Study of Sustainable Technology for Energy Recovery from Waste

Submitted By

Rahul Baidya

Doctorate of Philosophy (Engineering)

Department of Mechanical Engineering
Faculty Council of Engineering & Technology
Jadavpur University
Kolkata, India

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JADAVPUR UNIVERSITY
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This is to certify that the thesis entitled **“Study of Sustainable Technology for Energy Recovery from Waste”** submitted by **Shri Rahul Baidya**, who got his name registered on **6th April, 2015** for the award of Ph.D (Engineering) degree of Jadavpur University is absolutely based upon his own work under the supervision of **Professor (Dr.) Sadhan Kumar Ghosh** and that neither his thesis nor any part of the thesis has been submitted for any degree/diploma or any other academic award anywhere before.

Signature of the Supervisor

Professor (Dr.) Sadhan Kumar Ghosh
Dean, Faculty Council of Engineering and Technology
Professor, Department of Mechanical Engineering
Jadavpur University, Kolkata, India

JADAVPUR UNIVERSITY
Faculty Council of Engineering & Technology
CERTIFICATE OF APPROVAL*

The foregoing thesis titled “Study of Sustainable Technology for Energy Recovery from Waste” submitted by Sri Rahul Baidya, is hereby approved as a creditable study of an engineering subject carried out and presented in a manner satisfying to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn therein but approve the thesis only for the purpose for which it is submitted.

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Rahul Baidya
Ph. D Researcher at Jadavpur University

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EXECUTIVE SUMMARY

Waste management is a major problem in most fast developing countries; India being no exception generates annually 277.136 million tonnes of municipal solid waste, 7.234 million tonnes of hazardous waste and 30 million tonnes of non hazardous industrial waste (excluding power plant waste and mining waste). Since the last decades, energy and resource recovery from waste is looked upon as an environmentally and economically effective way of disposing waste. In many countries, including India, energy and resource recovery from different waste streams, such as municipal solid waste (MSW), industrial waste and hazardous waste is yet to be implemented effectively. Selection framework of different technologies focusing mainly on thermo-chemical route for sustainable operations is still elusive. There dearth of literature which have compared the effectiveness and sustainability of the commercially available energy and resource recovery processes, for different waste streams.

The work, analyses four of the thermo chemical technology which are in use in either commercial or trial configuration in India and similar developing countries. The four processes, gasification, incineration, pyrolysis and co-processing were analysed based on sustainability pillars i.e. economical, operational, environmental and social. The different constructs applicable to all the related technology have been gauged qualitatively and quantitatively with special emphasis to Indian scenario. The technology domains that required qualitative analysis were ranked based on the analytical hierarchy process (AHP) and quantitative constructs were gauged based on numerical values obtained from literature and field study of different plants. The selection framework based on the score indicated that the most sustainable process/technology is co-processing in cement plants followed by gasification, incineration and pyrolysis. Incineration, although ranked third has been studied in detail due to its potential of handling the largest quantity of urban MSW, both unsorted and sorted. Additionally, currently six plants are operating and are at different stages of commercial viability across the country. So a specific study on the sustainability of waste to energy (WTE) plants operating on the incineration methodology was analysed. The work finds the issues and challenges in supply chain framework of the waste to energy plant specific to Indian scenario. The work was carried out based on three case studies in India utilizing MSW for production of energy. The findings revealed certain factors which are hindering the supply chain sustainability of the WTE plants in India and are common to a number of developing countries. The sustainability aspects are needed to be addressed for a holistic business model.

Co-processing being the most sustainable waste treatment methodology as per the selection framework, the following work was focused in detail understanding of co-processing of different waste through number of experimental trials and case studies. Co-processing in cement kiln achieves effective utilization of the material and energy value present in the wastes, there by conserving the natural resources by reducing use of conventional resources. In India, a number of initiatives have been taken that take into account the potential and volume of waste generation. This current work studied the factors which influenced the sustainability of co-processing of waste in cement kilns as a business model by considering the issues and challenges in the supply chain frame work in India in view of the four

canonical pillars of sustainability. A pilot study on co-processing was carried out in one of the cement plant in India for evaluating the environmental, economical, operational and social performance. The findings will help India and other developing countries to introduce effective supply chain management for co-processing while addressing the issues and challenges during co-processing of different waste stream in the cement kilns.

Cement production consumes 9.10% of the total industrial energy, making it the third largest consumer of energy. Each ton of cement generates approximately 0.7 – 0.93 ton of CO_2 depending on the kiln technology used. The top ten cement producing countries along with the European Union emit 1445 million tonnes of CO_2 each year. Therefore, increased focus is laid on different strategies of carbon mitigation and co-processing is looked upon as one of the most prominent methodology for making cement manufacturing a low carbon process. The work highlights low carbon manufacturing potential of cement plants in India based on the available literature and a number of case studies, considering economical and environmental sustainability. Different trials were carried out to understand the sustainability of co-processing in cement plants for different waste streams, both hazardous and non hazardous.

An integrated steel plant generates a large amount of blast furnace flue dust – about 18–22 kg/t of hot metal as a by-product of the production process. The major component of this flue dust is iron oxides and coke fines. The recovery and reuse of this iron and coke assumes significance with increasing price of conventional resources. Consequently, co-processing of the flue dust is a solution for both the industries. In this chapter the potential of flue dust utilization in a cement plant in India was gauged by conducting experimental trial of one month. The work also analysed the techno-economic feasibility of the co-processing route. Since flue dust contains iron which is a limiting constituent in the limestone deposit of this plant, feasibility of reducing the iron content in the flue dust was evaluated through the magnetic separation route. The main objective was to utilise maximum amount of flue dust with acceptable iron content and high energy content. It was observed that magnetic separation neither does effectively segregate the iron present in the flue dust nor increases the energy content. The cost analysis of the usage of flue dust also revealed that flue dust can be used effectively by the cement industry if its cost ranges in an acceptable range of USD 35–39.

India produces around 90% of world's marble stone, with the state of Rajasthan contributing 85% of the India's production. Marble processing involves operations such as grinding, cutting, polishing, which produces waste in the form of marble slurry which is 30% of the original unprocessed marble stone. The waste contains approximately 70% of water. Improper disposal of this industrial waste affects the environment, including the health of living organism. In this chapter, the co-processing of marble slurry as an alternative raw material (AR) in the cement production process was evaluated. The work analyses the effect of marble slurry co-processing on kiln emissions, clinker quality and cement property based on the four year plant data. The result reveals no adverse consequence on emission and on product quality when the concentration of magnesium present in marble slurry is limited up to the acceptable level of < 5%.

Another trial with industrial hazardous waste acid tar sludge (ATS) generated in steel plants as a process by-product was studied for disposal potential at cement kiln via co-processing path. ATS disposal is a major challenge for the steel industry around the world and specifically for developing nations. Hazardous wastes are usually disposed of in a dedicated expensive thermal treatment plant in accordance with existing rules. In view of this, co-processing of ATS in cement plant as an alternative way of disposal was studied based on a number of experimental trials. During the five trials of five day each, feed rate of ATS was maintained at 0.4 tph with an average coal feed rate of 10tph. Another experimental trial was carried out with purified terephthalic acid (PTA) waste mix produced during PTA production for polyester industry. The wastes primarily consist of scrap PTA, PTA contaminants liners, ETP sludge, process sludge and oily rugs. Disposal of this hazardous waste mix is a major challenge for the chemical industry. Co-processing of PTA waste mix in cement plant as an alternative method of disposal and resource recovery was analysed based on a five day trial. During the trial feed rate of PTA, waste mix was maintained at 22 tonnes per day with an average coal feed rate of 1000 - 1200 tonnes per day. Both ATS and PTA waste trails showed no incremental variations in emissions. The analysis of clinker quality, leach behaviour and cement property revealed insignificant impact. The study also revealed no impact on ambient air quality based on NOx, SO_2, RSPM and SPM values as measured at varying location around the cement plant. A specific metal mass balance analysis of trace elements was analysed during PTA trial and showed negative impact as such. Therefore, co-processing of hazardous waste like ATS and PTA waste mix in cement plant can offer an effective solution for industrial hazardous waste disposal in developing countries like India. The present work concludes that co-processing provides potential for handling different waste streams, both hazardous and non hazardous, in a sustainable way that ends up in economic gain. Co-processing not only reduces the amount of waste that goes to landfill but also leads to low carbon cement manufacturing, as traditional fuel and raw materials are saved and simultaneously, waste going to the landfill gets reduced, therefore making co-processing a holistic methodology for resource recovery that promotes circular economy.

Chapter 1

Introduction to Waste Management

1.1. Municipal Solid Waste Management

Solid waste management is one of the most challenging issues in urban cities (Kumar et al., 2009). Increased waste generation due to population, societal lifestyle, development and consumption of products that are non-biodegradable, have increased the challenges for municipal solid waste management (MSWM) across the cities throughout different countries (Assamoi and Lawryshyn, 2012). Waste generation has close relationship with population growth and urbanization and is directly linked to gross domestic product (GDP) per capita and energy consumption per capita (Bogner and Matthews, 2003; Nakicenovic and Swart, 2000). With increased affluence comes increased consumption and increased waste generation (Agamuthu et al., 2009). Although urbanization is not a problem but haphazard and unplanned growth results in many environmental problems which includes public space, riverbank encroachment, air and water pollution, and generation of waste (Troschinetz and Mihelcic, 2009). The collection, transport, treatment and disposal of MSW generated in medium and large urban centres, have become a relatively difficult problem to solve. Poor waste management practices can negatively impact human health, the environment and the economy in many ways (Agamuthu and Herat, 2014). To promote sustainable development, waste management has evolved into material flow management in many developed countries (Zhang et al., 2010). Municipal solid waste (MSW) is the most complex waste stream compared to more homogeneous waste streams resulting from industrial or agricultural activities (Wang and Nie, 2001). According to Organization for Economic Co-operation and Development (OECD), MSW is collected and treated by or for municipalities. It covers waste from households, including bulky waste, similar waste from commerce and trade centres, office buildings, institutions and small businesses, yard and garden waste, street sweepings, contents of litter bins, and market waste. The definition excludes waste from municipal sewage, and construction and demolition waste (Yay, 2015).

Waste cannot be responsibly dumped without giving due concern and preparation, because not only is it unsightly, unhygienic, and potentially disastrous to our environment due to uncontrolled combustion, generation of methane and production of dioxin and furans (Minh et al., 2003), it also requires the allocation of space and incurs disposal costs. In recent years integrated waste management is looked upon as a methodology to reduce waste at source before it even enters the waste stream (Ngoc and Schnitzer, 2009). Improper management of solid waste has serious consequence on environment and health (Güleç et al., 2001). In developing countries with mixed economies, the problem of implementing sustainable practices for the disposal of solid wastes is more difficult than in developed countries. MSWM can be separated into three main activities: collection, treatment and disposal (Di Maria and Micale, 2014). In most developing countries, municipal authorities lack resources which include trained staff, technology and an integrated management system to provide the population with the necessary facilities and services. Developing countries today face challenges of balancing economic growth with environmental progress (Turan et al., 2009).

As less developed countries such as India and China industrialise and their populations urbanise, huge amounts of municipal waste are needed to be disposed, though the production is currently less than 0.5kg/day/capita in India and less than 0.9 kg/day/capita in China compared to the other individual OECD counties (2.1 kg/day/capita in the USA) (Giusti, 2009). In India the MSWM is defined by Solid Waste Management Rules, 2016 of Ministry of Environment, Forest and Climate Change, India. India generates around 277.136 million tonnes of municipal solid waste annually out of which 52% is organic fragments and 23% inorganic fragments consisting of paper, plastic, rubber and textiles (figure.1-1). This 23% of the waste has high potential for energy and resource recovery and needs to be treated effectively.

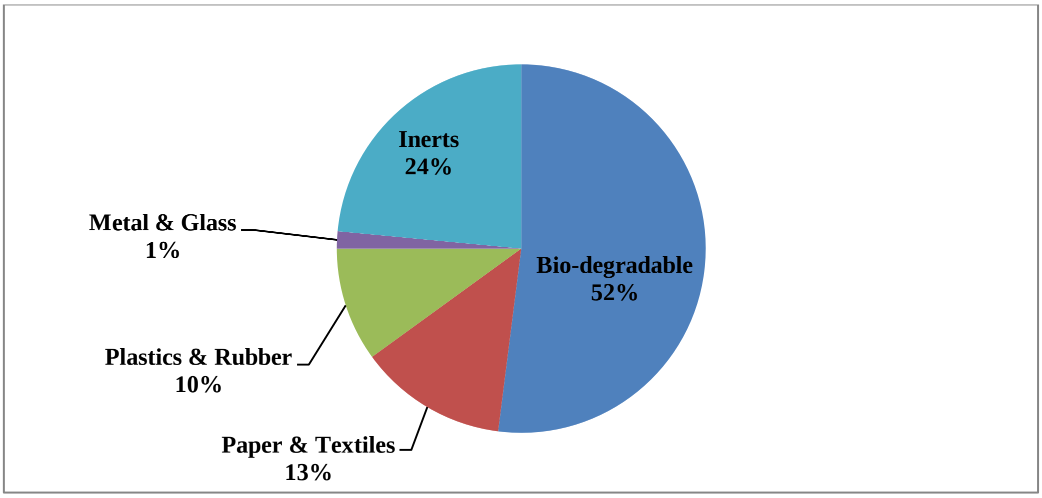

Figure.1-1. Physical composition of waste in India

Like any other developing country MSWM is a major environmental problem for Indian cities. Improper management of MSW causes hazards to inhabitants. Different studies revealed that 90% of MSW is disposed of unscientifically in open landfills, creating numerous problems to public health and environment. Rapid industrialization and population growth in India has led to the migration of people from villages to cities, which generate tons of MSW daily (Sharholy et al., 2008). The increase in the population and rapid growth in income has changed the lifestyle of urban residents across Indian cities, changing the composition of generated garbage. The presence of paper, plastic and metal is on the rise, resulting in disposal difficulty. The municipalities are unable to collect and dispose of this enormous quantity of waste being generated each day. Scavengers and rag pickers have helped the municipalities with the segregation of the waste in to recyclable and organic fragments (Narayana, 2009), although manual scavenging are forbidden by the law of land. A typical solid waste management system in developing countries displays an array of problems, including low collection coverage and irregular collection, open dumping and burning, breeding of flies and vermin and manual scavenging activities (Manaf et al., 2009). Municipalities, usually responsible for waste management in the cities, often face problems (Sujauddin et al., 2008) mainly due to lack of organization, financial resources, complexity and system multi dimensionality (Burnley, 2007).

Integrated waste management is a sustainable approach for solid waste management in any region and can be applied to both developed and developing countries, the difference lies in the approach taken to develop the integrated waste management system (Asase et al., 2009). As waste management system has developed through introduction of advanced technologies, different markets for waste treatment outputs (material, energy and nutrients) are coming to the existence; with it waste management planning has become more complex than ever. The responsibility for waste management may also be entrusted to different actors, thus increasing the planning problems even more (Eriksson and Bisaillon, 2011). The amount of waste produced is directly dependent on the country, urbanization, population, city size, culture, lifestyle and income. The traditional consideration of waste as pollution has progressively shifted towards a new perspective, in which it is regarded as a resource that could make societies more sustainable (Laurent et al., 2014). The closed cycle waste management, thus not only contributes to the environmental protection, but it also pays off economically (Nelles et al., 2016). Municipal wastes are generated from several sources in which different human activities are involved. Several studies indicate that much of the MSW are generated from households (55–80%), commercial areas (10–30%) streets, industries and institutions. Wastes from these sources are highly heterogeneous in nature (Valkenburg et al., 2008) and have variable physical characteristics. The heterogeneity of the generated waste is a major setback in its utilization as a raw material. Therefore, there is a need for segregation of waste before they can be treated. Source segregation of waste is the fundamental step in an integrated waste management system. However, the success of waste management system will largely depend on the active participation of the waste generators and how they comply with the principles of sorting and separation of the waste (Baidya et al., 2016; Miezah et al., 2015).

1.2. Hazardous and Industrial Waste Management

Industry has become an essential part of modern society, and waste production is an inevitable outcome of the developmental activities. These wastes may pose a potential hazard to the human health or the environment if not treated, stored, transported and disposed of properly (Misra and Pandey, 2005). A substantial amount of these generated wastes are potentially hazardous and dangerous to the living organisms. A hazardous waste (HW) is defined as any waste that possesses properties such as toxicity, flammability, carcinogenicity, reactivity, corrosivity, etc. Hazardous waste management systems (HWMS) entail collection of HW, their transportation to disposal facilities with proper processing technologies (Yilmaz et al., 2017). The improper disposal of these wastes may lead to contamination of air, surface water, ground water, soils, sediments and biota. Contamination of ground water by landfill leachate constitute the major environmental concern with the land filling of the HW (Christensen et al., 1994).

Waste characterization is an essential requirement for an effective industrial waste management plan (Sharma and Lewis, 1994). Prior to establishing strategies for control and treatment of waste, it is necessary to analyse, whether the waste contains hazardous constituents. The simplest systems for characterization of industrial waste (IW) is to review industries having potential to produce HW, e.g. electroplating, petroleum, tanning, pesticide, lead acid battery industries, etc (Misra and Pandey, 2005). Hazardous wastes include organic and inorganic wastes. Inorganic hazardous wastes, commonly found in aqueous solution or suspension, often require pre-treatment before they are land filled (Qian et al., 2006). Also, some household consumer products contain hazardous substances. Such products may include paints, cleaners, varnishes, car batteries, motor oil, and pesticides. The used up leftover contents of such consumer products or the remaining unused portion of the substances are known as “household hazardous waste” (Slack et al., 2005). This household hazardous waste needs to follow the HWMS path as otherwise they also pose a risk to human and environment. Management of the hazardous industrial wastes has become a serious concern for both environment and public health due to increase in quantity of hazardous materials that need to be treated (Kavouras et al., 2003). The hazardous waste management system must ensure safe, efficient and cost effective collection, transportation, treatment and disposal of wastes. Further the selection of treatment and disposal facilities and routing of hazardous wastes involve economic and social concerns. In order to ensure techno-economic feasibility as well as safety of public and environment; locations, technologies and capacities of hazardous waste treatment and disposal facilities are needed to be carefully selected. In the course of the decision-making process, sources that might create multiple types of hazardous wastes with diverse characteristics should be considered (Yilmaz et al., 2017).

Increasing pressure on resources such as land, energy, finance and strict environmental regulations have made the hazardous waste management problem more complex. Further diverse characteristics of different HW add considerable complexity to the hazardous waste management problem. Different types of waste streams have distinctly different handling protocols, treatment possibilities, and disposal alternatives (Nema and Gupta, 1999). It is essential to consider the influence of the system components on each other to arrive at an optimal plan for hazardous waste management system. There are several treatment methods for hazardous waste e.g. acid–base neutralization, incineration, chemical fixation/ solidification, etc., which may be used prior to ultimate disposal. The treatment technologies convert the waste into a more innocuous form, or immobilize toxic components, or reduce the quantity of waste (Misra and Pandey, 2005). The disposal facilities act as a permanent repository in hazardous waste management programme for the waste residues generated from the treatment facility (ReVelle et al., 1991; Millano, 1996); presently hazardous waste in cement kilns via co-processing in cement plants is also practised (Baidya et al., 2017).

Although it is commonly accepted that the environmental impacts of waste treatment are continuously reducing. New techniques have been developed for the treatment of hazardous waste and better management of problematic waste streams, such as waste oils, PCBs/PCTs and batteries are being carried out. Heavily polluting landfills and incinerators are being cleaned up and alternative efficient technologies based on the waste stream are coming up. The levels of dioxins and other emissions from incineration are being reduced with advent of new technologies. The perspective with time is also changing as increasingly hazardous waste is seen as a valuable resource for industry through different valorization routes. The final destinations for different industrial wastes are becoming critical, with severe legislation and environmental constraints. Those aspects need to be linked with economic vectors in order to achieve viable solutions for waste recycling. The common practice of land filling is not recommended and increased taxes are discouraging the same. This offers an opportunity to develop better sustainable systems, involving valorization of industrial wastes and by-products for a distant industry (Buruberri et al., 2015). By-products such as slag, scale or dust from steel industry which are typically sent to landfills, offer significant potential for cost savings or profits if properly reintroduced in the industrial system (Notarnicola et al., 2016).

In India, the HWMS is defined by the Hazardous and Other Wastes (Management and Trans-Boundary Movement) Rules, 2016. India generates around 7.2 million tonnes of hazardous wastes every year, out of which land fillable hazardous waste is 3.5 million tonnes, incinerable is 0.87 million tonnes and recyclable is 2.8 million tonnes as per CPCB. Around 12% of this HW has to be disposed of in incineration unit at treatment storage and disposal facilities as per the guidelines (figure.1-2). But there exists other thermo-chemical routes for effective utilization with energy and resource recovery. Around 30 million tonnes of (excluding power plant waste and mining waste) industrial non-hazardous wastes generated annually by different processes across industries are disposed of as per CPCB, guidelines for respective industry.

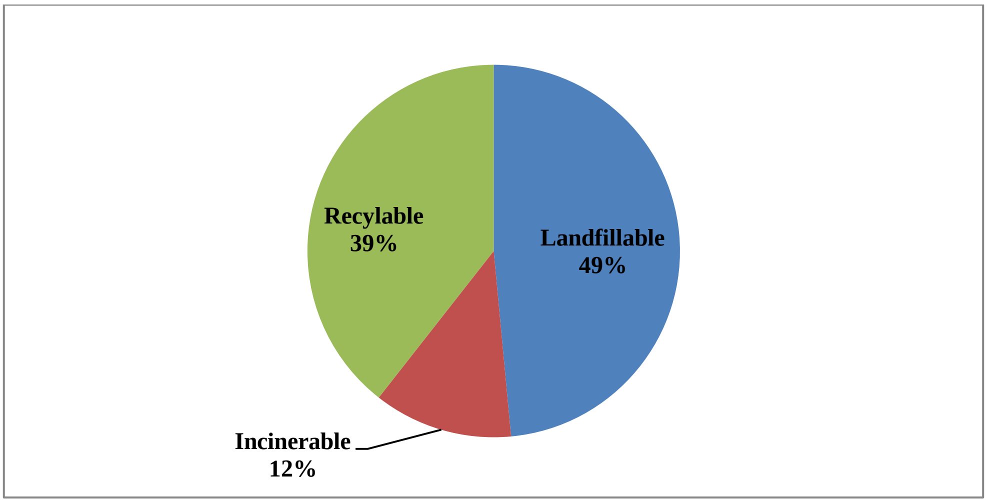

Figure.1-2. Hazardous waste treatment routes in India

1.3. Plastic Waste

Plastics are man-made long chain polymeric molecules. They are widely used economical materials characterized by excellent all-round properties with easy molding and manufacturing capability (Agamuthu, 2018; Zheng et al., 2005). Continuous innovation has increased the plastics production in an average of almost 10% every year on a global basis since 1950 (Panda et al., 2010). It is estimated that 4% of global crude oil being produced is dedicated for the plastics industry (Al-Salem et al., 2017) while another 4% is consumed to supply energy for the plastic manufacturing industries itself (Shahul Hamid et al., 2018). The rising needs of the middle class and cheaper price has contributed to an increase in the consumption of plastics in the last few years (Narayan et al., 2001). The rapid rate of plastic consumption throughout the world has led to increased amount of waste and this in turn poses greater difficulties for disposal. This is due to the fact that duration of life of plastic wastes is very small (roughly 40% have duration of life smaller than 1 month) (Achilias et al., 2007;

Datta and Halder, 2018). Their presence in the waste stream poses a serious problem due to lack of efficient end of life management (Panda et al., 2010). Plastic wastes are classified as industrial and post consumer plastic wastes or municipal plastic waste according to their origins; these groups have different characteristics and qualities and are subjected to different management strategies (Buekens and Huang, 1998). Post consumer plastic wastes remain a part of MSW as they are discarded and collected as household wastes. The various sources of post consumer plastics includes domestic items (food containers, packaging foam, disposable cups, etc.), agricultural (feed bags, fertilizer bags etc.). Thus, the post consumer plastic waste collected as a MSW are mixed, consisting of polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene etc. The percentage of plastics in MSW has increased significantly (Buekens and Huang, 1998). In order to recycle municipal plastic wastes, separation of plastics from other household wastes is required. For mixed plastics different mechanical separation technique is currently available, by using wet separation method mixed plastics can be separated into two groups: one with density greater than water (polystyrene and polyvinyl chloride), and other with a density lower than water (polyethylene, polypropylene, and expanded polystyrene) (Panda et al., 2010). The large plastics manufacturing, processing and packaging industry is the source of industrial plastic wastes. The industrial plastic waste also constitutes plastics from construction and demolition sector, electrical and electronics and automotive industries. Most of the industrial plastic waste have comparatively good physical characteristics i.e. clean and free from contamination and are available in large quantities (Panda et al., 2010). Currently there is no authentic estimate available on the total generation of plastic waste, although, considering the fact that 70% of total plastic consumption is discarded, approximately 5.6 million tonnes of plastic waste is generated annually in India, which accounts for 15342 tpd as on 2013 (Singh et al., 2017). By far the largest share of all postconsumer plastic waste is packaging waste.

Packaging plastics are ubiquitous and have short life spans, especially when compared to other streams such as construction & demolitions, automotive and consumer products. Excluding polyvinyl chloride (PVC), all the other polymers type high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP) and polyethylene tereftalate (PET) have primary applications in packaging, thus dominating the composition of plastic waste stream (Ragaert et al., 2017). The increase in demand for plastics can only lead to the accumulation of more plastic solid waste (PSW) taking up large chunk of the MSW sector in developed and developing countries alike. Recent statistics reveal that 25.8 million tonnes of plastics ends up in the waste upstream of Europe of which 39% gets land filled (Al-Salem et al., 2017). In addition, developing countries rely primarily on land filling as a strategy for MSW disposal without giving due consideration to the advantages, that different recycling schemes could have on the economics (Al-Jarallah and Aleisa, 2014; Al-Salem et al., 2009). Increasing cost and decreasing space of landfills are forcing alternative options for PSW disposal (Zia et al., 2007). There are a number of treatment, recycling and recovery methods for PSW that are economically and environmentally viable (Howard, 2002). The different routes of PSW treatment include primary (in-situ), secondary (mechanical), tertiary (chemolysis & thermolysis) and quaternary (energy recovery) schemes. Primary recycling involves in situ re-introduction of clean scrap of single polymer to the extrusion cycle in order to produce products of similar type. This method is primarily applied in the processing line itself, although theoretically this method can be used for different post consumer plastics but is seldom applied by the recyclers, as recycling materials rarely possess the required quality and are usually always contaminated. The various waste products, mainly post consumer plastics waste, act as a feedstock for secondary routes.

Tertiary treatment schemes have recently contributed greatly to the recycling status of PSW. Advanced thermo-chemical treatment methods cover a wide range of process and produce fuels or petrochemical feedstock depending on the process. Quaternary route is primarily energy recovery from PSW by incineration, co-combustion and co-processing depending upon the suitability (Al-Salem et al., 2009). Due to their high calorific value (CV), comparable to conventional fuels (e.g. gasoline, kerosene, diesel, etc), plastics can be used as a throughput material to produce electrical power, steam and heat (Dirks, 1996; Williams and Williams, 1997). The use of plastic waste as alternative fuel will help the cause of carbon mitigation and will reduce the energy cost. During co-incineration of PSW in blast furnace the PSW is completely burnt and slag formed are further utilized for cement and road construction (Singh and Sharma, 2016), while co-processing PSW in cement kiln makes it an integral part of the clinker (Baidya et al., 2017). However, use of PSW presents numerous challenges that make this type of treatment route very demanding and questions its economical sustainability versus its advantages in reduction of volume and energy production. Such problems include inconsistent feed resulting from inadequate sorting, fluctuating heating values, combustion instability, complex pollutant emissions control (Fu et al., 2015). Social acceptance and accountability are also key issues that need to be considered for a sustainable energy recovery scheme (Al-Salem, 2019).

1.4. Waste and Resource Recovery

The recovery of resource and energy are the two means that can turn waste into a valuable asset. The variety of methods and technologies available to carry out material and energy recovery gives a number of ‘‘recovery paths’’ (Consonni et al., 2011). Uses of waste for production of energy, becomes increasingly interesting when considering two perspectives that is, management of waste and the production of energy (Münster and Meibom, 2011). Energy recovery from waste or Waste-to-Energy (WTE) has become an attractive solution for many countries for an effective waste management system. A sustainable waste management system must extract the full energy and environmental value from MSW (Jamasb and Nepal, 2010). Energy recovery methodologies or processes can provide valuable alternative energy, reducing the burden on landfill and simultaneously mitigating greenhouse gas emissions. As a result – and despite of the recent economic slowdowns – the global market for WTE has experienced substantial growth with over 1200 operating plants across 40 countries (Yap and Nixon, 2015) with many of them in different stages of commissioning. MSW can be considered as an available source of domestic energy, because of its energy values and its regular generation (Lombardi et al., 2015). Its calorific values range in between 8 to12 GJ/t, approximately 42% of the value of bituminous coal (24 GJ/t). Therefore, whenever material recovery and re-use is not possible, different treatment technologies are effectively used for resource and energy recovery, leading to economical and environmental gain (Baggio et al., 2009; Ionescu et al., 2011; Poulsen and Hansen, 2009; Sakai, 1996). In Germany, only 1% of the waste was land filled, consisting of mainly inert and the WTE share was around 35% of the waste treatment, higher than the Europe Union (EU)'s WTE ratio of almost 24%. Sweden is another successful case of WTE in the EU with 50% of waste incinerated for energy recovery (Tan et al., 2015), simultaneously also utilizing the landfill gas for district heating, vehicle fuel, and even for power plants operations (Dahlquist et al., 2011).

Utilization or treatment of the waste can be done in several ways based on whether the waste is incinerated or whether fuel is produced. The production of fuel from waste can take place either by thermo-chemical or biological processes (Tabasová et al., 2012). WTE and resource recovery approaches can be categorised into three types, thermal or thermo-chemical treatment, biological treatment and landfill. The thermal or thermo-chemical treatment can produce electricity, fuels or simply act as a resource for substitution of traditional fuel and raw materials in industrial process; it includes different process like incineration, pyrolysis, gasification and co-processing. Biological treatment includes anaerobic digestion with the production of biogas (Rathaur et al., 2018). Landfill with methane gas recovery system can also produce electricity and heat (Tan et al., 2015). The current work is primarily focused on commercially available thermal or thermo-chemical based energy and resource recovery methodology, other non thermal process/ technology being excluded from the discussion. The aim of thermal treatment of the waste is to lower its volume and to utilize the chemical energy in the waste. Mass burn incineration (MBI) is the most commonly used thermo-chemical based technology and includes large-scale combustion of waste in a single-stage chamber, at high operating temperatures (Papageorgiou et al., 2009). Present generation of incineration plant is characterized by an improved performance of chemical conversion process, with advanced technologies for pollution control systems (Arena and Di Gregorio, 2013). Consequently, today it is considered as an efficient process for destroying hazardous organic substances, recovering energy and materials from different waste streams, and saving landfill space (Vehlow, 2015). Non-combustible materials, e.g. glass, metals, inert waste and organic fraction of waste are eliminated before incineration (Solheimslid et al., 2015). It can treat different types of waste including solid, liquid (e.g. domestic sewage) and gaseous waste. However, municipal solid waste (MSW) represents the most common application (Fazeli et al., 2016). Incineration of MSW has numerous advantages which includes volume reduction (approximately 90%) and mass reduction (approximately 70%), complete disinfection and energy recovery. It is a major component of an integrated waste management system for large cities (DQ Zhang et al., 2010) although the by-products the process: fly-ash, bottom-ash and stack emissions is an area of concern (Hu et al., 2011). Another energy recovery methodology is gasification technology, it is the conversion of solid waste to fuel (syngas) through gas-forming reactions. It is a type of ''indirect combustion'' of the waste in the presence of an oxidant amount lower than that required for stoichiometric combustion (Arena, 2012). The minimum operating temperature for gasification is 1100°C. The products of the process are char, hydrogen, nitrogen, sulphur, CH_4 and oxygen – although the specific products depend on the feed materials used. The syngas, can be further converted to a liquid fuel using a catalytic Fischere Tropsch process and can be used for production of electricity or combusted for heat recovery, or used for the production of different chemicals (Pan et al., 2015). Similar type of energy recovery process is pyrolysis, which is thermal degradation either in the complete absence of an oxidizing agent, or with only a limited supply (i.e. partial gasification) in order to provide the thermal energy required for pyrolysis. Relatively low temperatures (400-900°C) are employed as compared to the gasification. Three products are obtained: pyrolysis gas, pyro-oil and solid coke, the proportion of each of the product depends on the pyrolysis method and reactor process parameters (Bosmans et al., 2013). The energy recovery methodology produces residue in the form of ash and char, although co-processing of waste in cement kiln recovers calorific value from it, but doesn't produce by-products since the waste residue forms a part of the clinker. Co-processing in cement kilns has been proposed by a number of literature for its technical, economical, environmental and social sustainability (Kikuchi and Gerardo, 2009).

Chapter 2

Literature Review and Problem Statement

2.1. Energy and Resource Recovery Processes

It is generally recognized that a modern municipal solid waste management system should include four fundamental options, for an efficient and sustainable management of waste: recycling of the dry fraction, biological treatment of the organic wet fraction, thermal treatment of the remaining waste, and land filling disposal for the residues of the recycling, biological and thermal processes. In this framework, thermal/thermo-chemical treatments are an essential component of a sustainable waste management system. The main advantages are: (i) reduction of the waste by about 70% in mass and more than 90% in volume; (ii) environmentally compatible exploitation of waste for energy; (iii) destruction of organic contaminants; (iv) concentration and immobilization of inorganic contaminants; (v) utilization of recyclables from thermal residues, including metals from bottom ash and slag; (vi) reduction of methane emissions from anaerobic decomposition of organic wastes; (vii) avoided environmental burdens (Arena, 2011). Consequently it is very clear that the use of landfills must be residual and devoted to pre-treated wastes (Lombardi et al., 2015). Thermal or thermo-chemical treatment of waste is an inalienable part of any integrated waste management system (Porteous, 2005). For an effective waste management of a city using of suitable energy and resource recovery facilities, it is absolutely essential to understand the characteristics and compositions of the generated waste (Yadav and Samadder, 2017).

Thermo-chemical treatment is characterized by higher temperatures and higher conversion rates compared to most of the other biochemical and physicochemical processes, thus allowing an efficient resource and energy recovery methodology for different streams of waste, in particular for unsorted residual waste (i.e. the waste left downstream of separate collection, which cannot be conveniently recycled from an environmental and economic point of view) (Arena, 2012). Technological advancement, improved pollution control systems, governmental incentives and stringent regulations have made energy and resource recovery processes a potential alternative for both the developed and developing countries. It not only acts as a source of resource and energy, but also reduces the potential harmful impacts on the environment, if left untreated. For example 1 tonne of MSW when incinerated for electricity generation, instead of land filling (without gas recovery), around 1.3 tonnes of CO_2 equivalent emissions are avoided (ASME, 2008). The technological advancement, process-cost reduction, and incentives for government bodies have made renewable energy sector including energy and resource recovery process more competitive and sustainable in the energy market (Münster and Lund, 2010).Treatment and processing of different waste stream including MSW, industrial waste (hazardous and non hazardous) should minimize the volume of land filled waste while recovering as much resources and energy out of it as possible. Waste is actually a resource with huge potential of material and energy recovery (Arafat et al., 2015).

Sustainability is a cross-disciplinary topic that is analysed by researchers, policy makers and community members. Protection of people and the environment and conservation of resources are the goals of waste management (Brunner, 2010; Stanisavljevic et al., 2015; Stanisavljevic and Brunner, 2014). In the context of sustainable waste management (SWM), sustainability is defined as the assessment of environment, economic, and social impacts of available waste treatment options (Soltani et al., 2016). SWM is tangible when the generation of waste and harmful substances is minimised, the reused (using materials repeatedly), recycled (using materials to make new products) or recovered (producing energy from waste) materials are maximised, and disposal of waste is minimised in order to preserve resources for the future (Nelson, 2016; Singh and Ordoñez, 2016; Tot et al., 2016). Different thermo-chemical technologies are available and they to be gauged based on the sustainability constructs. Numerous processes for energy and resource recovery exist but the current work is limited to the thermo-chemical processes which are at different stages of commercialization in India. The process considered for the current work is pyrolysis, gasification, incineration and co-processing.

2.2. Pyrolysis

Pyrolysis is thermal degradation either in the complete absence of an oxidizing agent, or with only a limited supply (i.e. partial gasification) in order to provide the thermal energy required for pyrolysis. The process is carried out at temperatures of 400 - 900°C, but usually lower than 700°C. Pyrolysis is an endothermic process, of the order of 100 kJ/kg (Khiari et al., 2004). Pyrolysis process can reduce the waste volume by 50 - 90% (Nixon et al., 2013). Pyrolysis unit for treatment of waste usually include preparation and grinding, drying (depends on process), pyrolysis reactor and secondary treatment setup for pyrolysis gas and pyrolysis coke (Bosmans et al., 2013). The pyrolysis process recovers 80% of the stored energy in carbonaceous waste to liquid fuel and char (Ouda et al., 2016) (figure.2-1).

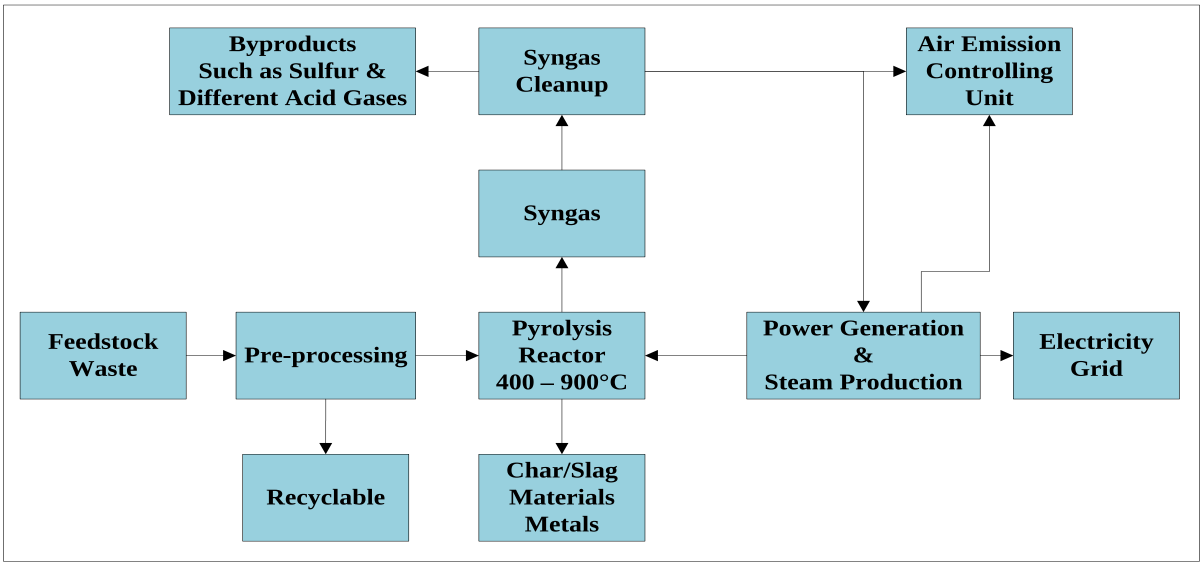

Figure.2-1. Process schematic of pyrolysis unit

Conventional pyrolysis reactors usually have one of the following configurations: fixed bed, fluidized bed, moving bed, entrained flow, rotary kiln, ablative reactor, etc., and often require pre-treatment of waste. The interaction between a large numbers of thermo-chemical phenomena results in different products and increases the complexity of the process. Several hundred different compounds are produced during waste pyrolysis, and many of these are yet to be identified. A thorough understanding of the characteristics and composition of waste to be processed is essential, especially when the waste is of hazardous nature (Helsen and Van den Bulck, 2001). Three types of products are produced from pyrolysis process: pyrolysis gas, pyrolysis oil and char, the proportion of the products depends on type of pyrolysis process and waste compositions (Bosmans et al., 2013). Pyrolysis technologies are classified as slow, intermediate, fast and flash pyrolysis (Ahmad et al., 2014; Homagain et al., 2014), but most commonly used systems are the slow and fast pyrolysis process. Bio char/char is the main product of the slow pyrolysis process and takes place at moderate temperature, low heating rate and longer residence time. In contrast, pyro-oil is the main product of fast pyrolysis and is carried out at rapid heating rate and short residence time. Fast pyrolysis produces a higher quantity and quality of bio oil relative to slow pyrolysis (Brown et al., 2011; Jahirul et al., 2012). The bio-oil has low alkali metal content and can be used as an alternative fuel by blending with conventional liquid fuels (Hossain and Davies, 2013). The yield and properties of the pyrolysis products depend on the operating conditions and process type, as a result of which each process has a different application. If a higher yield of bio char is required, then slow or intermediate pyrolysis process can be used, if pyro-oil is the goal, then fast/flash pyrolysis is used. The quality and quantity of pyro-oil and bio-char that are produced from a certain feedstock can be optimized by varying the operational parameters, specifically the reaction temperature and heating rate (Roy and Dias, 2017).

Pyrolysis gas is useful as it contains methane and hydrogen, although its calorific value is lower than convention fuels due to the presence of nitrogen and carbon dioxide, while the bio-char can act as a carbon sequestration material and can be used for soil amendment (Park et al., 2004; Pütün et al., 2004; Tsai et al., 2006). Due to lower operating temperatures and the absence of oxygen the process is less polluting, oxygen and particularly the temperature being the primary precursors for the production of furans and dioxins (Conesa et al., 2009). The low operating temperature also helps in removal of heavy metals from the pyrolysis gas, which remain trapped in the resulting solid carbonaceous char (Menendez et al., 2002). Though pyrolysis has started to gather much interest in the field of energy recovery due to economical potential of the alternative products, but no installed commercial facilities exists in India and research activity into these types of systems remains limited to lab scale (Singh and Gu, 2010) and due to lack of economic viability the technology is not established (Samolada and Zabaniotou, 2014) although several cases suggest economical viability on a larger scale.

2.3. Incineration

Incineration is an integral part of waste management in many countries worldwide (Arena, 2012), around 65–80% of the energy stored in the waste materials can be recovered (Chakraborty et al., 2013). The process efficiency of incineration is 25–30% (Kirby and Rimstidt, 1993). The end product of incineration is hot combusted gases, consisting of nitrogen (N_2), carbon dioxide (CO_2), flue gas, oxygen (O_2) and non-combustible materials

(Tan et al., 2015). Incineration is the most commonly used thermo-chemical treatment applied for different types of waste, including MSW, intended unsorted residual waste (i.e. the waste left downstream of separate collection), solid refuse fuels (SRF), industrial waste (IW), and industrial hazardous waste (IHW). Incineration of waste is generally associated with energy recovery, in the form of electricity and/or heat production, only, IHW is disposed of without energy recovery due to the presence of several pollutants in the generated flue gas (Lombardi et al., 2015). Incineration is used as a treatment process for a wide range of wastes and the process leads to volume reduction of up to 90% (Di Maria et al., 2016; Sakai et al., 1996; Yap and Nixon, 2015). While the incineration/combustion of MSW is quite an old practice, its use as a viable waste management strategy in recent time has increased (Grosso et al., 2010) (figure.2-2).

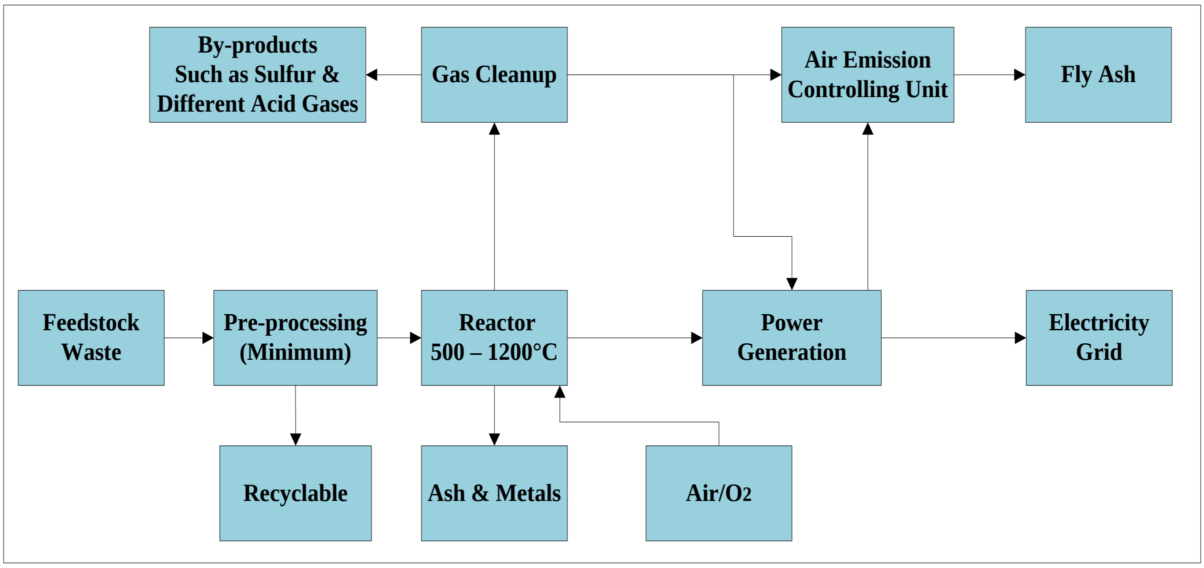

Figure.2-2. Process schematic of incineration unit

The main stages of the incineration process are: drying and degassing, pyrolysis, gasification and finally oxidation. These individual stages generally overlap, meaning that spatial and temporal separation of these stages may only be possible to a limited extent. Although it is possible to influence these stages in order to reduce pollutant emissions (Bosmans et al., 2013). Incineration is usually classified as a recovery treatment rather than disposal technique, additionally incineration also meets certain energy efficiency standard (Consonni et al., 2011). The main objective of an incineration plant is decreasing of MSW going to the landfill; therefore, it should not be compared with the energy generation from fossil fuels. The amount of energy recovery which can be achieved depends on MSW ratio of biogenic to fossil carbon and on the energy transformation efficiency of the incineration technology used. The conventional mass burn systems required 40-100% excess air over the stoichiometric value, resulting in a large amount of flue gas to be scrubbed. The incineration process produces harmful emissions of acidic gases (SO_2, HCl, HF, NOx etc.) and volatile organic compounds (VOCs) and heavy metals; additionally, the final process residues also constitute a major problem (Liu and Liu, 2005). Particulate matter can also cause a range of respiratory problems. Dioxins, furans and PCBs are carcinogenic. And mercury, along with other heavy metals, is toxic. The GHG emitted in the flue gas from incinerators are significant and estimates for CO_2 are in the region of 0.5 kg CO_2/kWh. Although the quantity of CO_2 and other emissions emitted during incineration is highly dependent on the operating condition and characteristics of the waste (Nixon, Wright, et al., 2013). To minimize and address the air pollutants emissions, most contemporary incinerators use an extensive pollutant/emissions control system. The use of latest pollution control technologies has reduced the emissions to the levels at which pollution risks from waste incinerators are now considered to be very low (Yap and Nixon, 2015). The proportions of solid residue (fly and bottom ash, slag, filter dust, other residues from the flue gas cleaning) vary greatly according to the process design, composition and types of waste.

In MSW incinerators, the bottom ash constitutes approximately 25 to 30% and fly ash in between 1 to 5% by weight of the input waste. The bottom ash can be used based on its characteristics, in concrete aggregates and other construction materials (Bosmans et al., 2013). Similarly slag and fly ash can be incorporated into cement or other similar building materials, or marked for landfill if its characteristics are appropriate as per the guidelines (Arena, 2012). The capital cost of incineration plants for 100 – 200 ktpa in India has been reported to be around 136 – 295 $/tpa (Salvatore, 2013; Yap and Nixon, 2015). Operational costs for incinerators in India are estimated to be around 85$/tonne (Chakraborty et al., 2013). Nevertheless, waste incineration can be an environmentally friendly method if it is combined with energy recovery, control of emissions and an appropriate disposal mechanism (Nixon, Wright, et al., 2013; Yap and Nixon, 2015). Although the capital cost of incineration is lower in comparison to other energy recovery technologies, but it does not directly correspond to its economical viability. Ancillary facilities like pollution control systems, feedstock handling unit, building requirements, and other supporting features for incinerators can represent approximately 40–70% of total project cost (Ouda et al., 2016).

2.4. Gasification

Gasification in particular, is the conversion of solid waste to fuel- or synthesis-gases through gas forming reactions. It is carried out by partial oxidation of the waste in presence of an oxidant amount lower than what is required for stoichiometric combustion. Gasification processes have more possibilities of being compatible with front-end processes and producing solid residues that are more suitable for re-use and have economical value unlike direct combustion by-products. Gasification processes can be modified to employ more efficient energy conversion systems like gas engines and turbines. They also benefit from flexibility of scale, as they can be built in a modular manner (Yassin et al., 2009). Gasification has several potential advantages over direct combustion, mainly related to the possibility of combining the operating conditions and the features of the specific reactor to obtain a desired syngas for specific uses as per different applications (Arena, 2012). The solid waste gasification is a complex process which includes different physical and chemical interactions (Arena and Mastellone, 2009). The products of the process are char, hydrogen, nitrogen, sulphur, methane and oxygen depending on the type of feed materials used. The total process is self-sustaining and energy input is not necessary under steady state operation (Samolada and Zabaniotou, 2014). Gasification of solid materials is an old technology but its only recently that it has been applied to waste management for energy recovery. During the gasification process, the waste is combusted in a controlled amount of oxygen to supply sufficient amount of heat for the syngas reaction, with temperature ranging in between 780°C to 1650°C (Tan et al., 2015) (figure.2-3).

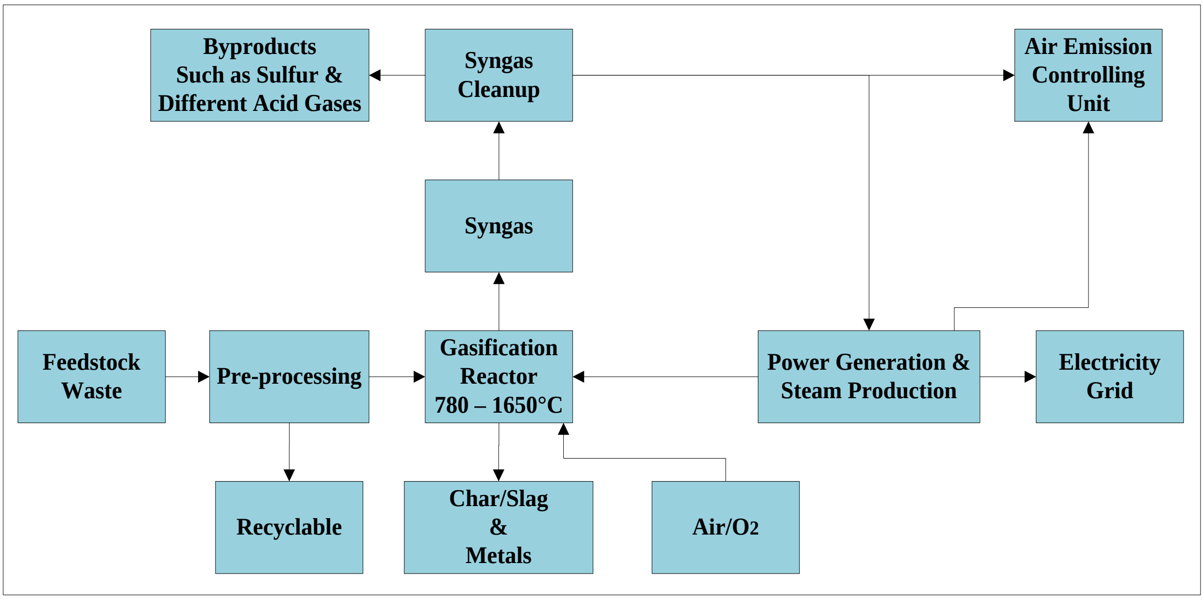

Figure.2-3. Process schematic of gasification unit

A typical gasification gas is characterized by a high hydrogen content of 8.89–11.17 (vol%). It contains also other combustible compounds, including CO (6.28–10.77 vol%), CH_4 (1.26–2.09), C_2S (0.75–1.2 vol%), CO_2 and the gasification medium (Fytili and Zabaniotou, 2008). A gasifier can use air, O_2, steam, CO_2 or a mixture of all these as gasification fluids. Air gasification produces a syngas with small lower heating value (LHV) ranging from 4 - 6 MJ/Nm^3, while O_2 gasification produces a syngas with a medium LHV ranging from 10 - 20 MJ/Nm^3 (Leckner, 2015). Different types of waste cannot be treated by gasification without pre-treatment. The cost of gasifier ranges from 180 to 270 $/kWh for thermal based applications and 540 - 810 $/kWe for mechanical and electrical based systems. For small gasifier plants in India (20 - 1000 kW), capital costs are on the higher side at around 900 - 1200 $/kW (Nixon, Wright, et al., 2013). Generation costs are pegged at around 0.05 - 0.07 $/kWh (Wu et al., 2002). For electricity production using gasification process, the parasitic electrical demand is around 20% and carbon dioxide emissions are around 114 g CO2/kWh. Gasification reduces volume by up to 90% with virtually zero hazardous emissions (Kumar, 2000). The syngas produced has a heating value in the range of 15-20 MJ/Nm^3. Moreover, gasification process generates less CO_2 than an incinerator of similar capacity (Murphy and McKeogh, 2004). (Kumar and Samadder, 2017) reported that, modern gasification units come with enclosures, which effectively reduce the chance of water and soil contamination. Asia has seen a huge leap in the gasification technology in last few years (Ouda et al., 2016). Although operations and maintenance costs for gasification systems are on the higher side due to tar and volatile gases which damages gas engines. Regular maintenance of the cleaning system is therefore required (Kumar, 2000). Also there are yet to be any established waste gasification plant of large scale across the world (predominantly in developing countries) for energy recovery (Luz et al., 2015) due to poor efficiency and gas cleaning systems requirements, heterogeneity in waste composition & particle size and high moisture content (Kumar and Samadder, 2017). While there are many gasification systems in India, there are no reported established gasification plants processing MSW or industrial waste currently in a commercial scale (Yap and Nixon, 2015).

2.5. Co-processing

Co-processing is the use of waste as raw material, or as a source of energy, or both to replace natural mineral resources and fossil fuels in industrial processes such as cement industry etc. Waste materials used for co-processing are usually referred to as alternative fuels and raw materials (AFRs) (Baidya et al., 2017). Co-processing of waste in cement kiln is a waste management technique that offers the benefits of simultaneous energy and resource recovery from waste and production of cement. Co-processing of waste in cement kilns offers economic, technical and environmental benefits, making it an attractive and promising waste treatment technique (Jin et al., 2016). The use of AFRs for cement clinker production is not only of high importance for the cement manufacturer but also for society as a whole (Michael Schneider et al., 2011). Coupled with resource conservation and reduced carbon emissions, co-processing is a preferable alternative for sound and environmentally sustainable waste treatment methodology over traditional incinerators and non-scientific methods. It is not only a solution to the waste disposal menace, but also reduces the burden on secured landfills (Tiwary et al., 2014). Cement industry offers vast potential for supplying preferable solutions for the management of wastes. Energy recovery from waste is also important for the reduction of CO_2 emissions (Kara et al., 2009). Various types of AFRs can be used in a cement kiln, with adequate equipment and fixtures. The use of AFRs in cement kiln also reduces emissions from landfills (Benhelal et al., 2013). Cement rotary kiln are able to burn a wide range of materials due to the long residence time of around 14 second at high temperatures of around 1450°C, intrinsic ability of clinker to absorb and lock contaminants, such as heavy metals into the clinker and also the alkaline environment of the kiln acting as a natural scrubber (Baidya et al., 2017) aids the co-processing methodology(figure.2-3).

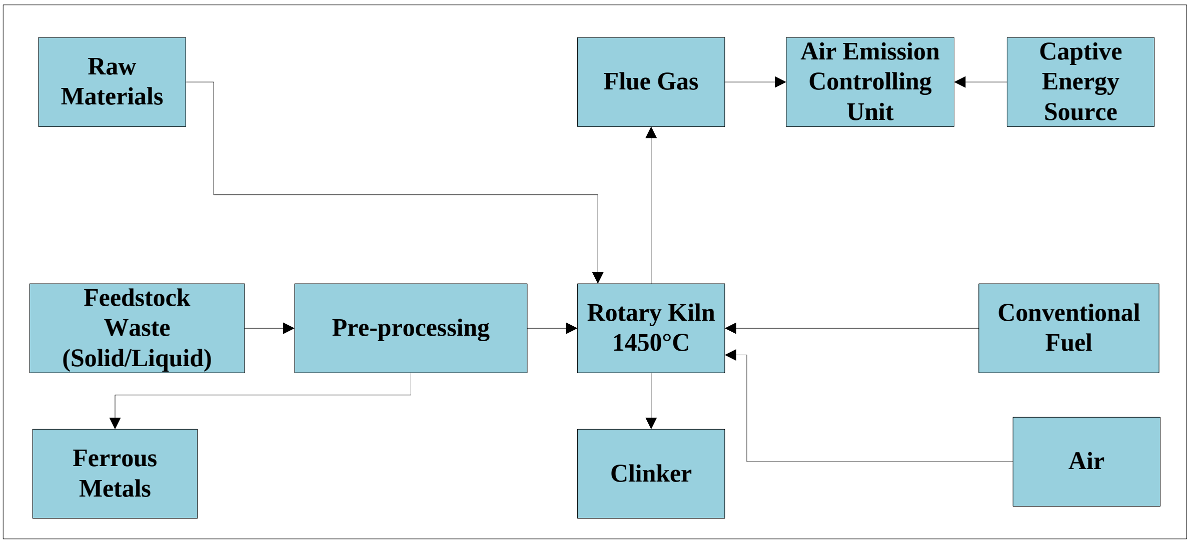

Figure.2-3. Process schematic of co-processing system in cement kiln

The clinker firing process is highly suited for different alternative fuels and raw materials; the goal is to optimise the process and AFRs feeding rate so as to maintain the clinker quality. Industrial experience has shown that the use of AFRs by cement plants is both ecologically and economically justified (Chatziaras et al., 2014) and has no effect as such on emissions and quality of the produced clinker (Garcia, Moura, Bertolino and de Albuquerque Brocchi, 2014). Currently, wide array of waste materials are co-processed, like rubber residues, pulp sludge, used tyres, plastic residues, wood waste etc. Industrial hazardous wastes are also co-processed which include tar, chemical wastes, distillation residues, waste solvents, used oils, wax suspension, and oil sludge, ETP sludge etc (Kääntee et al., 2004). Waste materials derived from fossil fuels such as solvent, plastics and used tyres are not considered as carbon neutral. Although it is important to note that transferring waste from incineration plants to cement kiln results in a significant net CO_2 reduction because cement kilns are more efficient. Another advantage is that no residues are generated as the AFRs form a part of the final product (Baidya et al., 2017; Karstensen, 2008). The co-processing of AFRs, in particular, has played a pivotal role in reducing emissions (CO_2), conserving natural resources and fossil fuels, and enhancement of waste management operations (Helftewes et al., 2012; Supino et al., 2016) thus providing a effective waste management methodology.

2.6. Research Gap Mapped with Problem Statement

Research Gap	Problem Statement
1. Sustainability issues of WTE Plants In India. 2. Issues and challenges in supply chain framework of waste management	1. What are the issues and challenges for an effective supply chain frame work of WTE plant considering waste management status of India?
3. Decision support framework for selection of technology or process for waste to energy and resource recovery in India 4. Sustainable thermo-chemical technology or process for Indian case	2. What is the best possible waste to energy and resource recovery thermo-chemical technology or process for India based on waste management practises and waste composition?
5. Issue and challenges for implementation of co-processing in Indian cement kiln. 6. Present supply chain framework and practises of co-processing in India.	3. What are the issues and challenges in supply chain framework and technical requirement of co-processing in cement kiln in generic and specific to India?
7. Possibilities of treating different waste stream via co-processing route specifically industrial hazardous and non hazardous waste.	4. How co-processing can reduce environmental impact and enhance the sustainability of waste management practises of different waste stream?
8. Techno-economical feasibility and requirements for sustainable co-processing in India.	5. How to address the issues related to waste characteristics, pollution control, and sustainability of waste management practises in India for an effective waste to energy and resource recovery business model?

Chapter 3

Objective & Methodology

3.1. Objective of the Study

1. To study the supply chain framework of MSW in India specific to WTE plant requirements, mapping the same and outlining the drawbacks.
2. Development of selection framework for effective thermo-chemical technology for WTE and resource recovery based on the waste characteristics, management practices and supply chain drawbacks considering sustainability pillars using decision support system.
3. The study will explore the potential and issues in co-processing of waste in the cement plant as an alternative fuel and raw materials (AFRs).
4. The study will analyse the hazardous waste treatment potential in cement kiln by experimental trial.
5. The study will examine the sustainability based on the four sustainable pillars and evaluates the potential of waste co - processing in Indian cement industry and also for waste to energy plant.

3.2. Problem Statement Mapped with Objective and Different Chapters

Problem Statement	**Objective**	**Chapter Number and Title**
1. What are the issues and challenges for an effective waste management emphasising on the supply chain frame work of WTE plant requirements, specific to the Indian scenario?	1. To study the supply chain framework of MSW in India specific to WTE plant requirements, mapping the same and outlining the drawbacks.	Chapter 4: Sustainability of waste to energy plant in India
2. What is the best possible waste to energy and resource recovery thermo-chemical technology/process in India considering the present waste management practises and waste composition?	2. Development of selection framework for effective thermo-chemical technology for WTE and resource recovery based on the waste characteristics, management practices and supply chain drawbacks considering sustainability pillars using decision support system.	Chapter 5: Selection framework of sustainable thermo-chemical technology for energy and resource recovery in India
3. What are the issues and challenges in supply chain	3. The study will explore the potential and issues in co-	Chapter 6: Co-processing of Waste in Cement Kiln Issues and Challenges

framework and technical requirement of co-processing in cement kiln in generic and specific to India?	processing of waste in the cement plant as an alternative fuel and raw materials (AFRs).	Chapter 9: Co-processing of Blast Furnace Flue Dust as AFRs in Cement Plant
		Chapter 10: Utilization of Marble Slurry as a Sustainable Substitution for Conventional Resource in Cement Kiln
4. How co-processing can reduce environmental impact and enhance the sustainability of waste management practises of different waste stream?	4. The study will analyse the hazardous waste treatment potential in cement kiln by experimental trial.	Chapter 11: Acid Tar Sludge Disposal in Cement Plant
		Chapter 12: Purified Terephthalic Acid Disposal in Cement Plant and Metal Mass Balance Analysis
5. How to address the issues related to waste characteristics, pollution control, and sustainability of waste management practises in India for an effective waste to energy and resource recovery business model?	5. The study will examine the sustainability based on the four sustainable pillars and evaluate the potential of waste co - processing in Indian cement industry and also for waste to energy plant.	Chapter 7: Co-processing of Industrial waste as AFRs in Cement Plant
		Chapter 8: Low Carbon Cement Manufacturing in India by Co-processing of Alternative Fuel and Raw Materials

3.3. Methodology of the Study

A structured literature review was carried out to gauge the present status in waste management practices, energy recovery and waste treatment technology usage around the world and specifically, India. The source of the problem was analysed with the help of literature and field studies/case studies and solution techniques have been suggested by employing a step by step, exploratory and descriptive research methodology. Across the country four energy recovery plants and four cement plant were studied through field visit over the years. The energy recovery plant field visit allowed understanding of the pertaining issues in the supply chain framework based on waste management practices. The problem and issues were analysed and a solution to the problem were proposed and further selection framework was developed to gauge the most effective thermo-chemical technology/process for energy and resource recovery from waste considering four sustainability pillars namely operational, economical, environmental and social. The qualitative constructs were gauged using multiple criteria decision making process - analytical hierarchy process (AHP). A questionnaire as per saaty scale was used to collect the ratings for pair-wise comparison in line with AHP methodology. The ratings were obtained based on the consensus of the experts. The quantitative constructs were gauged based on the secondary data from literature and field study. The ranking obtained provided the overall assessment for the sustainable technology in terms of the Indian waste management practices. The top ranked technology that is co-processing was analysed in depth with the support of the literature and filed study comprising numerous experimental trials with different waste streams. The sustainability analysis of different industrial waste co-processing at cement plant was carried out based on the four sustainable pillars namely environmental, economic, operational and social aspect. The supply chain network was critically analysed for challenges and issue in co-processing in cement kiln. The sustainability of co-processing at cement kiln was established for different industrial hazardous non hazardous waste steam for the first time as no report in literature was established. The experiments were carried to help in framing the standards of the co-processing. The specific experimental trials were in range of five days to a year. The experimental trials were carried out with hazardous and non hazardous industrial waste which includes marble slurry, acid tar sludge, purified terephthalic acid, blast furnace flue dust, FMCG trade rejects, ETP sludge, spent carbon etc. Individual methodology of each trial is discussed in the respective chapters.

Chapter 4

Sustainability of Waste to Energy Plant in India (Addressing Objective – 1)

4.1. Introduction

In the 21st century, the sustainable management of MSW will become necessary at all phases As a consequence, the spectrum of new and existing waste treatment technologies and managerial strategies have also spanned from maintaining present environmental quality to meet sustainability goals in the future. Such an orderly evolution allows both waste management industries and government agencies to meet common needs of waste management (Pires et al., 2011). A conventional MSWM system is composed of many enterprises such as waste collection and transportation centres and disposal plants. The management of MSW is increasingly becoming a challenging task for the municipal authorities due to increasing waste quantities, changing composition, decreasing landfill space and increasing awareness of the environmental affects (Srivastava and Nema, 2012).

There is a tremendous amount of loss in terms of environmental degradation, health hazards and economics due to direct disposal of waste. The waste must be segregated at the initial generation stages rather than going for a later option which is inconvenient and expensive. There is a need for an appropriate planning for proper waste management by means of analysing the waste situation of the area (Ahmed et al., 2006). Waste-to-energy (WTE) technologies involve converting different fractions of MSW such as paper, plastics and food wastes to generate energy either by thermo-chemical or bio-chemical processes. The thermo-chemical techniques consist of combustion/incineration, co-processing, gasification, thermal de-polymerization, plasma arc gasification and pyrolysis, which produce high heat in fast reaction times (Baidya et al., 2017; Kayes and Tehzeeb, 2009). Incineration can be classified as a recovery treatment rather than disposal (Bianchi et al., 2014; Consonni and Viganò, 2011; Cucchiella et al., 2010). The use of incinerator for waste management presents environmental risks; indeed, this facility can create toxic air pollution and toxic ash. Thus increasing the necessity of using appropriate technology at new facility and the application of advanced regulation scheme to prevent and minimize any risks that can be detrimental to the environment or health (Damgaard et al., 2010; Themelis and Ulloa, 2007; Zhang et al., 2013). Incinerator facilities also contribute to externalities, but not only the direct externalities are to be considered (i.e. due to waste incineration) but also the indirect one are needed to be considered (i.e. due to avoided emissions from conventional energy production) (Chakraborty et al., 2013). An effective waste management system requires that several aspects be integrated; local governments have to consider sustainable development approach, additionally, environmental, economic and social impacts of investments in waste sector have to be well integrated. All steps of waste management i.e. minimization, segregation and containerization, intermediate storage, internal transport, centralized storage are needed to be integrated for an optimal and correct waste management framework (Ochoa et al., 2013; Pires et al., 2011). The objective of the current work is to study the present issues in waste to energy supply chain frame work and find possible answers to these issues. Further the ultimate and proximate analysis of the waste and feed of each case have been analysed to obtain the heating potential of the waste.

4.2. Field study methodology

The field study was carried out in three WTE plants in India. The plants were visited and a discussion at the managerial level was carried out to map the supply chain and process flow framework. The organizational members were asked for the issues and challenges, being faced by them due to prevailing waste management practices. The waste management practices being carried out by the local corporation were also mapped and the results were correlated with the expert opinion of the WTE plant officials. Although waste management practises is governed by Solid Waste Management Rules, 2016 of ministry of environment, forest and climate change, India, the WTE supply chain frame work is still directly dependent on local practices. In order to make the WTE plant sustainable, the reverse logistic of the plants should be made holistically connected to the local municipalities waste management practice as the rule is yet to be implemented effectively.

4.2.1. Case study-1

The WTE plant is situated in East Delhi; it is located adjacent to the existing landfill site. The plant had started operation in the early quarter of 2015. It has a capacity of handling waste of 2000 tonne/day but presently the Eastern Delhi Municipal Corporation (EDMC) is supplying 1300t/day. The company maintains a MSW pit in which the EDMC trucks deposit their mixed waste. The waste received by the plant consist of approximately 35% organic, 7% paper, 5% clothes, 3% plastic, 5% glass/metal and 45% inert materials, which varies on a seasonal basis. The plant has two working line each of 1000 tonne/day capacity. The plant has employed 60 rag pickers as permanent employee for manual segregation. The plant lines are all mechanized; however a manual segregation process exists in the process lines. The leachate developed from the waste in MSW pit is collected by the drainage system inbuilt in the pit which is then drained to a specifically designed tank and is then treated in the treatment setup. The treatment is a two stage process consisting of primary treatment stage and secondary treatment stage. In the primary stage the sediments, biochemical oxygen demand (BOD), organic nitrogen, organic phosphorus, and heavy metals associated with solids and suspended solids are all removed by primary sedimentation and the sludge formed is removed to the anaerobic digester for further treatment. The primary effluent is further treated by activated sludge process. And finally, this treated effluent and the sludge is used as a fertilizer in nearby farmyards. The manual segregation is the primary segregation method used by the plant for segregating large size, inert, recyclable materials from waste stream, consisting of the combustible waste. The waste is dumped by the EDMC at the MSW pit, as shown in figure.4-1 where two EOT crane for each line, lifts the waste by using a grab bucket, and drops it into the hoppers. Each line has three hoppers, as a result of which the two lines combined have four EOT crane and six hoppers. The waste via hoppers falls on to the moving conveyor belts below it where they are manually segregate by the workers in to three fragments: large size materials, inert materials and recyclable materials. These three types of materials are taken off from the conveyor belt and kept aside and the combustible fragment goes to the trommel. This large size combustible fragment is transferred to the shredder. The recyclable materials were disposed to the 3rd party buyers.

The inert materials are again disposed off to the adjacent land fill site. The line-1 and line-2 has a separated trommel arrangement. There are two trommel in each line in which the trommel-1-1 and trammel-2-1 is used to separate the materials with less than 100 mm size the larger size materials above 100mm is transferred to the conveyor belt-3 which goes to the shredder. The less than 100mm materials are transferred via a conveyor belt-1-2 and conveyer-2-2 to the trommel-1-2, trommel-2-2 which is a 16/25 type separating device with two sections. In the first half of the trommel less than 16 mm material is removed as it was found to be inert by the field study which had been carried out for the received waste based on the locality. The second section separates the waste in two parts, one less than 25mm which falls to the bottom conveyor belt-1-4 and conveyer belt-2-4 for line-1 and line-2 respectively, and gets transferred to the composting plant, a sister plant at Okhla, Delhi. The 16 to 25 mm material contains mainly organic fragments and greater than 25 mm but less than 100 mm is transferred to the dryer via conveyer belts. The waste after shredding also is routed to the same conveyer belt-1-3 via conveyer belt-4 which goes to the magnetic separator. The magnetic separator removes all ferrous material which are then sold to the 3rd party recycler. The waste then passes through a rotary dryer fuelled by hot air generated by combusting refuse derived fuel (RDF). The dryer removes approximately 60% of the moisture; this dried waste is then transferred via conveyor belt-6. The waste after drying is passed through an air density separator (ADS), where the heavy material, mainly inert material is removed and disposed off to the landfill site, the RDF being blown off and deposited to the other side of the ADS. The RDF obtained is having approximately calorific value in the range of 4100-4300 kcal/kg. The RDF is fed to the boiler; the boiler uses RDF at the rate 476 tonnes/day and the same RDF is used to fire the dryer; around 100 tonne of RDF is used up in the dryer per day for generating the hot air.

The boiler has been designed specifically for RDF firing. The boiler has a moving grate which reciprocates as well as tumbles so that proper burning of the RDF is obtained as RDF has a tendency of forming small ball of mass which hinders effective burning. The steam generated in the boiler is used to run a turbine generating 12 MW/day of power via an alternator. The boiler steam parameter at outlet is 6.276MPa of pressure and steam temperature 485°C. Around 46% of power generated by the alternator is sold to the regional electricity distribution company, 3% of the generated power is utilized in-situ by the plant and the remaining 51% is sold to other buyers. The ash generated is disposed of in the adjacent landfill site. The WTE emissions which are of concern are trace organic compounds, dioxins and furans, heavy metals such as mercury, lead and cadmium, total particulate matter, and acidic gases such as hydrogen chloride, hydrogen fluoride, sulphur dioxide and nitrogen oxides. The emissions of these elements are arrested by combining wet scrubbers, electrostatic precipitators (ESPs) and fabric filters. The emission control unit is of European standards, so it easily adheres to the guidelines of Ministry of Environment, Forest and Climate Change, India. The fly ashes arrested by the emission control unit are disposed as per guidelines in a treatment storage and disposal facilities (TSDFs) (figure.4-1).

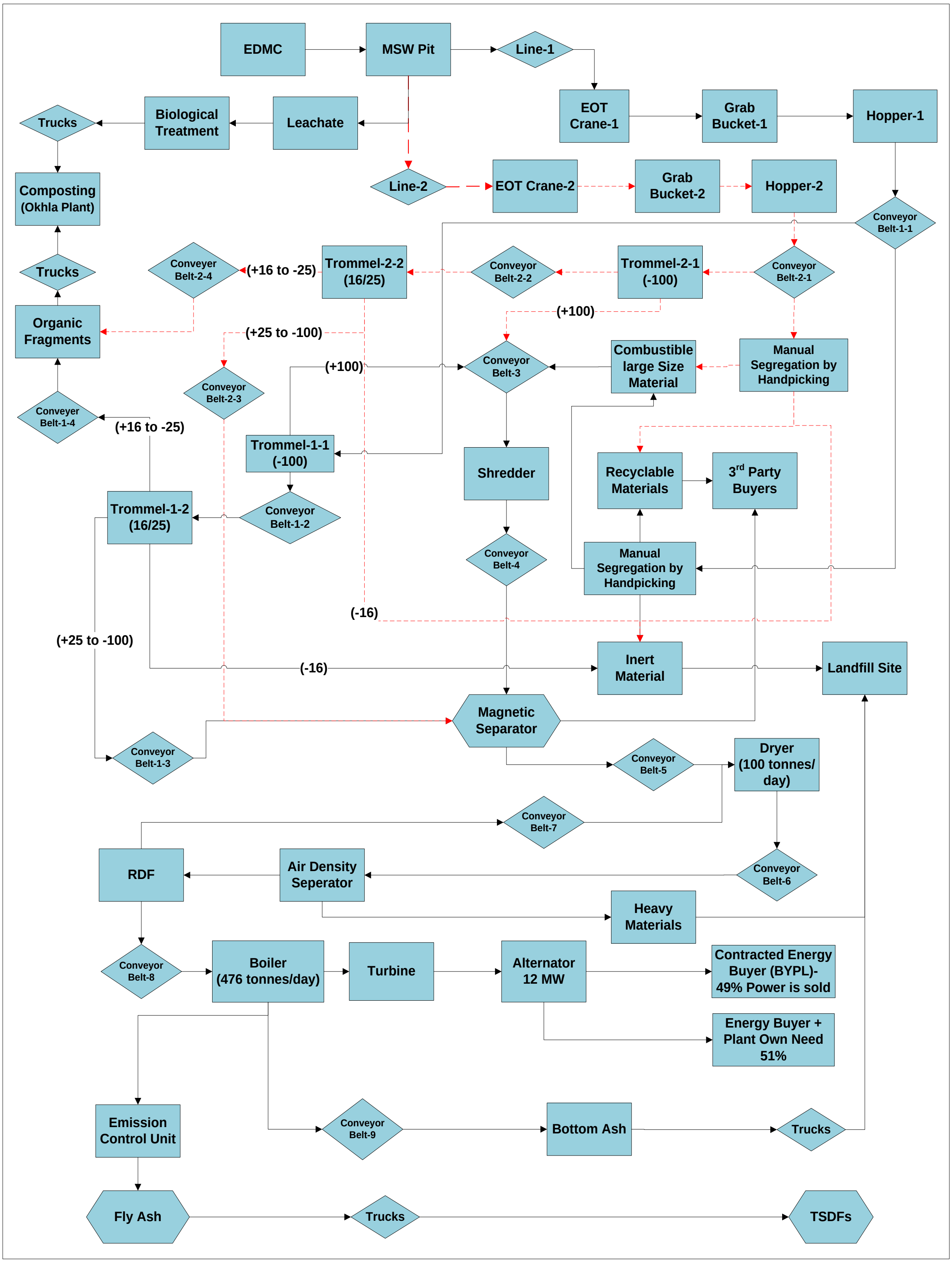

Figure.4.1.Process flow of waste in Case-1 WTE plant

An analysis was carried out to calculate the approximate heating value and mass energy balance of the process; the average value of the typical waste characteristics of the feed waste received by the plant is shown in table.4-1. The table gives the typical composition of the discarded solid waste with mass percentage and moisture percentage. Volume of each component is calculated with the help of density of each component.

Component	Mass (%)	Moisture (%)	Density (kg/m^3)	Calorific value (Kcal/Kg)	Dry weight	Volume (m^3)
Food waste	35.00	50-80	120-480	3114.24	22.246	0.13
Paper	7.00	4-10	30-130	3546.21	0.66	0.04
Cloths	5.00	20.00	150.00	4414.4359	0.8	0.05
Plastic	3.00	1-4	30-156	5850.86	0.15	0.03
Glass/metal	5.00	1-4	90-260	38.24	0.185	0.01
Inert silt, construction and demolition (C&D) waste	45.00	6-12	800-1500	0.00	25.75	0.02

Table.4-1. Estimated waste composition coming into the plant

The detailed chemical analysis in the laboratory revealed the following chemical composition of the received waste. The typical chemical composition of the various constituents of solid waste with percentage of chemical proportion of carbon, hydrogen, oxygen, nitrogen, sulphur and ash in various waste components have been analysed and given in table.4-2. The one with higher percentage of carbon has higher calorific value and the one with higher percentage of inert material has lower calorific value.

Component	Composition (%)					
	C	H	O	N	S	Ash
Food waste	48	6.4	37.6	2.6	0.4	2.8
Paper	43.5	6	44	0.3	0.2	6-20
Clothes	50.00	5.00	30.00	5.00	0.00	10.00
Plastic	60	7.2	22.8	0.00	0.00	6-20
Glass/ metal	0.00	0.00	0.00	0.00	0.00	100.00
Inert silt, C&D waste	0.00	0.00	0.00	0.00	0.00	100.00

Table.4-2. Typical chemical composition of the various constituents of solid waste

Based on the calculation and data in table.4-1 & 4-2, the chemical composition by weight for a sample of 100 kg, of discarded solid waste is as shown in table.4-3. The amount of carbon, hydrogen, oxygen and sulphur in 100 kg of the discarded solid waste is given in table.4-3.

Component	Dry Weight	Composition, kg					
		C	H	O	N	S	Ash
Food Waste	22.246	8.8984	1.1123	8.45348	0.33369	0.11123	3.3369
Paper	0.66	0.198	0.033	0.33	0	0	0.099
Clothes	0.8	0.4	0.04	0.24	0.04	0	0.08
Plastic	0.15	0.06	0.0075	0.045	0	0	0.0375
Glass/Metal	0.185	0	0	0	0	0	0.185
Inert, Silt, C&D waste	25.75	0	0	0	0	0	25.75
Total	49.791	9.5564	1.1928	9.06848	0.37369	0.11123	29.4884

Table.4-3. Waste chemical composition coming into the plant

To increase the calorific value of the waste input, the MSW is processed, as discussed, to produce RDF. The RDF is then fed into the furnace as fuel. The chemical analysis and the study of RDF shows increased energy production from RDF feeding. The analysis of the chemical composition of the original waste coming from the municipalities has been shown in table.4-4 and chemical composition of the RDF formed is shown in table.4-5.

Element	Mass, kg	Kg/mol	Moles	Mole Ratio (approx.)	Components (%)
C	10.63	12.01	0.885096	29.68	10.63
H	1.325	1	1.325	44.43	1.325
O	10.05	16	0.628125	21.06	10.05
N	1.9175	14	0.029821	1.00	1.9175
S	0.1225	32	0.003828	0	0.1225
Ash	26.705	0	0	0	26.705
Moisture	49.25	0	0	0	49.25

Table.4-4. Chemical analysis of the waste composition received

The calorific value was calculated from the data obtained from Table 4-4 & 4-5, by applying the Dulong's formula $[\frac{kJ}{Kg} = 337C + 1428(H - \frac{O}{8}) + 9S]$ (Reza et al., 2013) and the calorific value obtained for the waste in term of received basis is 879.91Kcal/kg and based on the processed RDF is 4298.67Kcal/kg.

Element	Mass, kg	Kg/mol	Moles	Mole Ratio (approx.)	Components (%)
C	38	12.01	3.167	35.58	38
H	7	1	7	78.65	7
O	27	16	1.687	18.95	27
N	1.25	14	0.089	1	1.25
S	0.35	32	0.0109	0	0.35
Ash	12	0	0	0	12
Moisture	14.4	0	0	0	14.4

Table.4-5. Chemical analysis of RDF with external moisture

4.2.2. Case study-2

The WTE plant is situated in Karimnagar district of Andhra Pradesh. The plant's electricity generating capacity is 10 MW/day. The plant uses Refuse Derived Fuel (RDF) which is obtained by processing MSW in the WTE plant itself. The waste is received from the nearby town of Adilabad and Karimnagar Districts. The quality of garbage is not consistent, hence overall RDF generation varies from 25% to 35%. The final moisture content in the RDF obtained is below 10%. The composition of the waste received by the plant consist of 50% organic, 5% paper, 7% clothes, 4% plastic, 5% glass/ metal and 29% inert materials. The plant has been operational since July, 2008. The plant has two operating unit, one unit is the RDF and composting plant while the other unit is the incineration based WTE plant. RDF prepared in one unit is transferred to another unit by the use of trucks. The maximum electricity generation capacity is 20 MW while the average electricity generated is 8-9 MW. Approx 200-300 tonne of MSW is provided by the municipality every day. There is no tipping fee from the government for disposing the municipal corporation waste. In the feed, 15% coal is added to increase the calorific value of the feedstock, the coal which is fed to the furnace has calorific value in the range of 3600 - 4200 kcal/kg. The transportation cost is the most expensive process in the total supply chain of the waste flow of this plant, the average cost is USD 15 per tonne depending on the distance. In the RDF and composting plant, mixed waste received is segregated by the rag pickers who collect the recyclable items including plastics and sold them in the market. Sorting in the plant is done to further remove the inert and recyclable materials which are still left in the waste. The removal of plastic reduces the RDF calorific value and quantity as Indian waste approximately contains 40-60% of organic fragments. From the 200-300 tonne of MSW received daily the RDF generation is hardly 10-

15 tonne/day. The municipalities collect wastes from the adjoining municipal areas and transfer it to the plant's covered storage area. The waste is then transferred to the pre-sorting area by a dumper. The pre sorting process allows the rag pickers to remove the plastic and recyclable items to be sold off to the 3rd party recycler. After the pre sorting the waste is passed through a magnetic separator to separate out the magnetic fraction. The metallic portions are sent to the market for resale while the larger inert materials are removed from the conveyer belt and disposed of to landfill site by trucks (figure.4-2).

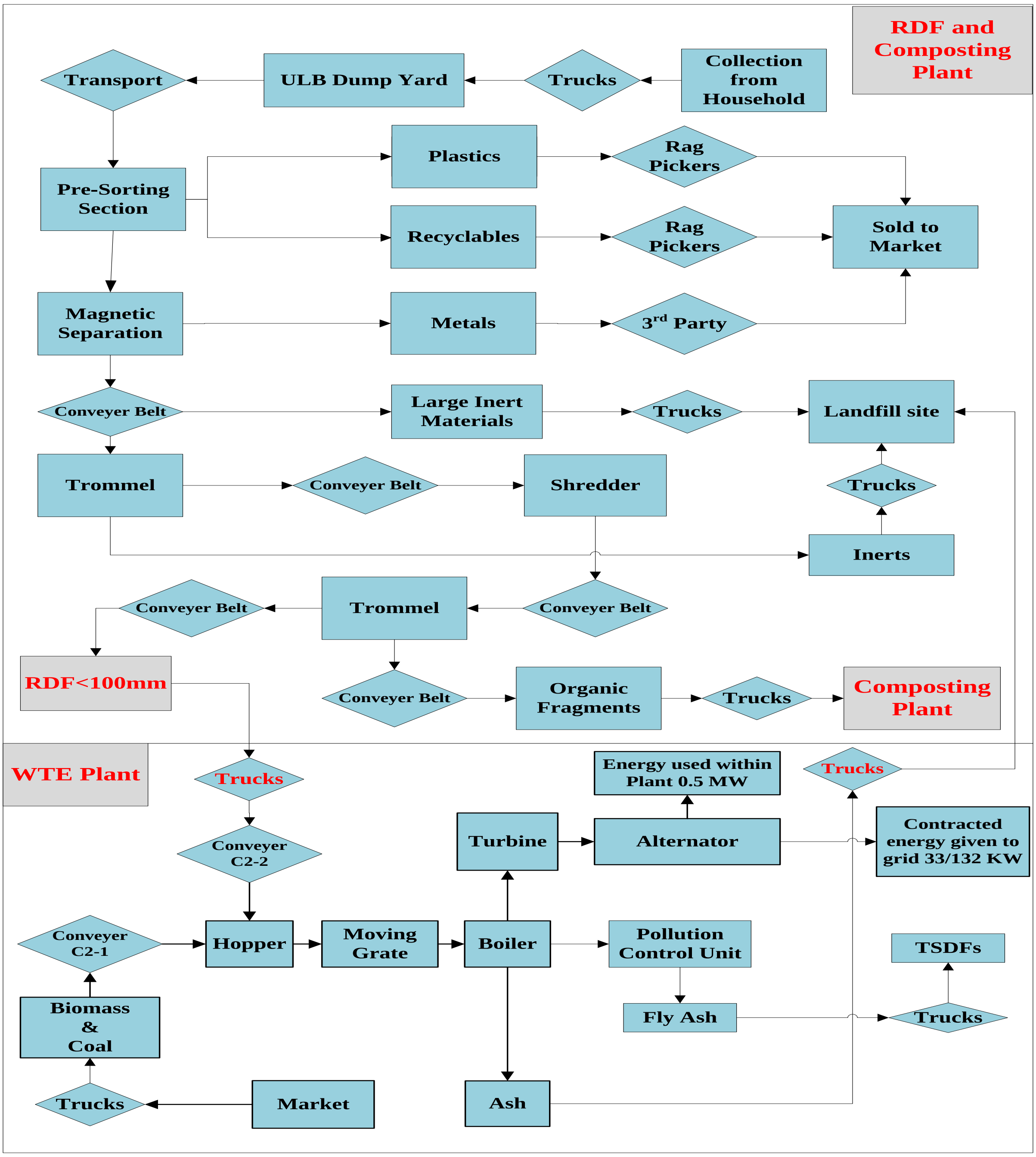

Figure.4-2. Process flow of waste in Case-2 WTE plant

The waste is then passed through a trommel by conveyer belt followed by a shredder and further segregation by the second trommel to produce the final product, that is RDF (<100). The remaining part is separated out as organic fragments and small fraction of inert which is further processed to separate out the inert and organic fraction. The organic fraction ends up as compost and sold to the farmers. The RDF is then transported to the other unit by trucks; on reaching second plant it is mixed with coconut fibre, rice husk and coals to increases the calorific value of the feed stock. The rice husk, coconut fibre and other biomass are bought from market. The purchased material is stored in unit-2. The conveyer line C2-1, C2-2 takes the biomass, coal (15%) mix materials and RDF respectively into the hopper for firing in to the furnace, the furnace, which is of moving grate type. The furnace runs the boiler which drives the turbine and generates 8-12 MW via alternator. Maximum capacity of waste intake of the plant is 400 tonnes/day. If pre-decided amount of electricity is not supplied to the grid, a fine is levied at the rate of difference from threshold at USD 0.01/KWh. The emission control devices are as per the standard of Ministry of Environment, Forest and Climate Change (MOEF&CC), India. The bottom ash generated is collected and sent to the landfill site by trucks. The fly ash is disposed off to a treatment storage and disposal facilities (TSDFs) as per MOEF&CC guidelines. The two kinds of ash generated are bottom ash and fly ash. The electricity generation is of 10.5 MW out of which 0.5 MW of energy being used up by the plant leaving a net 10 MW of energy to be supplied to the grid. Contracted energy given to grid is 33V/132KW. The plant faces issue during closure. There have been closures due to failures in the boiler. Poor quality of the waste corrodes the boiler shell. The corrosion in boilers is usually caused by chloride compounds which deposit on the furnace, super heater and boiler tubes. Several modes of chloride corrosion usually occur which include corrosion by hydrochlorides (HCl) in the combustion gas, corrosion by metal chlorides (mainly $ZnCl_2$ and $PbCl_2$), corrosion by NaCl and KCl deposits on tube surfaces. The shutdown of the plant puts an extra burden of penalty on the plant. The mass percentage of the various components obtained from the MSW is shown in table.4-6.

Component	**Mass (%)**	**Moisture (%)**	**Density (kg/m^3)**	**Calorific value (Kcal/Kg)**	**Dry weight**	**Volume (m^3)**
Food waste	50.00	70.00	400.00	3201.54	15.00	0.13
Paper	5.00	10.00	130.00	3897.54	4.50	0.04
Cloths	7.00	20.00	150.00	4012.59	5.60	0.05
Plastic	4.00	10.00	150.00	5239.32	3.60	0.03
Glass/metal	5.00	5.00	1500.00	27.14	4.75	0.01
Inert silt, C&D waste	29.00	50.00	1200.00	0.00	14.50	0.02

Table.4-6. Waste composition coming into the plant

Based upon the calculations and data in table.4-6, the chemical composition by weight for a sample of 100 kg solid waste is shown in table.4-7. From table.4-7 the amounts of carbon, hydrogen, oxygen and sulphur in 100 kg of the solid waste were calculated using Dulong’s formula. To increase the calorific value of the waste input, the MSW is processed as discussed, to produce RDF. To increase the calorific value, more biomass and coal is added to the RDF. The RDF is then fed into the furnace as a fuel. The analysis of the chemical composition of the original waste coming into the municipalities is shown in table.4-7 and the chemical composition of the RDF-coal-biomass mixture formed is shown in table.4-8. The calorific value was calculated from the data (table.4-9), employing Dulong’s formula is 4957.52 Kcal/kg.

Component	**Dry weight**	**Composition, kg**					
		C	**H**	**O**	**N**	**S**	**Ash**
Organic waste	15.00	6.00	0.75	5.70	0.23	0.08	2.25
Paper	4.50	1.35	0.23	2.25	0.00	0.00	0.68
Clothes	5.60	2.80	0.28	1.68	0.28	0.00	0.56
Plastic	3.60	1.44	0.18	1.08	0.00	0.00	0.90
Glass/ metal	4.75	0.00	0.00	0.00	0.00	0.00	4.75
Inert silt, C&D waste	14.50	0.00	0.00	0.00	0.00	0.00	14.50
Total	47.95	11.59	1.44	10.71	0.51	0.08	23.64

Table.4-7. Chemical analysis of the waste composition coming into the plant

Component	**Dry weight**	**Composition, kg**					
		C	**H**	**O**	**N**	**S**	**Ash**
Organic waste	15.00	3.00	0.60	5.51	0.20	0.03	2.25
Paper	4.50	0.80	0.20	1.80	0.00	0.00	0.68
Clothes	5.60	0.24	0.10	1.38	0.11	0.00	0.56
Plastic	2.60	0.90	0.10	1.0	0.00	0.00	0.90
Biomass	5.00	0.65	0.02	0.02	0.00	0.00	0.95
Coal	15.00	6.00	0.50	1.0	0.20	0.06	1.5
Total	47.70	11.59	1.51	10.71	0.51	0.09	6.84

Table.4-8.Chemical analysis of the waste feed (RDF-coal-biomass mixture)

Element	**Mass, kg**	**Kg/mol**	**Moles**	**Mole ratio (approx) Nitrogen = 1**	**Components (%)**
C	51.59	12.01	4.29	47.66	51.59
H	6.1	1.00	6.1	67.77	6.1
O	30.5	16.00	1.9	21.11	30.5
N	1.28	14.00	0.09	1.00	1.28
S	0.08	32.00	0.00	0.00	0.08
Ash	3.64	0.00	0.00	0.00	3.64
Moisture	7.05	0.00	0.00	0.00	7.05

Table.4-9. Chemical analysis of RDF waste

4.2.3. Case study - 3

The plant chosen for third case study is situated in Okhla region of South Delhi. It is a mass burn incineration facility, disposing and processing 1300 tonnes of municipal solid waste per day. The waste is collected from six lakhs homes in the New Delhi Municipal Corporation area by the municipality. The approximately 1500 tonnes of waste is then transported by trucks and dumpers by the municipalities to the plant stockyard. The composition of the waste received by the plant consist of 31.78% organic, 6.6% paper, 4% clothes, 1.5% plastic, 3.7% glass/ metal and 51.5% inert materials. The organic fragment in waste is approximately 40-60%. There exists an uncertainty in the waste supply due to seasonal variation. In case of shortage of wastes, it is supplied from other municipalities on a case to case basis and also form rejects of the compost plant (inorganic fragments). The plant line is mechanized with single manual segregation stage. Manual segregation is the primary segregation methods used by the plant for segregation of large size, inert and recyclable materials from waste stream consisting of combustible waste. The waste, after dumping is stored for two days for removal of moisture (figure.4-3). After storing for two days, an EOT crane with bucket arrangement is used to churns the waste, to aerate the waste and to remove moisture, thus increasing the rate of drying. Approximately 50- 60% of the moisture is removed by drying process.

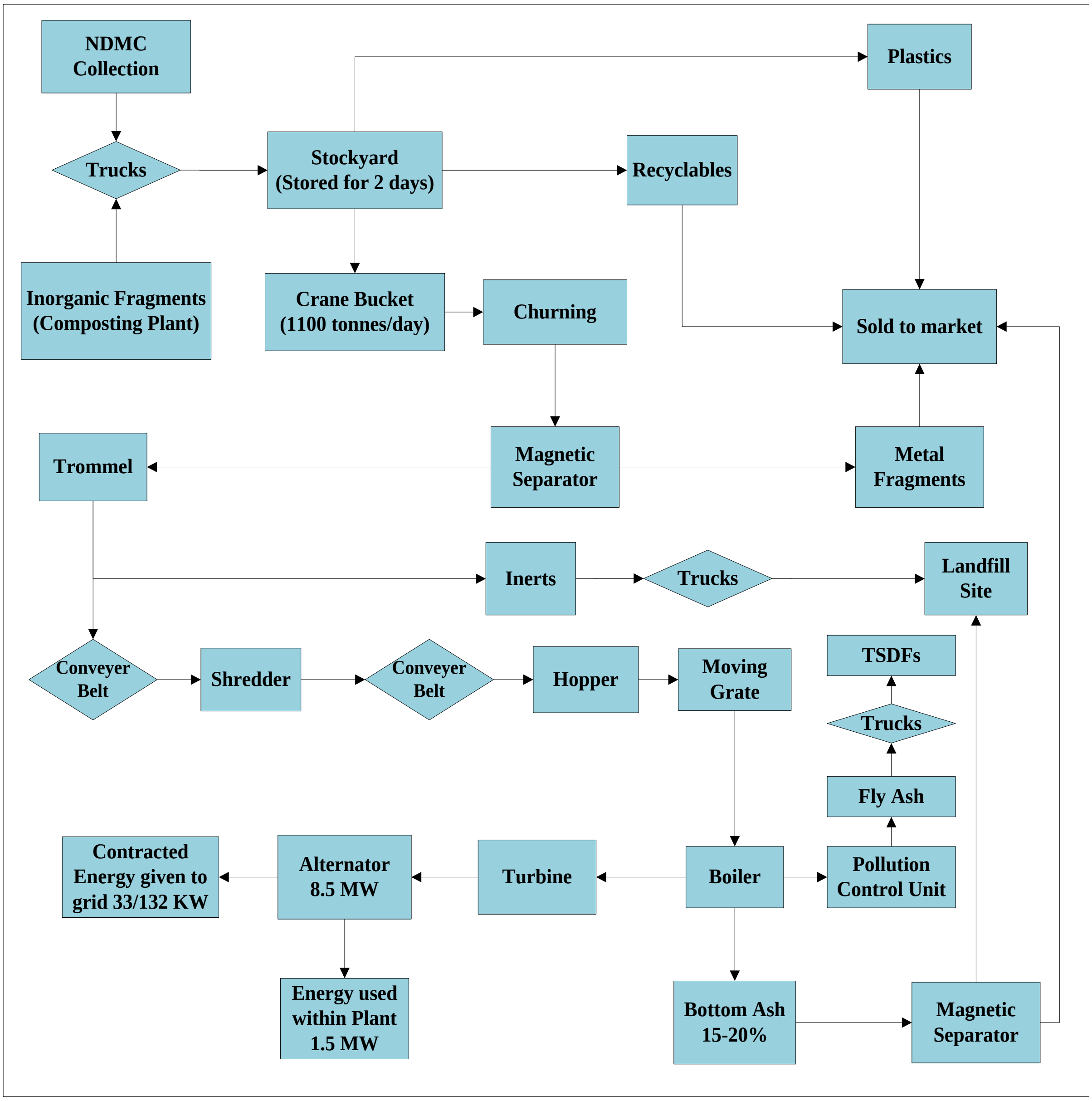

Figure.4-3.Process flow of waste in Case-3 WTE plant

The waste in it raw state constitutes 40 – 50 % of moisture. The calorific value of the waste is approximately 650-1000 Kcal/kg. The churned waste then moves into the incinerator through a conveyor belt. The incinerator is a moving grate type incinerator. The major issue faced by the plant is the presence of construction and demolition waste which leads to reduction of the calorific value. Poor quality of waste also leads to increase in the maintenance cost of the machinery. Being a mass burn type incineration plant there is very less segregation in the process line. The pre-sorting phase excludes plastics, inert materials and recyclable materials. This removal is carried out manually by the rag pickers. The removal of inert materials and recyclables is an effective segregation methodology of the process but removing of plastic reduces the calorific value of the feed stock thus ultimately this segregation reduces the quality of the wastes being burnt. The plant has been operational for last four years and the promised subsidy for disposing of MSW by the government is yet to be received hindering the sustainability of the plant.

A magnetic separator removes the metal fractions which are sold to the 3rd party buyer. The waste is then passed through trommel for separation of further inert material before falling on to a conveyer belt. The waste from the conveyer belt goes to the shredder and the shredded waste then empties in to the hopper of the feeding system. The waste via hoppers drops on to the moving grate for burning. As the grate moves the combustion of waste take place and this in turn produces superheated steam in the boiler. This boiler then drives a turbine which rotates an alternator to produce power. The power generated is approximately 8.5 MW/day of which the plant itself consumes 1.5 MW. The recyclable material and plastics which are collected are also sold to third party buyers. The inert materials along with the ash collected are sent to the adjacent landfill site. The prominent difference from the other two plants is that this plant doesn't use RDF for its firing. The emission arresting device is highly effective with bag filter to collect the fly ash generated during the combustion. The bottom ash collected contains metal which are being separated by a magnetic separator and the remaining ash is transported and dumped in the nearby landfill site. The fly ash is disposed of as per the guidelines of Ministry of Environment, Forest and Climate Change, India at a treatment storage and disposal facilities (TSDFs). The approximate heating value of the system was calculated, the average of the typical waste characteristics of the considered waste is shown in table.4-10. The study of the typical solid waste, received by the plant is considered to be comprising of the data as shown in table.4-10. The chemical analysis of various components obtained from solid waste is shown in table.4-10.

Component	**Dry Weight**	**Composition, kg**					
		C	**H**	**O**	**N**	**S**	**Ash**
Organic	22.246	8.8984	1.1123	8.45348	0.33369	0.11123	3.3369
Paper	0.66	0.198	0.033	0.33	0	0	0.099
Clothes	0.8	0.4	0.04	0.24	0.04	0	0.08
Plastic	0.15	0.06	0.0075	0.045	0	0	0.0375
Glass/Metal	0.185	0	0	0	0	0	0.185
Inert, Silt, C&D Waste	25.75	0	0	0	0	0	25.75
Total	49.791	9.5564	1.1928	9.06848	0.37369	0.11123	29.4884

Table.4-10. Waste composition coming into the plant from the municipality

Based upon the calculations and data in table.4-10, the chemical composition by weight for a sample of 100 kg, discarded solid waste is given in table.4-11. Based on the Dulong's formula the calorific value obtained is 785.03 Kcal/kg. The characteristics of the waste obtained from the municipalities in the case-1 and case-3 stands approximately similar due to the municipal solid waste coming from the same locality. The calculated calorific value of available energy from the waste is similar but the technology used by case 1 is more efficient, further case-1 uses RDF, which increases the calorific value of the feed. Case-2 makes RDF and is successful in reducing the moisture content of the RDF to below 10% of the mass of waste input feed and also augments the feed with coal and biomass, thus improving the operating calorific value. As can be seen from the calorific value in term of per tonne basis of feed, the case-1 is most effective over other cases and case-3 is the worst in term of sustainability as the calorific value obtained is meagre and the business model lacks sustainability.

Element	Mass, kg	Kg/mol	Moles	Mole Ratio (approx)	Component (%)
C	9.5564	12.01	0.795	30.57692	30.7
H	1.1928	1	1.192	45.84615	46.17
O	9.06848	16	0.566	21.76923	21.92
N	0.37369	14	0.026	1	1.01
S	0.11123	32	0.003	0	0.11
Ash	29.4884	0	0	0	0

Table.4-11. Chemical analysis of waste with external moisture and inert

4.3. Results and Discussion

The WTE plant sustainability largely depends on the reverse logistics of the waste management practice in India. The reverse logistic comprises collection, secondary storage, transportation and in some cases segregation after collection. The WTE plant in India till date hasn’t been sustainable due to an ineffective supply side. The WTE plant’s foremost requirement is segregated waste with lesser organic fragments but in all the plants the characteristics of waste is of mixed waste with varying organic composition from 40 - 60% depending upon the plant location. The waste quality is a major issue as the high calorific valued items are generally removed by the rag pickers from the secondary storage the left over is mainly organic fragments. The WTE plant’s backward side supply chain is also lacking in number of important factor like ash treatment, effective emission control, social acceptance etc. The internal supply chain is also not robust due to unavailability of indigenous technology. All the plants that were studied use imported technology which is unsuitable for the Indian waste characteristics; the technology needs to be compatible with Indian environment and waste management practices. Indian waste management practices lack the foremost part of segregation at any level, even though in some places the waste is collected in to segregated form but ultimately it ends up as mixed waste. The basic supply chain frame work for waste management in cities has been elaborate below in figure.4-4.

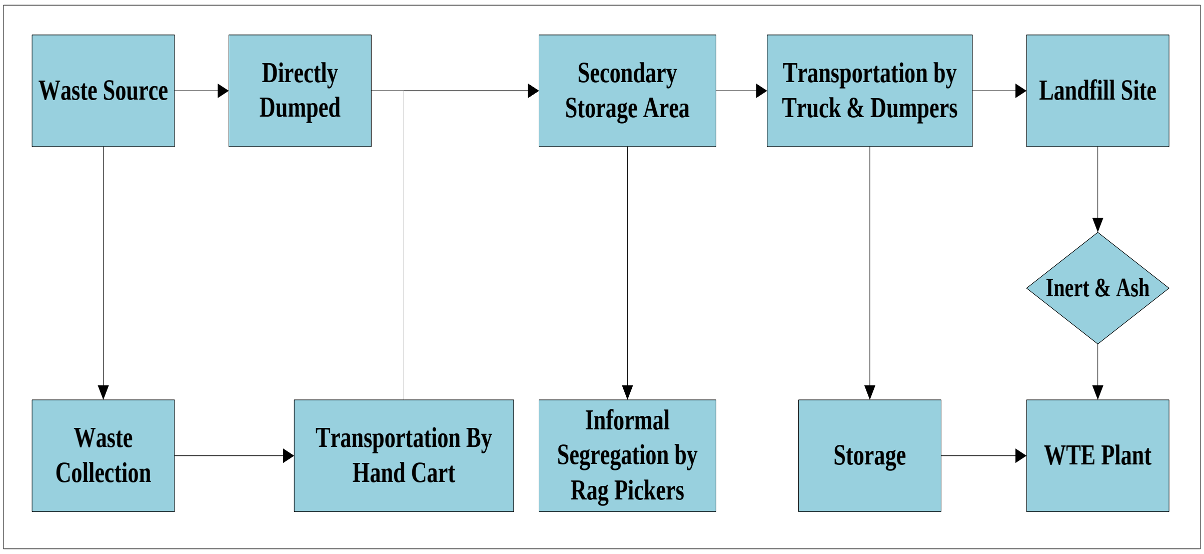

Figure.4-4. Basic supply chain of waste for WTE plant

The house hold waste in some cities is collected by door to door collection system. These wastes are collected by a small hand cart with capacity of 200 kg. The collected waste is dumped in to secondary storage area from where daily, trucks or dumpers carry the MSW to the landfill site and in some case to a WTE plant. The waste is also directly dumped in to the secondary storage area by the producer, due to lack of door to door collection system. The secondary storage area is inflexed with informal rag picker who usually removes/handpicks valuable recoverable items like plastic, papers, etc. Though manual scavenging is banned by the law of land, it is being practiced informally. Being an unhygienic practice that it is, the rag pickers usually increase the rate of recycling of waste which would have otherwise end up in landfill or would have been incinerated. But this removal is not good for the sustainability of the WTE plant as high calorific valued items are removed and the waste is left with high content of inert waste and organic fragments. For the supply chain to be sustainable, the system must be overhauled and rag pickers are need to be incorporated in the supply chain of WTE plant process as can be seen in the Case-1, in which around 60 rag pickers were formalized and absorbed in to the plant for manual segregation. Although Case-2 has also incorporated rag pickers in to their pre processing system but it acted as a negative factor for the WTE plants as the high calorific contents were removed.

A similar practice like Case -1 needs to be incorporated in other plants. The employment of rag pickers for wastes value creation can be a learning experience for industries where they segregate the low calorific value materials. The solution to this reduced calorific quality of wastes can be improved if the segregation of waste starts from the source. The wastes can be collected from household based upon end product. The collection if done category wise and if the wastes reach the plants in segregated form it will lead to an improvement in quality of wastes thus increasing the calorific value of the feedstock. The presence of slag comprising mainly of silt and construction and demolition waste, if avoided, can lead to improvement of the supply chain of the waste to energy plant as well as increase the sustainability of the plant. The supply chain can be made holistic if a well defined formal process of collection system of waste is practised and the waste supply being made to the plant by a well defined logistic system. Although the latest Solid Waste Management Rules, 2016 emphasises on segregated storage and collection but implementation is still lacking. Well defined logistics support would have a well demarcated area of coverage, source and destination. In the collection system, three bin collection system of waste exists in some areas but during their collection by municipalities they are mixed together, thus producing mixed waste.

The working of the plants needs high capital and investment costs so government support and subsidy is highly needed. The downtown time faced by the companies poses economic pressure on the stakeholders of the plant. The monetary aids in form of waiving off the penalties, gate fee and tipping fee can highly increase the sustainability of the waste to energy plants in India. People are getting aware of the need of an effective waste management practice and community participation is increasing. Based on the challenges and issues and as per the rule a waste management system specific to the requirement of the WTE plant has been proposed which addresses the hindering factors and incorporates them to make a holistic waste management system (figure.4-5).

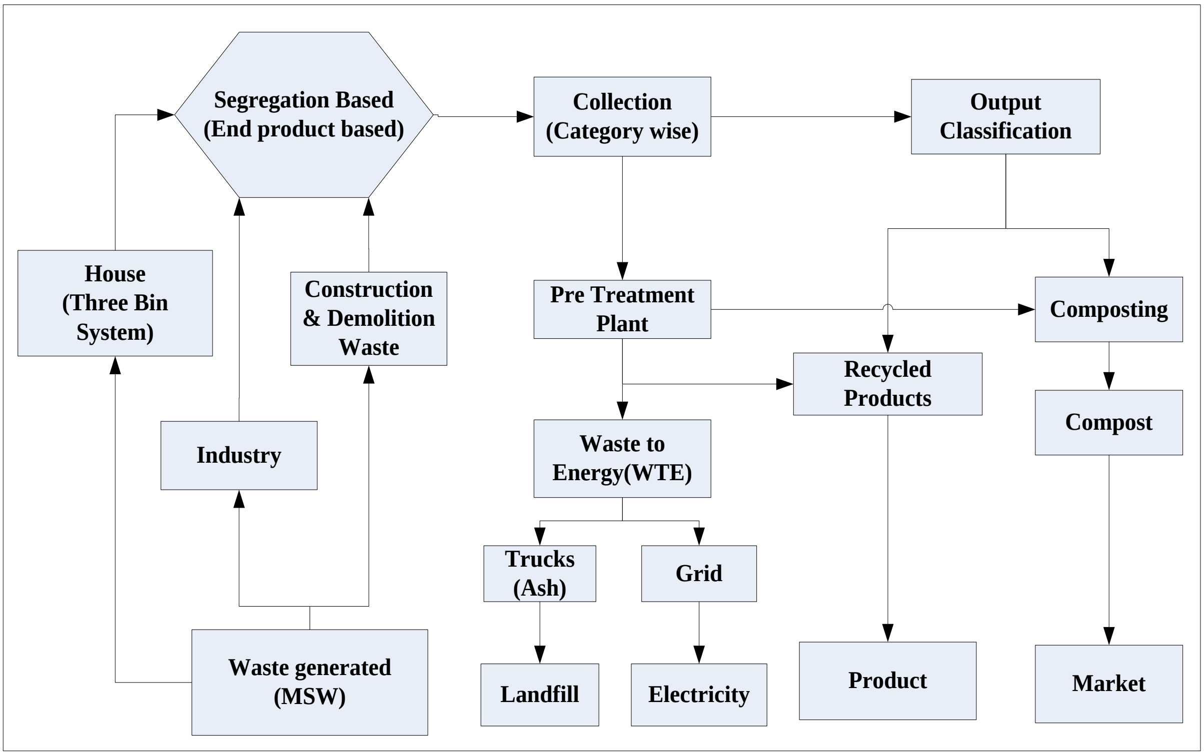

Figure.4-5. Proposed framework of waste for sustainable WTE plant

4.4. Conclusion

There are a number of constraints within the supply chain of the WTE plant. The supply chain is plagued with more issues and challenges in forward side of the WTE plant. Some of the challenges and issues as revealed from the literature and case studies are, steady flow of required quality of MSW, segregations of waste, low calorific value of the wastes and seasonal variation. The sustainability is largely depended on the administrative and economical aspects components like tipping fee, incentives in unit price of the electricity generated from the WTE plant. The WTE plants to become sustainable needs an effective policy implementation, as the law Solid Waste Management Rules, 2016 mandates number o aspect in this regards but the implementation is still lacking. The issues and challenges as found from the study are mandated in the rules which once implemented the sustainability may be improved. Thus the issues and challenges once addressed the whole supply chain network will become holistic and sustainable business model will be developed as for the Case- 1 is already a sustainable venture but if this issues are address the business model will become highly economical system.

Chapter 5

Selection Framework of Sustainable Thermo-chemical Technology for Energy and Resource Recovery in India

(Addressing Objective – 2)

5.1. Introduction

Municipal Solid Waste (MSW) is an unavoidable by-product of human activities (Akdağ et al., 2016).The management of municipal solid waste (MSW) is a big concern today for city authorities and planners due to increasing population, urbanization, and limited land space. Waste management constitutes one of the main problems of daily life in all the industrialized countries and its efficacy depends on multiple aspects such as the level of technological development, the characteristics of waste material and cultural level of the local population. Raising concerns about potential health effects and land value are increasing the cost for waste treatment (Barba et al., 2015). The traditional treatment and dumping of different solid waste has some key environmental challenges such as leachate generation and GHG emissions (Khan et al., 2016). Waste is being generated at a rate which outstrips the ability of the authorities to manage it (Tan et al., 2015). Improper land filling of waste has number of negative impact (i) the contamination of surface and groundwater; (ii) soil contamination; (iii) air pollution through burning of wastes; (iv) spreading of diseases by different vectors like birds, insects, and rodents; (v) odour from landfills, and (vi) uncontrolled release of methane by anaerobic decomposition of waste (Ngoc and Schnitzer, 2009).

Rapid development in India has led to severe problems with management of the waste. The management of MSW is complex due to its variable composition, which depends on local demographic and their habits (Nixon, Dey, et al., 2013). Waste management and disposal is a pressing issue facing India, since about 90% of waste is currently disposed of by open dumping (Narayana, 2009). India generated around 277.136 million tonnes of municipal solid waste, 7.234 million tonnes of hazardous waste and around 30 million tonnes of non hazardous industrial waste as of 2016 (Kaza et al., 2018). This enormous amount of waste has a huge potential in terms of resource and energy recovery. Thus, effective disposal operations have the advantages of energy and resource recirculation with added advantage of reduction in landfill able waste (Arafat et al., 2015). The acceleration in urbanisation and increasing income per capita further speeded up the waste generation rate (Ng et al., 2014) increasing the onus on energy and resource recovery strategies (Akdağ et al., 2016). The utilisation of MSW and other stream of waste as an alternative resource could overcome waste disposal challenges, generate power for fossil fuel displacement and mitigate GHG emissions by converting CH_4 to CO_2 (Tan et al., 2015). With proper waste handling, management practice and treatment environmental impacts can be reduced to a sustainable level (Fodor and Klemeš, 2012).

Assessment of the impact of major environmental factors have highlighted a range of environmental benefits to be gained through energy and resource recovery from MSW and other waste stream, including reduced GHG emissions, acid gas emissions, conservation of natural resources, impact on water (leaching), and reduced land contamination (Khraisheh and Li, 2010; Sonesson et al., 2000). Energy and resource recovery from waste plays a key role in sustainable waste management and energy security.

There are numerous technologies that vary in suitability for different economic condition and social climates (Yap and Nixon, 2015). Several studies have tried to clarify which waste to energy and resource recovery system or process is best suited, based on economical and environmental impact. As the technological alternatives for generating electricity and resource recovery grows in number and complexity, strategic decisions making for the effective evaluation of this technology becomes an area of concern. An optimal choice is subject not only to economic requirements but environmental regulation compliance requirements. Therefore, it is necessary to combine all of these factors in order to make acceptable trade-offs. From the point of view of technology, there is usually a choice of best available technologies – BAT (Stehlik, 2009); but a proper analysis based on the merits of each case with reference to existing situation and constructs is imperative before a selection is made. There are number of way in which energy and resource is recovered from waste by indirect or direct means. The current study is limited to certain thermo-chemical based technologies which are at different stages of commercialization in India, this process were assessed based on the different constructs considering four pillars of sustainability. The technology considers includes gasification, incineration, pyrolysis and co-processing (Baidya et al., 2017; Bolzonella et al., 2003; Young, 2010). The present work analysis different technology qualitatively and quantitatively considering number of key constructs of sustainability common to each of the technology. The constructs were gauged based on the secondary data and field study. Some of the constructs which were qualitative in nature were gauged with the help of multiple criteria decision making (MCDM) approach using analytical hierarchy process (AHP).

5.2. Materials & Method

The study involves qualitative and quantitative analysis of the different technology based on the literature findings and primary data. Firstly, a detailed literature review and primary data collection were done to identify the thermo-chemical technology/process and sustainability constructs for energy and resource recovery from waste considering four sustainability pillars namely operational, economical, environmental and social. The constructs considered for the analysis were applicable for all the process. Secondly, the qualitative constructs identified were gauged using multiple criteria decision making process - analytical hierarchy process (AHP). A questionnaire was developed as per saaty scale to collect the ratings for pair-wise comparison as per AHP methodology. The ratings for the pair-wise comparison were obtained from an expert group of person including scientists, researchers, academician, industry experts, operational and technical managers of energy and resource recovery plants. The ratings were obtained by developing a consensus among the expert panel. Thirdly, the ranking obtained from the AHP analysis were used for assessment of the qualitative constructs and ranking of the technology was done. Finally, the individual ranking score of each technology/process based on the individual constructs of all the sustainability pillars provided overall assessment for the sustainable technology in terms of the Indian waste management practices. The detail methodology applied for the AHP has been discussed below.

5.2.1. AHP methodology adopted for assessment of qualitative sustainability constructs

The methodology adopted for the AHP analysis has been adopted from the Saaty (Saaty, 1990; Saaty and Kearns, 2014). The AHP analysis used simply to gauge the importance of the constructs with each other through a pair wise comparison for each of the technology. The AHP has been used to prioritize, that is a ranking was obtained. The AHP analysis has been carried out by using the open source super decision software. The basic steps involved in AHP analysis have been elaborated below.

Step 1. Define the problem and determine its goal.

Step 2. Construct a set of pair-wise comparison matrices of size n×n for each of the lower levels with one matrix for each element in the level immediately above by using the relative scale measurement. The pair-wise comparisons are done in terms of which element dominates the other as per the saaty scale (table.5-1).

Step 3. There are n (n-1)/2 judgments required to develop the set of matrices.

Step 4. Hierarchical synthesis is then used to weigh the eigenvectors by the weights of the criteria and the sum is taken over all weighted eigenvector entries corresponding to those in the next lower level of the hierarchy.

Step 5. Having made all the pair-wise comparisons, the consistency is determined by using the Eigen value, λ_{max}, to calculate the consistency index, CI as follows:

$CI = (\lambda max - n) / (n - 1)$ ....equation 1

Where n is the matrix size. Judgment consistency can be checked by taking the consistency ratio (CR) of CI with the appropriate random index (table.5-2). The CR is acceptable, if it does not exceed 0.10. If it is more, the judgment matrix is inconsistent. To obtain a consistent matrix, judgments should be reviewed and improved.

CR = CI/Random Consistency ....equation 2

Numerical rating	**Verbal judgments of preferences**
1	Equal importance
3	Somewhat more important
5	Much more important
7	Very much more important
9	Absolutely more important.
2,4,6,8	Intermediate values

Table.5-1. Saaty scale

Size of matrix	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Random consistency	0.00	0.00	0.58	0.90	1.12	1.24	1.32	1.41	1.45	1.49	1.51	1.48	1.56	1.57	1.59

Table.5-2. Random consistency index

5.2.2. Methodology adopted for ranking sustainability of each technology/process

The qualitative constructs analysed by AHP provided the ranking, with rank value from 1 to 4 for each of the technologies, considering each of the constructs. The quantitative constructs were compared based on the quantifiable value, obtained from literature and field study. The sustainability ranking of individual constructs forms the basis for overall score of the technologies. Each of the four sustainable pillars was assessed separately and the ranking obtained under each of the constructs of operational, economical, environmental and social sustainability were added up to obtain the total sustainability score. The sustainability score thus obtained for each of the technology considering all the constructs both qualitative and quantitative provided the final sustainability ranking.

5.3. Results & Discussion

The assessment of the technology was done by considering numerous constructs under the four sustainable pillars considering Indian specific scenario. The qualitative constructs ranked with the help of AHP are pre-treatment/feed stock preparation requirements, specific emissions controlling requirements, pre-treatment cost, different waste streams which can be disposed/utilized in a single setup, by-product characteristics nature, people perspective issues/public acceptance, odour, perceived pollution issue, noise problem and expertise requirement. The quantitative constructs are retention/residence time /process time, overall system efficiency, volume reduction, land requirements, capital cost, operational and maintenance cost, CO_2 emission and by product generation by volume of input waste. All the constructs were identified based on the fact that they were common to the four technologies, assessed for Indian case, further the constructs forms the basis of the sustainability of the technology considering operational, economical, environmental and social pillars of sustainability. This AHP analysis of the pre-treatment/feed stock preparation requirements revealed incineration is the best followed by gasification, co-processing and finally pyrolysis. All the four process requires a pre–processing and feed preparation step but incineration process can handle a wide array of waste types and sizes. The feed preparation as such hardly requires any shredding or fingerprint analysis, the feed only needs to have a considerable calorific value. Mixed waste can be used although the waste composition and characteristics plays a major role in ash and flue gas emission production (Bosmans et al., 2013). The gasification process also requires high pre-processing and pre-treatment of the feed materials and different waste stream can’t be treated as it will have negative effect on the efficiency of the system. The feed requires being of certain nature (size, consistency) and must be within the predefined limits of that setup (Arena, 2012; Bosmans et al., 2013). The co-processing of waste requires a feed preparation. The composition of waste is very important although different waste stream can be fired in same system. The main lever is to know what are the components going in to the kiln and further the size of the waste are also needed to be controlled depending on the firing mechanism. The waste pre-processing and feed preparation is mandatory to achieve large substitution rate but without pre-processing waste can be fired but the quantity will be limited i.e. substitution ratio will be very small (Chatziaras et al., 2014). The pyrolysis process requires pre-processing and pre-treatment including shorting, shredding and drying so as not effecting the operation. The system is highly sensitive to the deviation of the feed characteristics, if not controlled emission increases and product formation gets reduced (Bosmans et al., 2013). All the system requires a specific emission control equipments except co-processing system, as the cement plant are equipped with emission arresting device and the substitution ratio usually practised has zero effect in any of the emission parameters thus making the system ideal for waste disposal in term of emission control equipments requirement (Baidya et al., 2017, 2018; Baidya and Ghosh, 2018; Garcia et al., 2014). The gasification process is also one of the cleanest in terms of emission, the process produces syngas. The produced syngas or synthesis gas is a mixture of carbon monoxide (CO), hydrogen (H_2) and CO_2 that can be directly used in gas turbine for electricity production, although it may contain minute quantity of H_2S, HCl, COS, NH_3, HCN, alkali, particulate matters, the gas can be cleaned easily to meets the standards and air pollution control system requirement quit less (Arena, 2012; Murphy and McKeogh, 2004). The pyrolysis process produces pyrolysis gas consisting of CO, H_2, CH_4 and other hydrocarbons. The gas also contains small quantity of H_2S, HCl, NH_3, HCN, particulate matters. Compared to gasification, pyrolysis process requires more effective gas cleaning system (Arena, 2012; Bosmans et al., 2013; Samolada and Zabaniotou, 2014). The incineration process with its diverse waste handling capability has an inherent problem of pollution thus requiring major flue gas treatment device. The flue gas usually contains CO_2, H_2O, SO_2, NOx, HCl, PCDD/F and particulate matters. Specific pollution control equipment is absolute necessary for flue gas cleaning and meeting the standards and even the air pollution control residue is hazardous and needs effective disposal (Arena, 2012; Murphy and McKeogh, 2004; Ouda et al., 2016).

The residence /retention/process time of each process reveals co-processing is taking the least time. The residence time of the process is 14 sec with operating temperature of 1450°C. Due to the operating condition the process there is negative chance of dioxin and furans formation (Karstensen, 2008). The incineration process is comparably faster than pyrolysis and gasification process, the usual solid residence time for incineration is 60 second. The gasification process solid residence time is around 1800 seconds depending on the type of gasification chamber and design it may get reduced or increased (Singh et al., 2011). The pyrolysis process has a wide array of residence time from 300 – 3600 second, again depending on the reactor and process type i.e. weather the pyrolysis is fast, slow or flash type (Singh et al., 2011). The overall system efficiency of the co-processing is above 80% as all the waste that goes in to the kiln forms a part of the clinker with 20% contributed to the losses through radiation, emission and insulation etc. The overall system efficiency of the pyrolysis is much better than the other two process with efficiency of 28-42%, depending on the waste composition and process type (Hammond et al., 2011). The gasification efficiency is on the lesser side and ranks third due to the fact that it requires auxiliary equipments and elaborates gas cleaning system thus increasing the parasitic load (Nixon, Dey, et al., 2013; Yap and Nixon, 2015). The incineration efficiency is the lowest with values ranging in between 18–26%. The low value is attributed to process parameter and mixed waste feeding which has a lower calorific value (Lombardi et al., 2015; Nixon, Dey, et al., 2013). The volume reduction of waste achieved is also very important factor as by product generation depends on the volume reduction of the process. The co-processing process can be considered a 100% volume reduction process as all the waste material forms a part of the clinker. The process net output is a product rather than any by-products (Baidya and Ghosh, 2018; Karstensen, 2008). The gasification process also reduces the volume of the waste by 80-95% followed by incineration with reduction of 80- 90% of volume and worst performance in term of volume reduction is pyrolysis with value of 50-90% depending on the waste characteristics, operating condition and type of process (Singh et al., 2011). The land area requirement is also a determining factor for the sustainability of the process although they are neck to neck, although the proximity to the transfer station or sorting facility is a factor to be considered. The land requirement for pyrolysis, gasification and incineration process of 300tpd is around 0.8 hectare and for co-processing it is around 0.6 hectare but for co-processing it is only pre-processing plant as the firing and kiln forms a part of the existing cement plant (Baidya et al., 2017; Lombardi et al., 2015; Saini et al., 2012; Yap and Nixon, 2015). The qualitative value indicates the same land requirements but there ranking defers due to the location and sub transfer station requirements and possible proximity towards urban area etc.

The capital cost for 100 – 200 ktpa plant reveals co-processing has the least cost with value of 80 – 100 $/tpa followed by incineration with cost of 136-295 $/tpa, gasification with 170 to 300 $/tpa and most expensive is pyrolysis plant with cost of 927 $/tpa (Yap and Nixon, 2015; Yassin et al., 2009). The operational and maintenance cost for 100-200 ktpa plants also shows similar trends, with co-processing having the lowest operating cost of 15-20 $/tonne followed by gasification 65–112 $/tonne (Nixon et al., 2014), incineration 85 $/tonne (Chakraborty et al., 2013) and finally pyrolysis at 185$/tonne (Murphy and McKeogh, 2004), attributed to the by-products cleaning requirements, low pyro-oil yield, corrosion of metal tubes and high requirements of secondary treatment of pyrolysis gas (Bosmans et al., 2013; Ouda et al., 2016). The pre-treatment cost is almost negligible in the case of conventional incineration as there is no requirement of any shredding or sorting at the plants, the mixed waste is directly fired to the chute of the incinerator (Nixon, Dey, et al., 2013). The co-processing process requires some level of segregation and requires a uniform mixture of a composite waste material, to be prepared before they can be fired. The waste needs to be sorted and ferrous based materials are needed to be removed. The gasification and pyrolysis process also requires the feed to be pre-treated for effective operation. In term of CO_2 emission co-processing is the least emitter as there is no evident added emission due to firing of AFRs in the cement kiln, rather it reduces the carbon emission of the cement manufacturing process by reducing the consumption of conventional resources. The gasification process emits around 114g CO_2/kWhe (Nixon, Dey, et al., 2013) followed by pyrolysis with emission of 138g CO_2/KWhe (Gaunt and Lehmann, 2008) and highest emission of CO_2 takes place during incineration at 220g CO_2/kWhe (Murphy and McKeogh, 2004). The by product generation by volume of input waste for co-processing is 0 % as all the waste forms a part of the clinker and comes out as a product. The by-product generation of gasification is around 5 – 25% (Al-Salem et al., 2009) followed by incineration 26 – 35%, constituting manly bottom ash (Bosmans et al., 2013). The worst performer is the pyrolysis process with by-product generation rate varying at 30-35% (Hammond et al., 2011). Different waste stream can be disposed off in the conventional thermo-chemical process and energy and resource can be recovered but optimization or adjustment of the process setup is required although co-processing in cement plant as such doesn't require any elaborate equipments and can take in almost all type of waste including MSW (pre treated), industrial waste both hazardous and non-hazardous waste stream (Baidya et al., 2017, 2018; Baidya and Ghosh, 2018; Karstensen, 2008). The incineration is ranked second as the system also can handle different waste stream without elaborate equipment change but operating process has to be adjusted so as to control the emission (Nixon, Dey, et al., 2013). The gasification and pyrolysis process on the other hand is unable to handle different waste stream and functions most effectively with particular fragments of waste (Bosmans et al., 2013). The co-processing process produces no by-product thus it is best in term of environmental perspective, gasification and pyrolysis process produces char which requires treatment before they can be used or disposed (Arena, 2012; Hornung et al., 2011). Incineration process produces fly ash and its immobilization is required in order to make it environmentally safe for landfill disposal (Bosmans et al., 2013). The technology when gauged under social implication or acceptance, co-processing comes out to be the most accepted with respect to all the considered constructs. In term of people perspective issue co-processing is the most accepted due to its zero land requirements as cement plants are already existing and co-processing takes place in the kiln which are situated in industrial zone situated in arid area. Further no perceive pollution issues exist as the cement plants are having appropriate emission controlling system, also the substitution rate practised is very less to have any impact on the emission parameters (Baidya et al., 2017). The gasification and pyrolysis are also accepted as the emission or pollution is minimal. The incineration process faces a major problem due to its perceived emission issues although with latest technology and optimized feeding of waste stream, has shown in numerous cases that the emission were adhering easily to the standards. The odour problem is also nonexistent for the co-processing process as the solid wastes are rid of moisture content and dried buy adding rice husk or saw dust while liquid waste are kept in sealed cylinder. The odour is a major problem for incineration process due to its mixed waste and untreated waste handling. The gasification and pyrolysis system also has a problem with odour due to wet waste handling and process types. The noise problem is least for the gasification process followed by pyrolysis, co-processing and finally incineration. The trend of noise emission is attributed to the production process and operating setup requirements. The expertise requirement to operate the system and handling is least for the incineration followed by co-processing, gasification and finally pyrolysis. The pyrolysis operation is very critical to operate thus requires high expertise (table.5-3).

Constructs for Sustainability Measurement	**Pyrolysis**	**Incineration**	**Gasification**	**Co-processing**
Operational Constructs				
Pre-Treatment/feed stock preparation Requirements	High Requirement (Bosmans et al., 2013)	Medium – High requirement (Bosmans et al., 2013)	High requirement (Arena, 2012)	High requirement (Chatziaras et al., 2014)
Sustainability Ranking	4	1	2	3
Specific Emissions controlling requirements	Less treatment to meet emission limits (Samolada and Zabaniotou, 2014)	Appropriate pollutant control systems required (Murphy and McKeogh, 2004)	Less intensive pollutant system is required (Murphy and McKeogh, 2004)	Separate pollutant control systems not required (Garcia et al., 2014)

Constructs for Sustainability Measurement	**Pyrolysis**	**Incineration**	**Gasification**	**Co-processing**
Sustainability Ranking	3	4	2	1
Retention/residence time /Process Time (Solid residence time)	300-3600 Sec (Singh et al., 2011)	60 Sec (Nixon, Dey, et al., 2013)	1800 seconds (Singh et al., 2011)	14 second (Baidya et al., 2017)
Sustainability Ranking	4	2	3	1
Overall system efficiency	28-42% (Hammond et al., 2011)	18–26% (Lombardi et al., 2015)	22-30% (Nixon, Dey, et al., 2013; Yap and Nixon, 2015)	>80% as the entire energy gets utilised except the system losses.
Sustainability Ranking	2	4	3	1
Volume reduction	50-90% (Singh et al., 2011)	80- 90% (Singh et al., 2011)	80-95% (Arena, 2012)	100% (as no by product is formed) (Baidya et al., 2017)
Sustainability Ranking	4	3	2	1
Land requirements	0.8 hectare (300 tpd – plant) (Saini et al., 2012)	0.8 hectare (300 tpd – plant) (Lombardi et al., 2015)	0.8 hectare (300 tpd – plant) (Yap and Nixon, 2015)	0.6 hectare (300-400 tpd – pre processing plant)
Sustainability Ranking	3	4	2	1
Economical Constructs				
Capital Cost for 100-200 ktpa	927 \$/tpa (Yassin et al., 2009)	136 - 295 \$/tpa (Nixon et al., 2013; Yap and Nixon, 2015)	170 to 300 \$/tpa (Yap and Nixon, 2015)	80 – 100 \$/tpa
Sustainability Ranking	4	2	3	1
Operational and Maintenance Cost for 100-200 ktpa	185\$/tonne (Nixon et al., 2014)	85\$/tonne (Chakraborty et al., 2013)	65–112 \$/tonne (Murphy and McKeogh, 2004)	15-20 \$/tonne
Sustainability Ranking	4	3	2	1
Pre-treatment cost	Medium–High (segregation and shredding)	None (Nixon, Dey, et al., 2013)	Medium–High (segregation and shredding) (Arena, 2012)	Medium (Mainly Segregation)
Sustainability Ranking	3	1	4	2
Environmental Constructs				
CO_2 emission	138g CO_2/KWh_e (Gaunt and Lehmann, 2008)	220g CO_2/kWh_e (Murphy and McKeogh, 2004)	114 g CO_2/kWh_e (Nixon, Dey, et al., 2013)	Negative Emission has been reported (Chatziaras et al., 2014)
Sustainability Ranking	3	4	2	1
By product generation by volume of input waste	30 – 35% (Hammond et al., 2011)	26 – 35% (Bosmans et al., 2013)	5-25% (Al-Salem et al., 2009)	0% (as the waste forms a part of the clinker) (Damtoft et al., 2008)
Sustainability Ranking	4	3	2	1
Different waste streams which can be disposed/utilized in a single setup	MSW (Pre Treated) Industrial Waste (Selected streams)	MSW (Pre Treated) Industrial Waste (All fragments of non hazardous)	MSW (Pre Treated) Industrial Waste (Selected streams)	MSW (Pre Treated) Industrial Waste (All fragments hazardous and non hazardous)
Sustainability Ranking	4	2	3	1
By-product characteristics nature	Char (Hornung et al., 2011)	Ash (Yap and Nixon, 2015)	Char (Arena, 2012)	No by product (Damtoft et al., 2008)
Sustainability Ranking	3	4	2	1

Constructs for Sustainability Measurement	**Pyrolysis**	**Incineration**	**Gasification**	**Co-processing**
Social Constructs				
People perspective issues/Public Acceptance	Accepted	Acceptance Issue exists	Accepted	Highly accepted as no new land requirement is there.
Sustainability Ranking	3	4	2	1
Odour	Medium	High – Medium	Medium	Low
Sustainability Ranking	3	4	2	1
Perceived pollution issue	Medium	High	Medium	Low
Sustainability Ranking	3	4	2	1
Noise Problem	Medium	High	Medium	Medium - High
Sustainability Ranking	2	4	1	3
Expertise requirement	High	Medium	High	High
Sustainability Ranking	4	1	3	2

Table.5-3. Framework for selection of thermo-chemical technology for waste to energy and resource recovery based on four sustainable pillars for India

The overall assessment of the technology, based on all the constructs considering four pillars reveals the best system for energy and resource recovery is co-processing with sustainability score of 24. The co-processing was ranked 1 in all the individual assessment of each of the sustainability pillars. The gasification process was second in term of operational, environmental and social sustainability, while third in term of economical sustainability. Over all, gasification is second most sustainable process for waste and resource recovery in India, considering different waste stream. The incineration process is third in term of operational, environmental sustainability and second in term of economical sustainability, while fourth in term of social sustainability. The system, considering all the pillars of sustainability is third best for the Indian case as per the selection framework. The pyrolysis system is fourth in term of operational, economical and environmental sustainability. The system is third in term of social sustainability and over all it is the most unsustainable (table.5-4).

Sustainability Pillars	**Pyrolysis Sustainability Score**	**Incineration Sustainability Score**	**Gasification Sustainability Score**	**Co-processing Sustainability Score**
Operational	20	18	14	8
Economical	11	6	9	4
Environmental	14	13	9	4
Social	15	17	10	8
Total Sustainability Score	60	54	42	24
Final Sustainability Ranking	4	3	2	1

Table.5-4. Overall assessment of the technology

The framework thus provides the basis for selection of the sustainable thermo-chemical technology for Indian case and for similar developing countries. The framework shows, co-processing in cement kiln is most effective waste management process with respect to all the sustainable pillars. The system although is highly sustainable in term of industrial waste stream including hazardous but when considering MSW the waste needs to be processed to RDF/SRF that is segregated or sorted, and in some case shredded depending on the feeding arrangement so as to reduce the logistic cost. The raw wastes are usually not economically sustainable for transportation thus a RDF/SRF processing plant is mandatory for disposal of MSW stream via a co-processing in cement plant. The cement plant being situated in semi arid area the logistic cost is a considerable factor and must be minimised, therefore RDF/SRF are to be transported after baling so that the MSW waste stream the largest waste stream can be utilized for energy and resource recovery.

5.4. Conclusion

The study examines sustainability of waste to energy and resource recovery technology, considering four pillars of sustainability. The sustainability pillars were analysed considering different qualitative and quantitative constructs applicable for all the thermo-chemical process which are at different commercial stages in India. The AHP decision making tool was used to gauge the ranking of the qualitative constructs. The technology/process selection framework reveals co-processing in cement kiln as the most sustainable methodology for Indian scenario. The analysis also ranks the other considered process, showing gasification as the second best, followed by incineration and pyrolysis. Although co-processing process has a problem with logistics and small firing rate compare to other available methodology but advantages like firing of multiple waste stream, negative impact on emission, zero by-products, low operating and capital cost makes the system one of the most sustainable process. The co-processing is also highly accepted when considered under social sustainability. The co-processing process is primarily based on resource circulation and resource recovery methodology without any secondary or direct electricity production like other process as considered. Although the result takes in to account the Indian waste management system and practises while ranking based on the latest legislation and waste characteristics, the method will be highly suitable for the others developing countries having similar waste management system.

Chapter 6

Co-processing of Waste in Cement Kiln - Issues and Challenges
(Addressing Objective – 3)

6.1. Introduction

Cement manufacturing is an energy and carbon-intensive industry. Cement is the main component of construction industry; it is the second most consumed material on earth, to produce one tonne of cement, an equivalent of 60–130 kg of fuel and 110 kWh of electricity is required (de Queiroz Lamas et al., 2013). The cement industry contributes approximately 5% of the global man-made carbon dioxide making it second largest after power plants. A wide range of options are available to considerably reduce CO_2 emissions (Ishak and Hashim, 2015). Cement manufacturing consists of raw meal grinding, blending, pre-calcining, clinker burning and cement grinding (Alsop, 2007). Portland cement is the most common type of cement used in industry it is made by heating raw materials consisting of oxides of silicon, calcium, aluminium and iron to temperatures of around 1450°C. This blended raw material is termed as raw meal or kiln feed and is heated in a kiln. The raw feed enters the kiln at the colder end and gradually passes down through the hot end of the rotary kiln and then falls out of the kiln and cools down. The modern day cement kilns are equipped with preheater towers and pre-calciners that help to improve the resource efficiency of the cement kiln production process. The material formed in the kiln is described as 'clinker' and is typically composed of rounded nodules between 1-25 mm across. After cooling, the clinker may be stored temporarily in a clinker silo or it may pass directly to the cement mill. The cement mill grinds the clinker to a fine powder (Hewlett, 2003). The properties of the cement clinker formed, influence the product property such as setting time, grindability, strength etc. To reduce the economical burden and to make the process less carbon potent, different types of waste including MSW (fragments), industrial hazardous and non hazardous are utilized as alternative fuel and raw materials (AFRs) for co-processing in cement kilns.

Co-processing is the use of waste as a source of energy or raw material, or both; in some cases, to replace natural resources & fuels in industrial processes, mainly in resource intensive industries (RII) such as cement, steel, glass, and power generation (Ziegler et al., 2007). Coupled with resource conservation and reduced carbon emissions, co-processing is an effective alternative for environmental friendly waste disposal, reducing burden on landfills & treatment storage and disposal facilities (TSDFs) (Tiwary et al., 2014). The use of AFRs in cement kilns is very important for cost reduction, fossil fuels saving and elimination of waste materials. Energy and resource recovery from waste plays an important role in reduction of CO_2 emissions (Kara et al., 2009). AFRs utilization in cement kilns is still progressing, while in some kilns around 100% substitution rates have been achieved, in others, local waste markets and permitting conditions are not allowing higher rates of AFRs substitution. Various types of alternative fuels can be used in a cement plant, with the adequate equipments. The use of waste in cement kilns also reduces emissions from landfills (Benhelal et al., 2013). The traditional fuel used in kiln includes coal, oil, petroleum coke, and natural gas. The substitution of traditional fuels and raw materials by AFRs in the production of clinker is of great importance for cement producers and society because it conserves conventional resources and in case of biogenic wastes, it reduces GHG emissions. The use of AFRs sometimes helps to reduce the costs of cement production. Energy costs and environmental concerns have led cement companies to explore the potential of different AFRs, like waste feedstock, trade rejects, expired consumer products, waste oils, plastics and paper, used tires, agro waste, gaseous waste, chemical and petrochemical process waste, ETP sludge etc. The clinker firing process is well suited for different AFRs, both hazardous and non hazardous.

Industrial experience has shown that the use of wastes by cement kiln is both ecologically and economically justified (Chatziaras et al., 2014). The environmental effects of co-processing cutting oil emulsions in cement kilns was studied by Giannopoulos et al. [9] and showed no effect on emissions. Tiwary et al., (2014) showed that co-processing is efficient, economical and environmentally sustainable, particularly for a developing country like India, as there was no adverse effect on quality and stack emission. Alkaline environment, high temperature of 1450°C and long residence time of 14 sec allow rotary kiln to burn a wide range of waste and hazardous material (Rahman et al., 2015). In order to choose the most suitable waste as AFRs, several factors other than the energy content has to be considered. Generally, the cement producers choose AFRs on the basis of price and availability. But it is also necessary to know the composition and characteristics of the waste including fixed carbon, moisture and volatiles contents. Different types of waste, from liquid to solids, powdered to big lumps need to be considered while dealing with AFRs. A flexible AFRs feeding system is required, whether they are fed directly into the burning zone in the kiln itself or into the preheating system (Kääntee et al., 2004). Consequently, the AFRs should be cost effective easy to handle, easy to store, must have longer storage life; else modifying the design of the manufacturing plant may discourage the usage of such fuel because it may not be cost effective.

Co-processing of hazardous wastes in cement kilns have for decades been thought to increase emissions of polychlorinated dibenzodioxins (PCDDs)/polychlorinated dibenzofurans (PCDFs) – but hundreds of PCDD/PCDF measurements conducted by the cement industry in last few years proved this perception false (Karstensen, 2008). Disposal of organic hazardous waste was analysed with PCB–oil in a cement kiln for assessing feasibility and destruction performance, the study showed PCBs can be disposed of in an environmentally sound manner (Karstensen et al., 2010). The addition of different types of waste requires an effective control of the temperature in the clinkering zone, as even slight exceeding of required temperature would fluidize the clinker and may cause damage to the refractory lining of the kiln (Trezza and Scian, 2005). There is a need for establishing and implementing standards and requirements for co-processing in general and for hazardous wastes in particular. Specifically, the commitment to continuous reduction of the CO_2 emissions from cement production by increased use of AFRs and introducing modified low-energy clinker and cements with reduced clinker content represents an effective way of supporting sustainable development (Yan et al., 2010).

6.2. Methodology

The methodology adopted in this work involves the following steps; firstly, an extensive literature survey was carried out to find the sustainability challenges and current status of co-processing at cement plant across the world. Secondly, the possible benefits of co-processing were studied based on the exiting cases from the literature. Thirdly, the issues and challenges for effective co-processing were gauged specifically for India. The issues in implementation of co-processing were analysed and the need for removal of the constraints were discussed with the aid of the literature. Addressing these issues, the several types of wastes can be utilised as resources, lowering the disposal volume of different waste stream.

6.3. Discussion & Analysis

There currently, exists number of challenges in implementing co-processing in different cement plant in India. These issues are hindering the sustainability of the co-processing. Based on the literature, number of key areas were gauged which are needed to be addressed to make co-processing sustainable for different waste stream including MSW fragments, industrial and hazardous waste. Depending on the location of cement plants, some alternative fuels may be more favourable than others. The cement plant location is a major issue as the waste generators are generally far away from the location of the source hence local waste availability is a concern. Further in the developing countries like India, cement producing organization and different industry like power plant is adding a competitive edge to the existing waste market hence the cost for certain type of waste mainly the biomass price are increasing and the tipping fees for the industrial waste are decreasing, due to the presence of new takers thus the availability of potential AFRs is obviously a system constraint for sustainable co-processing (Dutta and Mukherjee, 2010; Kääntee et al., 2004; Kookos et al., 2011; Strazza et al., 2011; Yan et al., 2010).

The transportation of the waste and its storage is a major factor which is effecting the implementation of co-processing in the cement plant. When the waste feedstock is hazardous industrial type, the transportation, handling and storage becomes a major concern for both the cement plant and also for the waste generators. Different kinds of waste produce different types of problems like, the meat-and-bone meals which result in the dust problems for the handler and also the fat content in it tends to stick all over the transportation systems. The biological activity of the meals also becomes prominent under high humidity conditions: digestion processes are initiated posing health hazard to the operating personnel (Duda et al., 2003). The water absorbability is another parameter which affects the storage of waste. This parameter is especially interesting because of considerable initial water content in sludge-derived materials. The safety of the personnel is a major issue when the, handled waste is hazardous, necessitating special preventive measures to avoid exposure, spillage and fire (Karstensen et al., 2006). The leaching of certain types of waste is also a major storage problem. Different types of waste from liquid to solids, powdered or big lumps can be encountered when dealing with AFRs, hence a flexible feeding system is required with a pre-processing setup. It may be fired directly into the burning zone in the kiln itself or into the pre-heating system (Kääntee et al., 2004). In general the size of the alternative fuel which can be fed in the pre-calciner stage is off around 100 - 150 mm. AFRs utilization requires the adaptation of the combustion process. Modern multi-channel burners designed for the use of AFRs and thermograph systems allow effective control of the flame shape, thus optimizing the burning behaviour (Wirthwein, 2010). Finding an ideal burner position is advantageous for the burning process and clinker quality. Oxygen enrichment of primary or secondary air is promising for optimizing AFRs combustion (Schneider et al., 2011). The installation for the co-processing, demands an economical expenditure, which is somewhat hindering implementation of co-processing in cement plant other issues like the availability, waste type, indigenous technology availability and absent of government support is affecting the implementation to a greater extent (Dutta and Mukherjee, 2010). To use any of the AFRs in a cement factory, it is necessary to know the composition of the fuel (Kääntee et al., 2004), although the choice is primarily based on the price and availability. The energy, ash, moisture and volatiles contents are also important. The composition of the AFRs plays an important role in deciding pre-processing requirements. The feeding percentage is controlled based on the composition of the AFRs as the materials going in to kiln is a deciding factor for the quality of the clinkers formed and emission from the stacks. The composition of the waste in co-processing in cement plant requires delicate controlling measures.

The burning behaviour of AFRs differs significantly from the behaviour of traditional fuels and raw materials due to large particle sizes, material densities and transport characteristics. This characteristic affects the temperature profile of the kiln including the sintering temperature, the length of the sintering zone and the cooling conditions. These changes affect different clinker characteristics like the burning grade of the clinker, the porosity of the granules, the crystal size of the clinker phases or their reactivity. The amount and composition of the ashes introduced by AFRs differ from those of traditional fuels and raw materials. Generally, the production process and the materials have to be monitored more closely when high ratios of AFRs are used. With adequate comprehensive production process control, the manufacturing of high-performance cement clinker is possible even with significant substitution rates (Schneider et al., 2011). In terms of air emissions, the performances of cement kilns appear independent from the use of AFRs at the percentages usually employed (Strazza et al., 2011). Van Loo (2008) evaluated around 2200 dioxin/ furan stack emission measurements which were collected from various sources and showed that most cement kilns can meet an emission level of 0.1 ng TEQ/Nm^3. Reducing the temperature to lower than 200°C at the inlet of the air pollution control unit can further limit dioxin formation and emissions at all types of cement kilns. Any chlorine introduced to the kiln system in the presence of organic material may cause the formation of PCDDs and PCDFs during combustion and wet-chemical processes. The formation of dioxins and furans is known to occur by denovo synthesis within the temperature window between 250-450°C. Thus it is important that the exit gases are cooled rapidly through this range. The overall emissions are well below the base limit in most of the kilns.

The co-processing business is supported by government in the developed countries as it mitigates one of the plaguing issues of waste management but for the developing countries the government support is one of the major issues for sustainability of co-processing. This is because the government neither provides any form of support for co-processing and nor ensures legislative backing for co-processing even though it reduces quantity of landfill waste. In India, getting a certificate for co-processing of hazardous waste material sometimes becomes a lengthy process even if all the norms regarding the emission are fulfilled. The certification process takes number of months. Although the legislative directive, emphasising co-processing as an effective waste disposal and resource recovery methodology has been presented in different Waste Management Rules, of 2016. As a result the investment on the co-processing business is sometimes difficult to justify. A detailed technical feasibility and comparative analysis should be carried with different waste streams to establish new sets of standard and legislation (Dutta and Mukherjee, 2010).

The co-processing option not only reduces the carbon foot print of the cement plant by reducing the consumption of conventional fuel it also reduces the carbon foot print of the industrial waste generated by the producer. Cement industry, due to its co-processing capabilities of different type of wastes act as an effective sink for CO_2 via reduction of landfill waste and extraction of energy out of the waste in an environmentally sound manner. The co-processing option also holds good for hazardous waste disposal. Resource consumption and conservation improves with the use of AFRs; due to the substitution of conventional resources in clinker production making it consistent with a “closed loop” strategy for industries (Albino et al., 2011). Even though there are multiple issues effecting a proper implementation of co-processing, co-processing is highly desired as is evident from the fact that issues and challenges outweigh the benefits which can be achieved, as the waste that would have ended up in landfill is decreased and a valuable energy and resource is recovered. The co-processing of industrial waste including the hazardous waste is the most prominent energy recovery process in term of its economical and environmental benefits.

6.4. Conclusion

The study, based on the literature review, gauged the sustainability of co-processing in cement kiln as a method of resource & energy recovery in cement plant. The challenges and issues which are acting as a hindrance for effective implementation of co-processing were analysed. The study revealed that the cement plants were able to reduce their carbon footprint by co-processing industrial waste as it reduces the use of conventional raw materials. The co-processing at lower substitution rate has no effect on emission. The AFRs has to be properly analysed so as to decide the co-processing percentage. The study showed co-processing has negative effect on the clinkering process and has no effect on the final products property. The study also revealed different aspect on which the future scope of the work should be carried out. Different waste stream co-processing is needed to be analysed experimentally so that the optimization of the feeding rate can be carried out and standards can be developed in India. The waste co-processing techno-economic analysis and sustainability based on the Indian scenario are needed to be analysed.

Chapter 7

Co-processing of Industrial waste as AFRs in Cement Plant
(Addressing Objective – 5)

7.1. Introduction

Cement will remain the key material to satisfy global housing and modern infrastructure needs. As a consequence, the cement industry worldwide is facing growing challenges in conserving traditional resources, as well as reducing its CO_2 emissions (Ishak and Hashim, 2015). According to the International Energy Agency, the main levers for cement industry are increase of energy efficiency and use of alternative materials, be it as fuel or raw materials. Accordingly, the use of alternative fuels and raw materials (AFRs) has already increased significantly in recent years, but potential for further increase still exists (Schneider et al., 2011). Cement production involves heating, calcining and sintering of blended and grounded raw materials. Clinker burning takes place at a material temperature of 1450°C in rotary kilns, i.e. inclined rotating cylinders lined with heat-resistant bricks. After cooling, the clinker is ground with a small amount of gypsum to give Portland cement, the most common type of cement (Karstensen, 2008).

It has been estimated that the annual global cement production is expected to increase to some 4 billion tonnes per year. Major growth is taking place in countries such as China and India as well as in regions like the Middle East and Northern Africa (WBCSD, 2009). Many of these countries are also facing immense problem with disposal of waste. Economical and ecologically beneficial approaches point to co-processing waste in cement kiln and recover substantial energy and resources from it, with reduction in the use of conventional raw materials. A wide range of alternative resources can be used in cement industries due to long residence time and high operating temperature. Almost 100% alternative fuel firing at the pre-calciner stage has been achieved (Schneider et al., 2011). The use of alternative fuels in rotary kilns of cement plants is very important not only for the cement plant but also for other waste producing industries; as co-processing leads to reduction in cost, savings in fossil fuels and also elimination of waste materials which would otherwise have been gone to landfill. Cement industries have an important potential in addressing waste management problem. Energy recovery from waste is also important for the reduction of CO_2 emissions (Kara et al., 2009).

Alternative fuels and raw materials which have been used are tires, animal residues, sewage sludge, dry fragments of MSW, waste oil and industrial waste. Although the clinker firing process is well suited for different AFRs; but proper optimization is essential (Chatziaras et al., 2014). There has been significant research one co-processing different waste stream. Cutting oil co-processing was analysed for quantifying NOx, CO and VOC emission and its effect on environment (Giannopoulos et al., 2007). Generally the cement producers choose the alternative fuel on basis of price and availability, but the composition of the fuel including fixed carbon, moisture and volatiles contents is also necessary. The fuel material should be cost effective, easy to handle, easy to store and have longer storage life; else modifying the design of the manufacturing plant may discourage the usage of such fuel on account of it not being cost effective. The use of waste co-processing in cement furnaces as a substitute for a portion of the fuel can provide energy gains without changing the gas emissions and quality of the produced clinker (Garcia et al., 2014). (Baidya et al., 2016) specifically showed the effectiveness of the co-processing in cement plants in India based on a number of case studies as a way for effective utilization of energy and recover raw materials locked in the industrial waste. (Parlikar et al., 2016) analysed the result of 22 co-processing trial with different waste stream to analyse the concern of different stake holder. The trial was evaluated based on the inputs like process parameters, emissions and product quality. (Baidya et al., 2015) reviewed the present status and sustainability of co-processing of the industrial waste in cement kiln through literature review, specifically for India. The review identified the challenges and issues in implementation of effective co-processing of industrial waste for cement kiln as AFRs. (Conesa et al., 2011) analysed the thermal decomposition of solid recovered fuel (SRF) for emission of dioxins and furans (PCDD/Fs). It was revealed that sulphur presence plays an important role in PCDD/Fs formation, although all the emitted pollutants were under the legal limits. No correlation between SRF input and metal emission was observed. (Rivera-Austrui et al., 2014) characterized atmospheric emissions of polychlorinated dibenzo-p-dioxins (PCDDs)/ polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) from a cement plant which was co-processing recovered derived fuel (RDF) and WWTP sludge as alternative fuels with conventional fuel. The kilns emission values were well below the limit established by the European Waste Incineration Directive 2000/76/CE (EWID) of 100 pg I-TEQ/Nm^3. (Liu et al., 2015) carried out a pilot study to evaluate the formation, distribution and emission of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) from cement kilns which were co-processing fly ash from municipal solid waste incineration (MSWI). Stack emission and particulate samples from multiple stages in the process were analysed for PCDD/Fs and all values were below the European Union limit for cement kilns (0.1 ng TEQ m−3). (Jin et al., 2016) studied the polychlorinated naphthalene (PCN) formation and emission from cement kilns, co-processing sorted municipal solid waste, sewage sludge, and waste acid. PCNs were analysed in stack emission samples and solid samples from different stages of three cement production runs. PCN destruction efficiencies were on the higher side when waste was co-processed (93.1% and 88.7% in two tests) than when waste was not co-processed (39.1%).

Cement kilns have proven to become an effective way of recovering value from waste materials and co-processing of AFRs is now an integral component in the spectrum of viable options for treating different waste stream including hazardous industrial wastes (Balbo et al., 1998). (Kara et al., 2009) investigated the potential use of refuse derived fuel (RDF) as an alternative fuel in cement production in Istanbul, Turkey. The substitution of traditional materials in cement plants not only allows a reduction of CO_2 emission, but it also acts as an alternative way to address the residual materials, such as sewage sludge, industrial waste and MSW, which should otherwise be disposed somehow/somewhere (Rovira et al., 2010). (Li et al., 2012) carried out a study on dioxins formation and suppression mechanisms in RDF fired cement kiln by analysing the dioxin concentrations of solid and gas samples in different critical points and showed that dioxins emission was below the international standard limit of

0.1ng TEQ/Nm^3. The objective of the study is to identify the factors which influence the sustainability of waste co-processing in cement kiln in India. The study evaluates the sustainability aspect based on the four pillars of sustainability, namely environmental performance, economic performance, operational performance and social performance. The study reveals the supply chain issues in India based on a pilot study in one of the largest capacity cement plant in South Asia along with the positive effect of co-processing waste in cement plant.

7.2. Material and Methods

7.2.1. Methodology

This study adopts a case study method. Firstly, a literature review has been carried to identify the status of co-processing in cement kiln around the world. Secondly, an organisation was identified to conduct a pilot study. Thirdly, the case organization was studied and the sustainability analysis was carried out based on the four sustainable pillars namely environmental, economic, operational and social aspect. Fourthly, the supply chain network was critically analysed for challenges and issues. Fifthly, the possible benefits of co-processing were discussed based on the findings of the pilot study. The study utilises a mixed method strategy with a two stage linear qualitative analysis. Separate qualitative analyses were carried out using data sourced from a case study and from literature. The primary data consisted of textual documentation of the plant co-processing waste, which were supported by interviews to confirm the interpretation of the documents.

7.2.2. Pilot study

The organisation chosen for the pilot study is one of the largest cement kilns in South Asia. The plant has two kilns in operation with five stage cyclone pre heater and in-line pre calciner. The kiln -1 has length of 74 m, diameter of 4.8 m and capacity of 3600 tpd. Kiln -2 is newly developed, having length of 96 m, diameter of 6 m and capacity of 12500 tpd. The kiln -1 and kiln -2 is equipped with waste heat recovery systems. The stack emission is controlled by an arrangement of bag filter and electrostatic precipitator.

Since 2007, the kiln-1 is being fed by alternative fuel and raw material (AFRs) and kiln -2 is under trial run and is yet to be commissioned. The AFRs feeding capacity in kiln-1 is 2 tonnes/hour and in kiln -2 is 20 tonnes/hour. While the kiln -2 process line has a state of the art pre-processing facility, kiln -1 process line has a basic manual setup, requiring four workers for operating it. The line -1, being a basic setup without pre-processing facility, has limited capacity, as large size feeding material cannot be fed into the kiln. Moreover, the rate of feed is low due to lack of automation. The detailed supply chain framework of waste from generators point to kiln inlet with process flow for dosing system has been mapped (figure.7-1). Although the plant is equipped to co-process RDF, but due to unavailability of feed and lack of economy of scale it is currently co-processing only industrial waste.

Once the waste is generated by the respective industry, it is suitably packed for transportation. The waste is loaded on to trucks and a transport emergency (TREM) card is generated before the journey, as is mandated by co-processing guidelines. Waste is then transported to the cement plant by trucks; the logistic support is provided by the waste generator. Biomass like rice husk, saw dust, cotton stalk etc., which were co-processed, is usually brought by the cement plant's own logistics. The industries which send their waste for disposal also provide tipping fee to the cement plant, thus adding to the economical sustainability. Once the waste is received at the plant, it is weighed and TREM card is collected. The waste laden truck is kept at a temporary storage area. The waste is then sampled and a finger print analysis is carried out to determine the type. On conformation of the right kind, acceptance is given. If the sampling result comes out to be different from what is intended, the truck is detained and a discussion with the industry is carried out for possible resolution of the issue. Usually the waste is taken in with increase in tipping fees, unless proscribed by norms. The waste is then unloaded to a permanent storage area. Further, the waste is homogenised and pre-processed, based on the requirement and waste characteristics. The waste is then loaded in bags and lifted by a bucket hoist. Then the waste is discharged in to the apron extractor, which then flows to a weigh belt feeder and into the hopper. The hoppers open to a chute with three shutoff gates and finally, the waste enters the kiln inlet at the cyclone end.

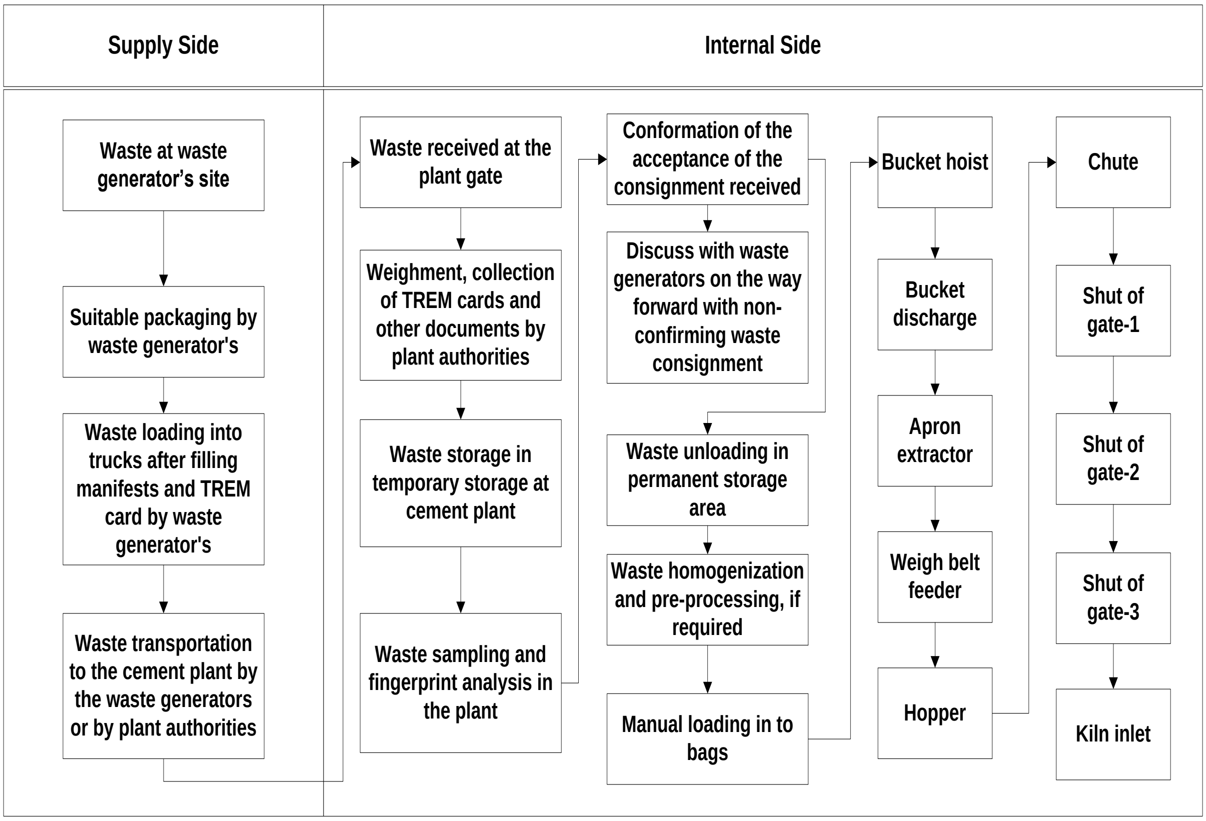

Figure.7-1. Supply chain framework of waste from generators point to kiln inlet with process flow for dosing system

7.3. Results and Discussion

The detailed discussion has been elaborated under the four sustainable pillars. The study revealed a number of aspects which provides ample indication of the sustainability of co-processing in India. The pilot study also indicates a number of issues, which if addressed can effectively make co-processing the most sustainable waste disposal and management process in India. The major issues that affect sustainability, according to past research and also revealed by our study at the plant, were availability of waste, transportation and storage, installation technological requirement, composition of the waste, quality of clinker, emission factors and government support (Dutta and Mukherjee, 2010; Kääntee et al., 2004; Schneider et al., 2011; Strazza et al., 2011; Wzorek, 2012). Co-processing is socially sustainable, irrespective of whether the cement plant uses industrial waste or MSW fragments as both the stream, if not utilized or disposed of properly will finally end up in the land filled site. This leads to a rise in GHG emission and also affects the public health adversely. Co-processing reduces the use of virgin material and conserves natural resources. Also, co-processing has enormous economical potential as earnings from tipping fee are supplemented by substitution of conventional fuel by AFRs which reduces the cost towards virgin materials. The plant will have reduced carbon footprint and society will also benefit in terms of lower emission and also less waste in land filled site. The methodology of co-processing will be an effective waste management solution if the related issues in the supply chain are addressed. The details have been discussed in term of each of the sustainability pillars.

7.3.1. Environmental aspect

The case study organisation presently uses industrial waste and biomass in the kiln-1; the set up doesn't allow firing of large size material. Due to absence of pre-processing platform the large sized RDF/SRF/MSW (dry fragments) waste cannot be shredded. Rather the kiln-2 is highly equipped for firing large size waste due to existence of pre-processing facility, although it is yet to be commissioned. The industrial waste has varying characteristics, which includes spent carbon, benzofuran, and chemical sludge from ETP, ETP sludge, tooth paste waste and biomass. The plant disposes bulk of the industrial waste as alternative raw materials (AR). The AR includes commodities like iron slag and red mud. The waste having higher calorific value or of hazardous nature are treated or disposed as alternative fuel by the feeding system in the primary side. Waste having lower calorific value and of non hazardous in nature are treated from cold side or in some cases used during the preparation of the silo. The waste is supplied by different industries and are analysed for their varying composition and characteristics, as the feeding rate and quantity is defined by the waste characteristics (table-7-1).

Industrial Waste	**% Moisture**	**%Volatile Matter (ODB)**	**% Ash (ODB)**	**% Fixed carbon (ODB)**	**Calorific Value gross Cal/g**	**% S**	**% Cl**
Spent carbon	38.8	39.8	11.8	48.4	3267	2.58	3.01
Benzofuran	0.8	85.4	0.3	13.5	4692	0.1	35.2
Chemical sludge from ETP	51.7	31.68	68.32	-	-	-	-
ETP sludge	37.8	19.1	43.1	-	-	0.1	0.088
Tooth paste waste	33.2	47.2	19.6	-	2185	0.3	0.693

Biomass	**% Moisture**	**%Volatile Matter (ODB)**	**% Ash (ODB)**	**% Fixed carbon (ODB)**	**Calorific Value gross Cal/g**	**% S**	**% Cl**
Saw dust	33.1	51.7	2	13.2	4512	0.1	0.05
Bagasse	21.0	67.8	2.5	8.7	4382	0.8	0.08
Rice husk	6.9	58.1	19.1	15.8	3677	0.1	0.02
Cotton stalk	9.7	83.8	1.0	5.5	4108	0.04	0.02
Coal/Traditional fuels	$\%SiO_2$	$\%Al_2O_3$	$\%Fe_2O_3$	%CaO	%Ash	NCV cal/g	
Coal	63.40	26.50	3.50	3.50	35.5	4150	
Pet coke	41.00	26.00	5.00	9.00	2.0	8050	
Alternative raw materials	**% Moisture**	**$\%SiO_2$**	**$\%Al_2O_3$**	**$\%Fe_2O_3$**	**%CaO**		
Red mud	22.9	6.8	20.4	40.3	8.4		
Iron slag	9.0	25.5	15.5	44.5	0.8		

Table.7-1. Different industrial waste type and there characteristics

The total quantity of industrial waste which would have otherwise been sent to landfill site is enormous as can be interpreted from the figure.7-2. In 2013, 68606 tonnes of industrial waste with biomass content of 3085 tonnes had been utilized effectively for co-generation of energy. The graph shows an increasing trend of waste disposal rate over the years from 2007 to 2013: only deviation in the trend was reported in the year 2009; this was attributed to the unavailability of the waste and production process deviation.

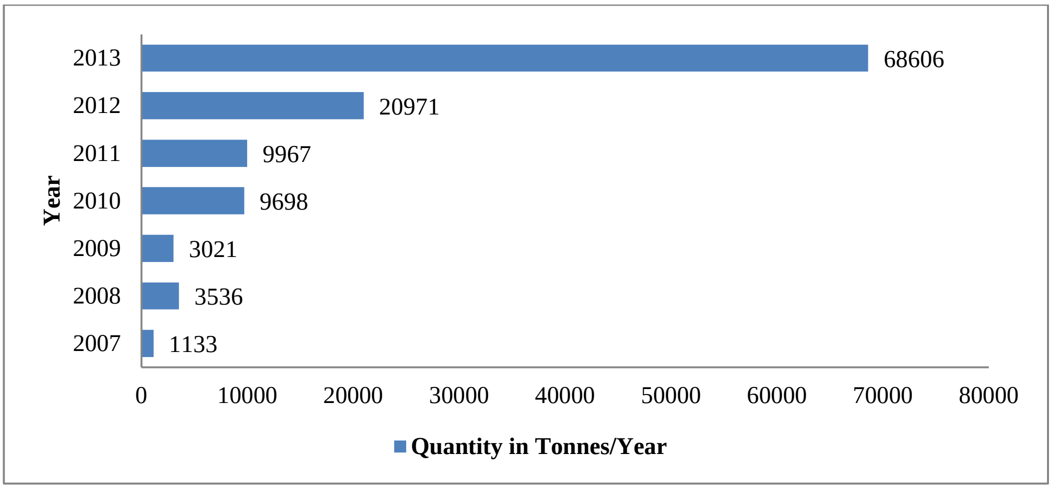

Figure.7-2.Quantity of AFRs consumed in tonnes/year

The effects of waste feeding on different emission parameters were analysed during different co-processing run, so that the negative implication of co-processing on emission could be revealed. The analysis was carried out by dividing the co-processing run in three stages: pre co-processing, during co-processing and post co-processing. The parameters which were critically analysed for different waste stream are dioxin and furan, total organic carbon (TOC), sulphur dioxide, suspended particulate matter mercury and heavy metals. Each category of waste was analysed for the different parameters and the trends were plotted. The co-processing emission norms for dioxins and furans are 0.1 ng TEQ/Nm^3. During the analysis it was revealed that for the entire waste stream, the emissions were well below the norm; maximum emission was reported at 0.004 ng TEQ/Nm^3 for spent carbon and minimum was reported at 0.001 ng TEQ/Nm^3 for benzofuran (figure.7-3). Similar analysis of the total organic carbon (TOC) reveals maximum emission of 5.17 mg/Nm^3 for spent carbon and minimum for tooth paste waste at 3.08 mg/Nm^3. The emission norm for TOC is 20 mg/Nm^3 and all the emission were well below the limit (figure.7-4).

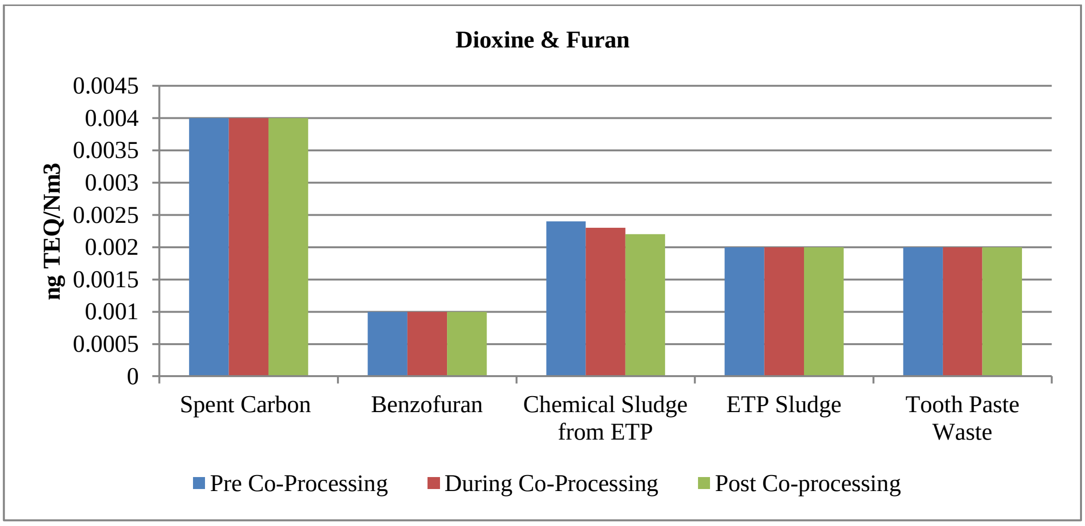

Figure.7-3. Dioxin and furan emission from different waste stream during co-processing

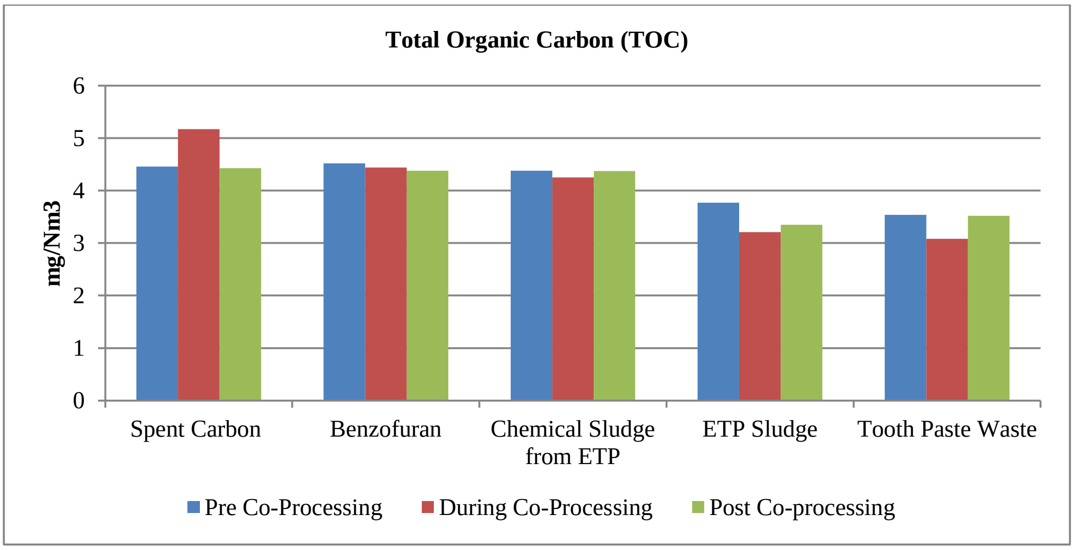

Figure.7-4. Total organic carbon emission from different waste stream during co-processing

The emission of sulphur dioxide (SO_2) during the co-processing was also below the limit as maximum emission was reported at 14.13 mg/Nm^3 during the ETP sludge feeding, were the norms was 200 mg/Nm^3. The minimum emission of 0.91 mg/Nm^3 was reported from chemical sludge from ETP (figure.7-5). The suspended particulate matter (SPM) measurement reveals 18.6 mg/Nm^3 for chemical sludge from ETP and minimum was for spent carbon at 13.66 mg/Nm^3. All the emission measurement of different waste stream was well below the norms of 50 mg/Nm^3 (figure.7-6).

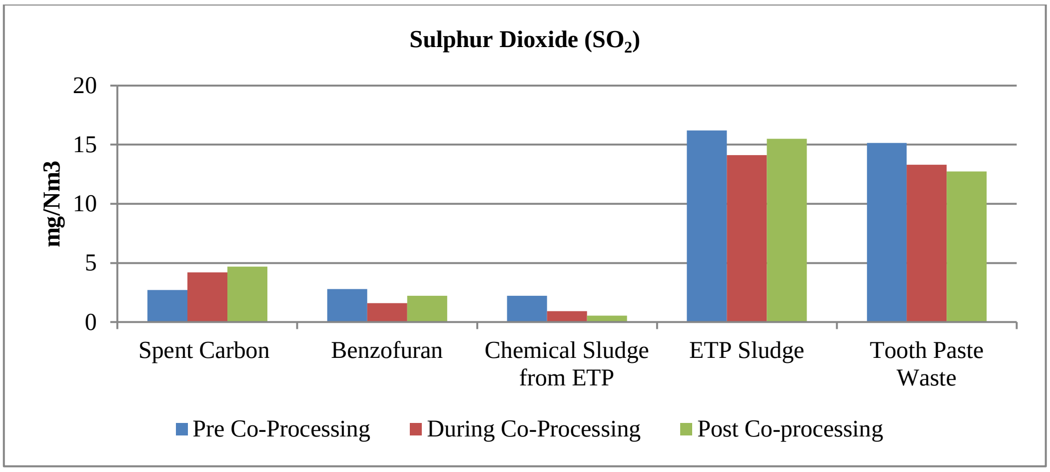

Figure.7-5. Sulphur dioxide emission from different waste stream during co-processing

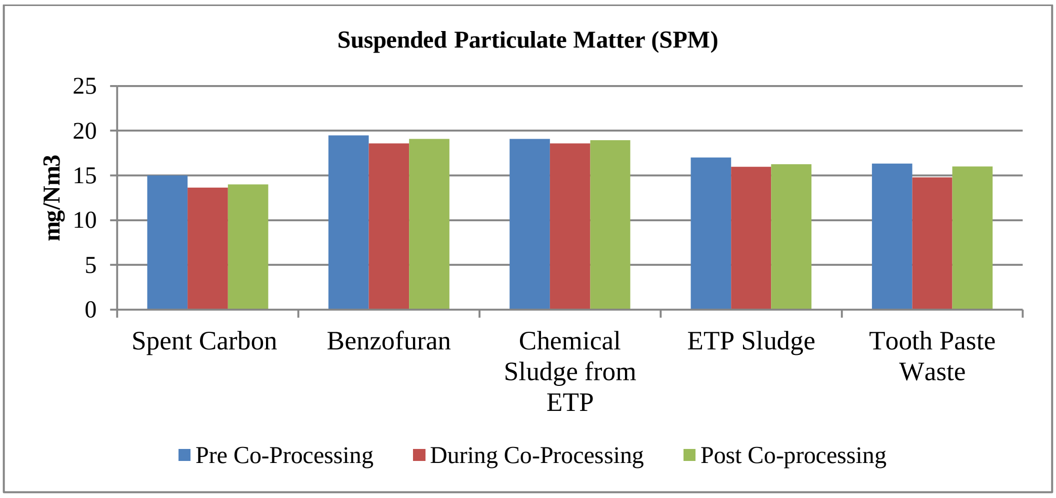

Figure.7-6. Suspended particulate matter emission from different waste during co-processing

The mercury emission measurement shows that benzofuran is the only waste stream which produced mercury at the level of 0.002 mg/Nm^3, with the limit being 0.05 mg/Nm^3 (figure.7-7). The heavy metal measurement reveals maximum emission at 0.07 mg/Nm^3 from chemical sludge from ETP and minimum was produced by tooth paste waste against the norm of 0.5 mg/Nm^3 (figure.7-8).

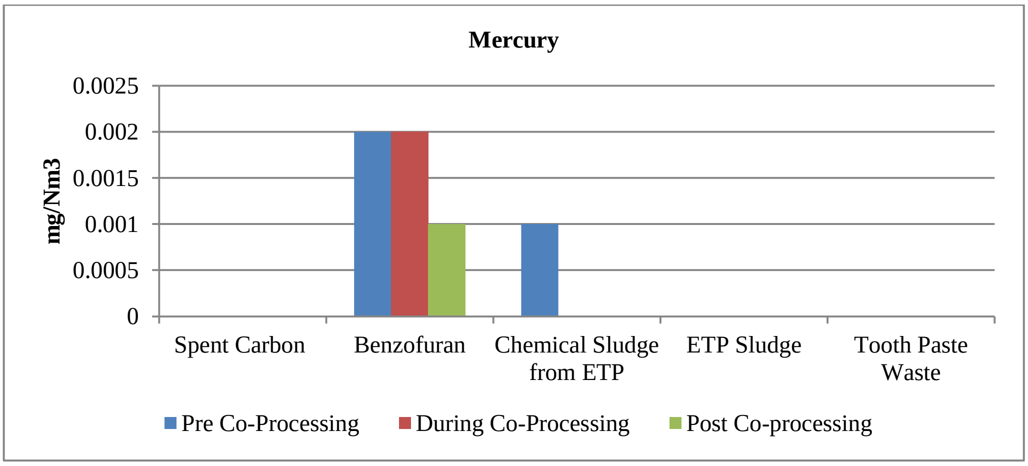

Figure.7-7. Mercury emission from different waste stream during co-processing

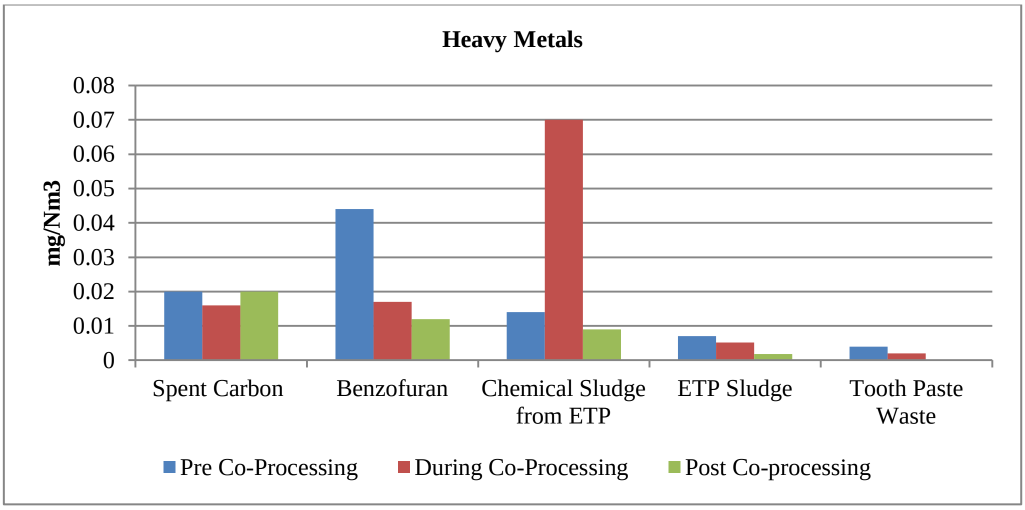

Figure.7-8. Heavy metals emission from different waste stream during co-processing

The leach test of the clinker was carried out to gauge the effect of co-processing on the final product. The analysis was conducted on toxicity characteristic leaching procedure (TCLP) leachate in accordance with ASTM D5233 and concentrations were expressed in terms of dry weight of solid used during analysis. Three sampling was carried out during the co-processing period. The measurement shows no changes in the parameter due to co-processing of different waste stream. The effect of co-processing on accumulation of heavy metal is also negative as there was no change in their values (table.7-2).

Thus, the waste disposal doesn't affect the emission or clinker quality as revealed by the analysis of different waste streams and leach test of the clinker. The waste can be disposed of without any change or incremental variation in the production process and without any by-product generation, as all of the waste forms a part of the clinker. Co-processing can be a very effective waste management solution and economic gains are also immense. The emission measures are also well under base line and economic gains run in to thousands of US Dollars.

Parameter	**Unit**	**Pre Co-processing**	**Co-processing**			**Post Co-processing**
			1st Sample	**2nd Sample**	**3rd Sample**	
Antimony	mg/kg	<5.00	<5.00	<5.00	<5.00	<5.00
Arsenic	mg/kg	<0.5	<0.5	<0.5	<0.5	<0.5
Cadmium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Chromium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Cobalt	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Copper	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Lead	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Manganese	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Nickel	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Thallium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Vanadium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Mercury	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Zinc	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Tin	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Selenium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00
Aluminium	mg/kg	7.00	4.00	11.2	4.4	<1.00
Iron	mg/kg	1.40	6.00	1.40	1.00	0.40

Table.7-2. Leach test of clinker

7.3.2. Economical aspect

The economical viability of co-processing in the plant can be gauged from the trends in savings as given in the figure.7-9. The co-processing of waste not only reduces the carbon footprint of the plant but also leads to economical sustainability of the business model. The economic effectiveness is achieved due to number of factors like tipping fees, high conventional fuel prices and low level of technological requirements for feeding system. During the year 2011 to 2012, due to un-availability of certain kinds of industrial waste and competition over preferred waste from other cement plants, reduction in use of AFRs consumption occurred. The waste consumption in the plant increased again in the year 2013 along with increase in economic benefit, as can be seen in the figure.7-9.

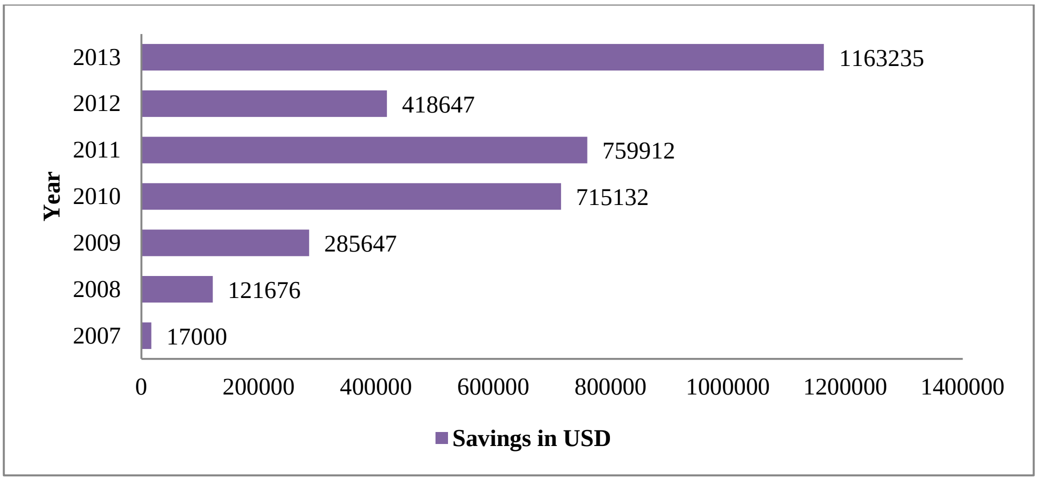

Figure.7-9. Trends in savings on the basis of AFRs in place of conventional resource

This is attributed to the increase in use of alternative raw materials in the form of iron slug and red mud. The industries responsible for reduction in supply of the waste, which in turn led to the lowering of economic gain, were FMCG companies, pharmaceuticals companies and chemical industries. The reduction was blamed on availability of new takers, which brought down the tipping fees, thus reducing the disposal bill for the waste producer. As a measure, the plant signed firm agreements with its suppliers for constant supply of industrial waste since 2013. Although the use of MSW fragments as feed could be most effective with regard to social and environmental benefits, it is yet to be implemented on account of unavailability and economic issues.

7.3.3. Operational aspect

The operational viability of co-processing is also highly sustainable as can be accessed from the pilot study of the plant. The waste firing operational requirements is not highly complicated as the technology requirement is less. The emission and quality of the clinker can be gauged and controlled from the central control room, based on the availability of existing technology, simply by controlling the feeding rate of waste. The manpower requirement is also less. The feed rate of waste is calculated based on the characteristics and composition of the waste analysis by the quality department. The operational ease and economic effectiveness can be realized from the thermal substitution rate percentage (TSR%)

achieved in comparison with conventional fuel, as given in the figure.7-10. Thermal substitution rate (TSR) is the percentage of energy from conventional fossil fuels which can be replaced by a lower carbon energy source. During the December month of year 2014, annual maintenance was carried out and as a consequence the entire production process was ideal: zero TSR% as is reflected in the figure.7-10. The analysis revealed high economic viability as well as operational viability of co-processing industrial waste in cement plant. The co-processing of AFRs doesn't have any effect on production process or quality of the clinker as the feed rate is strictly controlled in accordance with the characteristics of the waste. Further, the feed rate is quite less to affect the production process.

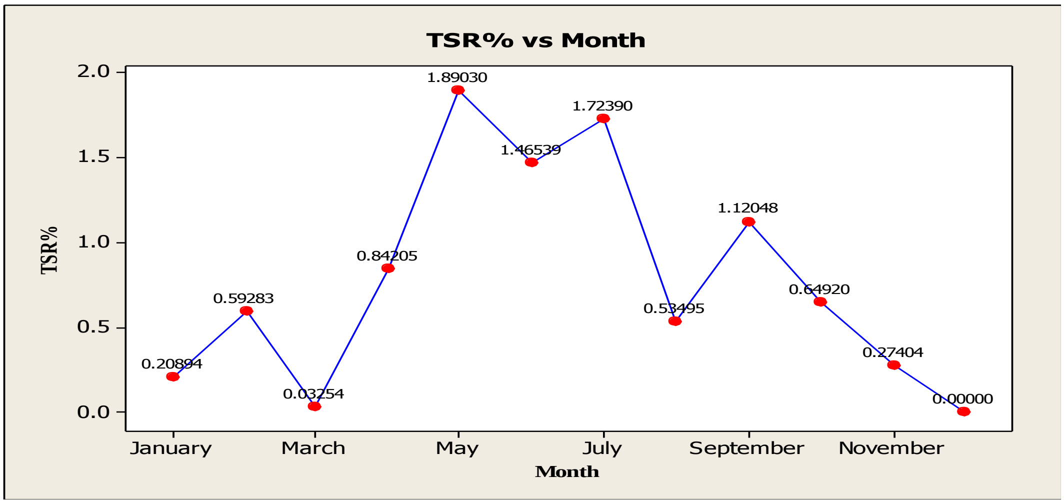

Figure.7-10. Thermal Substitution Rate % for each month of the year 2014

7.3.4. Social aspect

The social benefits were also brought to the notice of the study as less waste was available for landfill, with a major part of industrial waste or MSW being diverted for energy and resource recovery in the cement kiln. Co-processing of waste in cement plants provides a holistic methodology for waste management. The waste disposal reduces the deleterious effect on the environment, more specifically; minimizing open dumping improves the quality of life of the community around the landfill site. The co-processing also reduces CO_2 emission by reducing the use of virgin raw materials and fuel, causing an overall decrease in the carbon footprint of the cement plant as well as the waste producing industries it serves. The reduction in use of virgin fuel reduces the GHG in the atmosphere and it helps the industries to meet the carbon emission reduction goal. Despite the huge incentive of reduction in carbon footprint for co-processing, to be sustainable, the supply chain issues need to be handled effectively and MSW fragments need to be co-processed. The supply chain framework should be integrated with waste management system to handle the use of MSW fragments so as to facilitate MSW disposal.

7.4. Conclusion

The co-processing as a viable option for waste management and energy recovery with simultaneous economic gain has been presented in the study. The analysis, based on the pilot study, reveals certain sustainability issues and challenges before the cement industry. They needed to be resolved to device an effective business model of co-processing. The co-processing technology not only reduces the consumption of conventional material but also helps the industries to dispose of their waste as per the guidelines of the central pollution control board (CPCB), India. Co-processing also addresses the industrial goal of carbon mitigation as it reduces carbon emission, which would have otherwise taken place if conventional materials were used. The co-processing technique is a highly suitable business model in the Indian context and for other developing countries, based on the evaluation of the co-processing technique to environmental, economic, operational and social facets.

Chapter 8

Low Carbon Cement Manufacturing in India by Co-processing of Alternative Fuel and Raw Materials

(Addressing Objective – 5)

8.1. Introduction

Cement is one of the three main construction materials, which provides support for other related industries and fuels the economic growth (Song et al., 2016). The global construction sector approximately emitted 23% of total CO_2 amounting to 5.7 billion tonnes during the year 2009 (Huang et al., 2017). The cement industry contributes approximately 5% of the global man-made carbon dioxide (CO_2) emissions, thus becoming the second largest CO_2 contributor in industry after power plants (Ishak and Hashim, 2015; Kajaste and Hurme, 2016). Emission of CO_2 directly takes place during the cement manufacturing from the combustion of fossil fuels and calcinations of raw materials. An indirect and significantly smaller emission of CO_2 takes place from the consumption of electricity. Roughly half of the emitted CO_2 originates from the fuel and the rest originates from the raw material conversion (Hendriks et al., 1998). Approximately 40% of cement plants, CO_2 emissions are from the burning of fossil fuel in the kiln, 50% due to the manufacturing process and the remaining 10% are indirect emissions related to transportation and front-end production processes (Imbabi et al., 2012).

India ranks second in terms of cement production capacity, the cement industry in India emitted 102 million tonnes of CO_2 during the year 2014 (Olivier et al., 2015; WARMING, 2011). Cement making process is highly energy intensive accounting for nearly 35 – 50 % of the production costs. This provides ample opportunities for reducing energy consumption. About 30% of electric power is consumed for grinding, and a little less than 30% is consumed by the clinker burning process with the raw mill unit accounting for 24% of the energy consumption (Technology Compendium On Energy Saving Opportunities, 2013). The specific energy consumption levels of Indian cement sector are globally comparable. The range of electrical energy consumption varies from 65-110 kWhr/t of cement.

Cement production is the second largest contributor of anthropogenic CO_2, making the cement industry one of the primary sector for implementation of CO_2 mitigation strategies (Summerbell et al., 2016). Effective approaches to reduce the environmental impacts of the cement industry include optimizing the industrial structure in cement production, improving consumption efficiency of energy and raw materials, using industrial waste and by-products instead of limestone and promoting electricity recovery technologies (Chen et al., 2015). The study thus focuses on AFRs utilization via a co-processing, in cement kiln as a way of CO_2 emission mitigation strategy. The use of AFRs in the production of clinker reduces the amount of CO_2 intensive clinker in the final product. In order to contribute to lowering of energy consumption in clinker burning and reduction of associated CO_2 emission, suitable alternative materials should contain CaO; including other major constituent SiO_2, Al_2O_3 and Fe_2O_3 (Mikulčić et al., 2016).

The objective of the work is to show the co-processing potential as a low carbon manufacturing process which reduces the carbon footprint of the cement plant and waste producer (industries) based on the four constructs namely amount of AFRs co-processed, TSR%, traditional fuel (TF) and traditional raw material (TR) replaced and substitution benefit in term of monetary value.

8.2. Methodology

The study follows a case study approach based on a qualitative and quantitative analysis and involves the following steps. Firstly, literature review was carried out to gauge the practices of waste co-processing in cement kilns in different parts of the world. The different parameters with respect to low carbon constructs were identified and different sustainability issues of co-processing in cement plant were analysed. Secondly, two case studies were carried out in cement plants in different part of India to ascertain the present practices and status of co-processing in India. The case studies analysed different waste stream substitution potential and their effect on the plant production parameters. Thirdly, the low carbon potential of the process was analysed based on the statistical data of the year 2014 of the plants that is via savings of conventional resources. The statistical data were obtained from the plant production process running data. The data were obtained on a regular basis both in online and offline mode as per the parameters and their requirements with respect to norms. Number of low carbon constructs like traditional fuels replaced, alternative fuel and raw materials used, thermal substitution rate (TSR %) achieved and substitution benefit in term of monitory value were analysed. The clinker quality data was also analysed during the study period. Fourthly the study was concluded with emphasising on the benefits of waste disposal in cement plant and its implication as a low carbon cement manufacturing process in term of replacement of conventional/traditional raw materials and fuels by AFRs, which would have been ended up in landfills.

8.3. Discussion and Analysis of Case study

8.3.1. Case study-1

The cement plant is one of the oldest cement plants in India with clinker capacity of 2.23 million tonnes per annum; it has two modern cyclones pre-heater dry process type kilns. The plant uses AFRs in both the kiln; the plant has a waste pre-processing platform, for shredding, sorting and homogenising. A crane homogenizes the shredded waste with saw dust and rice husk to reduce the moisture contain. The waste are sampled by the in-house laboratory to measure the variable parameters namely calorific value, metal contents and different elemental constituents, based on the results the feeding rate is determined for a particular batch of waste. The pre-processing platform has a magnetic separator which takes out the ferrous based metal. The processed waste material is fed to the secondary inlet of the kiln via an arrangement of conveyer belts and screw feeder. A shut off gate arrangement is there to avoid back fire. Alternative raw materials (AR) is pre-processed in different pre-processing platform and fed through a separate conveyer belts; it is usually fed in to the secondary inlet or in some cases they are mixed in different proportion during the raw feed preparation. The AFRs are delivered by the waste producer with a tipping fee on a per truck basis to the cement plant. The rice husk and saw dust are brought by the cement plant authorities and there cost varies from 43-45 USD/tonne. The constituents of AFRs which are co-processed includes effluent treatment plant (ETP) sludge, bio sludge, spent carbon, plastic wastes, carbon black, water treatment plant (WTP) Sludge and fast moving consumer goods (FMCG) rejects. The average calorific value of the waste ranges in between 2020 – 6247 kcal/kg.

The production process of cement is highly energy intensive, with average specific electrical energy consumption of 79.41 kWh/tonne of cement produced. The use of alternative fuel thus reduces the overall carbon footprint of the plant which would have otherwise added to the plant directly or indirectly. Direct carbon emission may be attributed to the use of conventional raw material and conventional fuels at the plant and indirect may be attributed to the mining and processing of the conventional material at their manufacturing points including the electricity consumption. The analysis of the case study shows, high amount of thermal substitution rate (TSR%) during the co-processing (figure.8-1). The statistical data of the plant TSR% indicates maximum achieved substitution of 7.04% in the month of January; though the graphical trends reveals decreasing curve of TSR%. The fall in TSR% was due to the unavailability of the waste due to supply chain constraints which was mainly attributed to competition from other nearby cement plants which were taking the waste from the same supplier at lower tipping fees and also due to normal production process fluctuation.

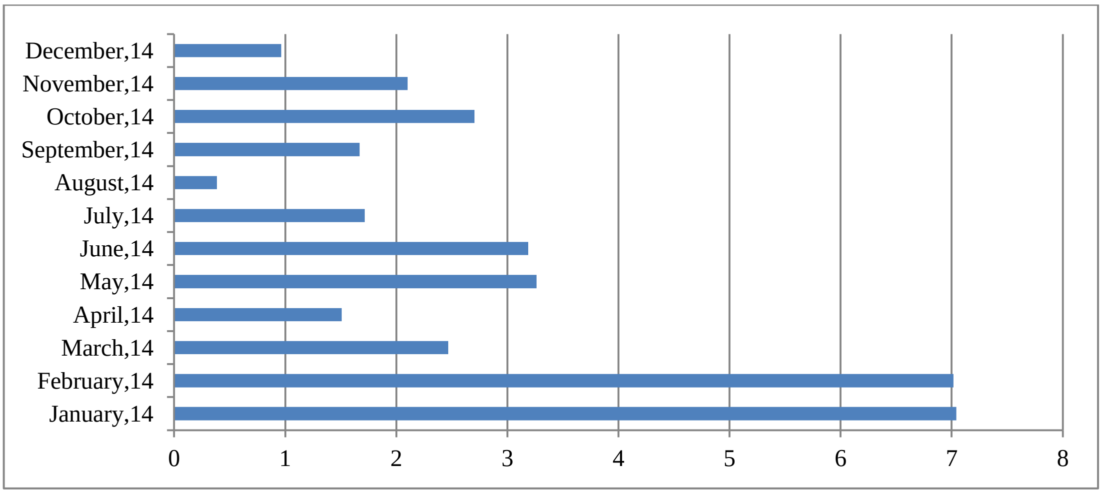

Figure.8-1. TSR% achieved during the year 2014

The quantity of AFRs co-processed in January is the highest (5,593 tonnes) after that a fall in quantity of AFRs was reported. Another noticeable trend was increasing quantity of alternative raw materials (AR) feeding, with decreasing quantity of alternative fuel (AF) feeding. This variation of AR and AF quantity was attributed to supply chain constraints and production process fluctuation (figure.8-2). Approximately 51,995 tonnes of traditional fuel and raw material was replaced in the year 2014. The feeding trend represents a fluctuation which is contributed due to the production deviation and process requirements as per the composition and characteristics of AFRs (figure.8-3).

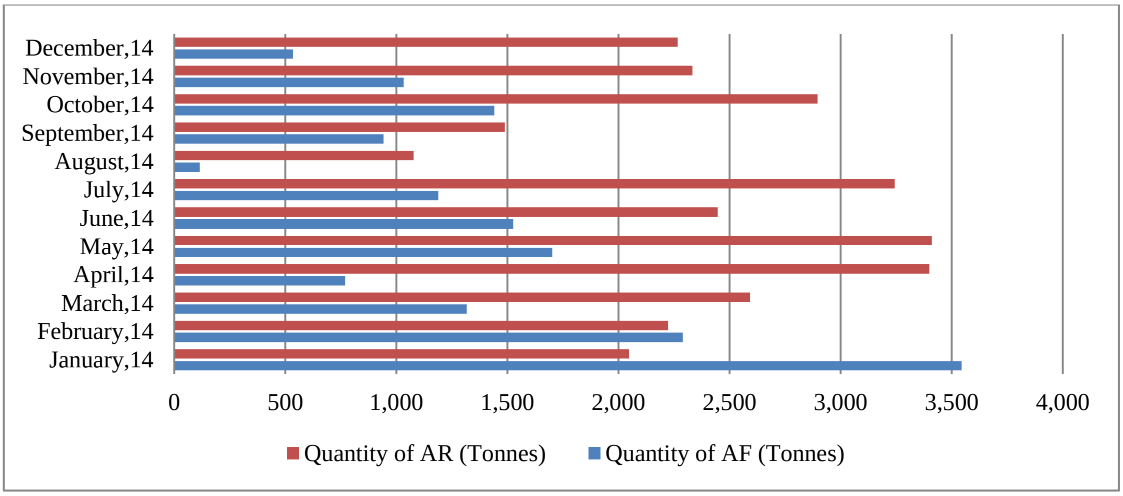

Figure.8-2. Quantity of AF and AR co-processed in the year 2014

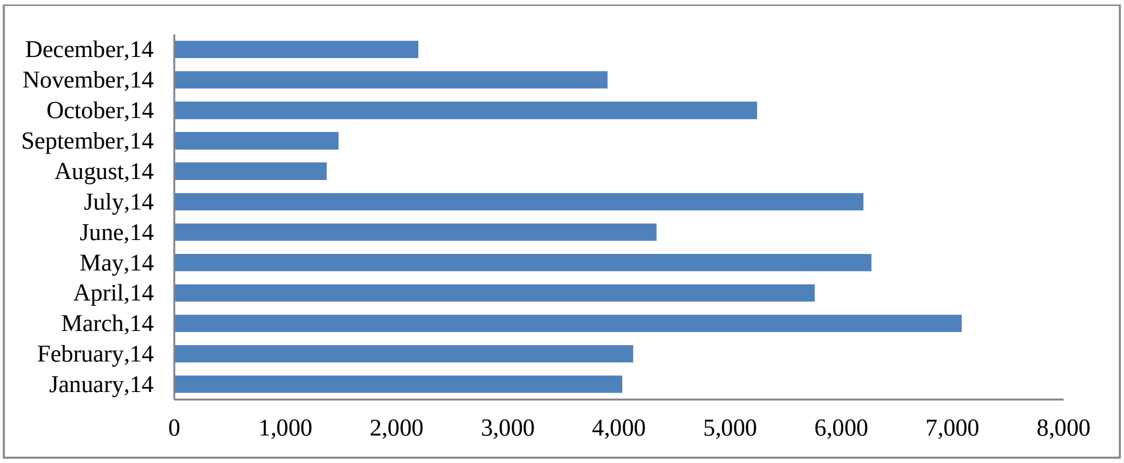

Figure.8-3. Quantity of traditional fuel and raw materials replaced by AFRs in the year 2014

The substitution benefit is enormous in term of monetary gain as co-processing of AFRs has effectively reduced both the cost towards raw material and conventional fuel resulting in savings running to millions of USD with highest substitution benefit of over 0.5 million USD achieved during the month of January (figure.8-4).

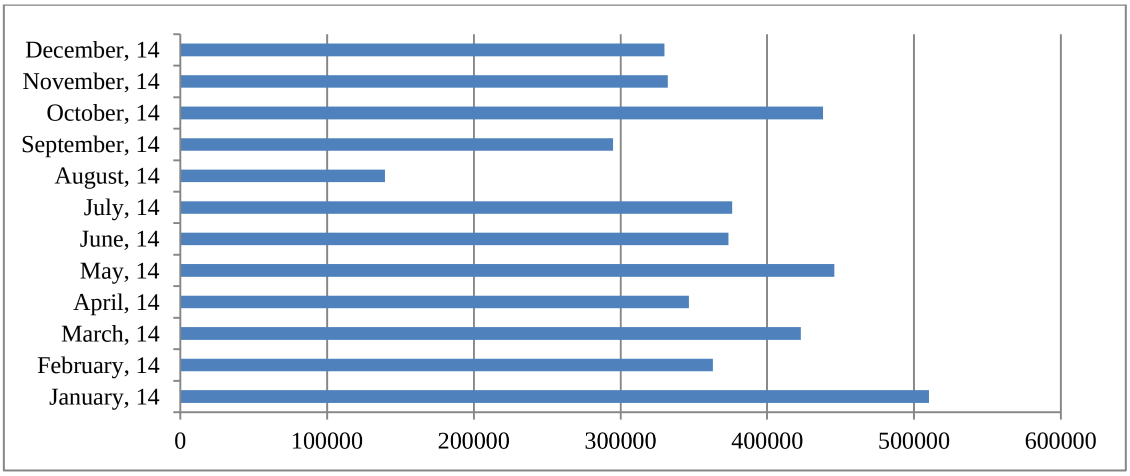

Figure.8-4. Substitution benefit of AFRs obtained in USD month wise for the year 2014

The fluctuation in substitution benefit is in line with feeding rate of AFRs. The stack emission of the cement kiln was also monitored during the period in both online and offline mode, based on the different parameters. None of the emission measured was above the co-processing guidelines of Ministry of Environment, Forest and Climate Change, India (table.8-1).

Parameter	**Unit**	**Method Used**	**Norms for Cement Plant Co-processing Waste**	**2014**
SPM	mg/Nm^3	USEPA 17	30	28.38
SO_2	mg/Nm^3	USEPA 6B	100	85.6
Hg	mg/Nm^3	USEPA 29	0.05	0.035
NOx	mg/Nm^3	USEPA 7E	800	396
Cd & Tl	mg/Nm^3	USEPA 29	0.05	0.028
Sb+As+Pb+Co+Cr+Cu+ Mn+Ni+V	mg/Nm^3	USEPA 29	0.5	0.10565
HF	mg/Nm^3	USEPA 26	1	0.41
HCL	mg/Nm^3	USEPA 26	10	6.31
TOC	mg/Nm^3	USEPA 25A	10	7.36
Dioxin/ Furan	ngTEQ/Nm^3	USEPA 23A	0.1	0.015

Table.8-1. Average stack emissions for each of the parameters during trial

Clinker quality is a defining property of the final finished products; it is monitored regularly during the production process. The properties of the clinker depend on the quantity of different elements going in to the raw materials. The parameters are kept fixed with in a tolerance level as per the industry practise. There were minimal reported changes during the overall study period throughout the year; all the critical parameters were below the production tolerance limit (table.8-2).

Parameter [%]	**Pre Co processing Monthly Average Value**	**During Co- Processing Average Value Every Quarter for the Year 2014**				**Post Co processing Month Average Value**
		1st Quarter	**2nd Quarter**	**3rd Quarter**	**4th Quarter**	
SiO_2	23.14	22.54	23.07	22.80	22.95	22.95
Al_2O_3	7.18	6.23	7.10	6.94	6.85	6.69
Fe_2O_3	3.16	2.82	3.03	3.05	2.99	3.00
CaO	62.35	61.91	61	61.20	60.20	60.10
MgO	2.64	2.55	2.71	2.26	2.75	2.74
SO_3	0.33	0.46	0.45	0.32	0.40	0.47
Na_2O	0.24	0.26	0.25	0.25	0.24	0.25
K_2O	1.31	1.42	1.36	1.18	1.25	1.43
Cl	0.00	0.00	0.00	0.00	0.00	0.00
TiO_2	0.38	0.34	0.39	0.32	0.35	0.38
Mn_2O_3	0.09	0.09	0.07	0.08	0.09	0.09
Free CaO	2.87	2.12	1.84	2.88	2.99	2.51
Lime Saturation Factor (LSF)	0.82	0.86	0.80	0.85	0.85	0.80
Silica Modulus (SM)	2.23	2.39	2.26	2.27	2.28	2.37
Alumina Modulus AM)	2.27	2.20	2.37	2.27	2.28	2.24
Liter Weight	1300	1320	1334	1317	1325	1314

Table.8-2. Clinker quality analysis during the trial

8.3.2. Case study - 2

The cement plant is situated in northern part of India with clinker capacity of 4.64 million tonnes per annum; it has two modern cyclone pre-heater dry process type kilns. The plant is co-processing AFRs in kiln – 2. The waste producer provides mixed waste with different size and characteristics. The pre-processing platform is fully mechanized and incorporates latest development in pre-processing technology. The pre-processing platform churns and shreds different waste and mixes them with the help of an excavator. The setup not only shreds the waste in to 10 – 15 cm but also removes ferrous based materials through a magnetic separator. The kiln-2 has a feeding capacity of 20tonnes/hr. The waste after shredding is impregnated with biomass consisting of rice husk and saw dust, to reduce the moisture contents of the homogeneous mixture. The wastes after sampling are taken by truck or dumpers to the walking floor; the waste mix is then fired via an arrangement of conveyer belt to multiflex system. The multiflex system is a hopper with screw conveyer arrangement, and finally through a pneumatic shut of gate it enters the kiln at the secondary inlet. The chemical sampling carried out determines the feeding rate for a particular homogenised batch of waste, the characteristics of the waste plays a key role in clinker property and emissions. The addition of biomass like rice husk or saw dust not only reduces the moisture content but also enhances the calorific value of the AFRs. The waste producer provides a tipping fee on a per truck basis and delivers the consignment of waste at the plant gate, only the biomass are brought by the plants, the cost of the biomass varies from USD 42 – 48 per tonne. The AFRs in this plant constitutes FMCG trade rejects, plastic waste, carbon slurry, bagasse, fly ash, paint sludge. The average calorific value ranges from 2713 - 4021 kcal/kg. The co-processing solves a major problem of industrial waste disposal as all the waste fraction were of industrial origin, 20501 tonnes of AFRs were co-processed by the cement plant in the year 2014. Thus co-processing of waste in the cement plant not only reduces the use of traditional raw material and fuels, it also manages to reduce the carbon footprint of the product. The analysis of 2014 statistical data of the cement plant reveals high TSR% (figure.8-5). The maximum TSR% was achieved in the month of April with value of 7.37%, the graphical trends shows that the plant TSR% was fluctuating, which is attributed due to waste types and production fluctuations.

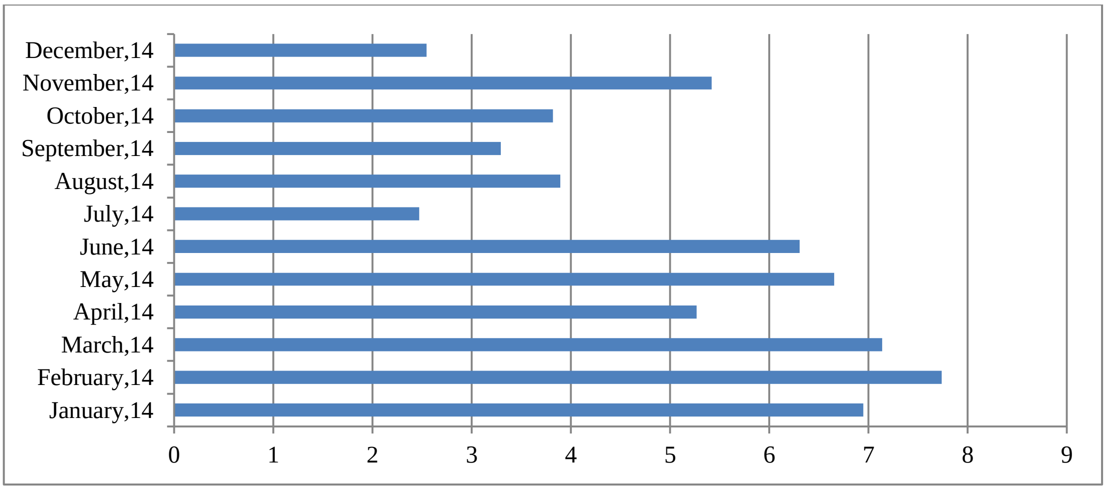

Figure.8-5. TSR% achieved for the year 2014

The quantity of AFRs co-processed in Aprils is the highest at 2781 tonnes; of which 1602 tonnes was AR and 1179 tonnes was AF. The analysis shows AF is the bulk of the material co-processed while AR is accounting to only 7648 tonnes during the twelve month period. The fluctuation which can be seen is due to the process fluctuation (figure.8-6). The quantity of traditional fuel and raw material which have been replaced due to co-processing is approximately 14,439 tonnes for the year 2014; indicating enormous saving of the conventional resources. The substitution of conventional fuel and raw materials led to the reduction of carbon emission both from indirect and direct source. The fluctuation in feeding trend of TF and TR is due to production deviation and process requirements (figure.8-7) and schedule maintenance.

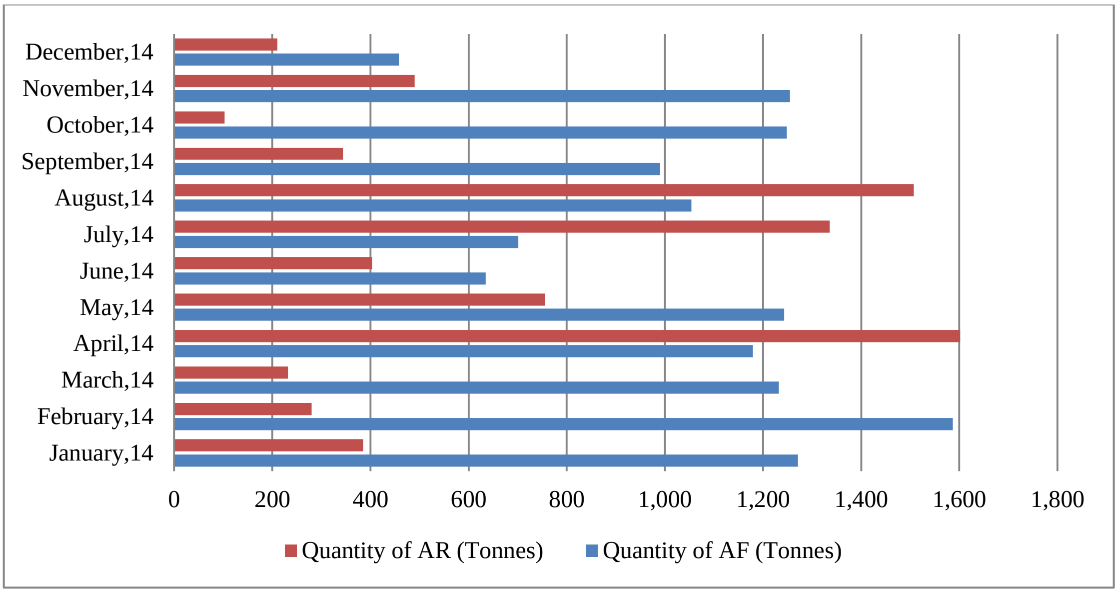

Figure.8-6. Quantity of AF and AR co-processed in the year 2014

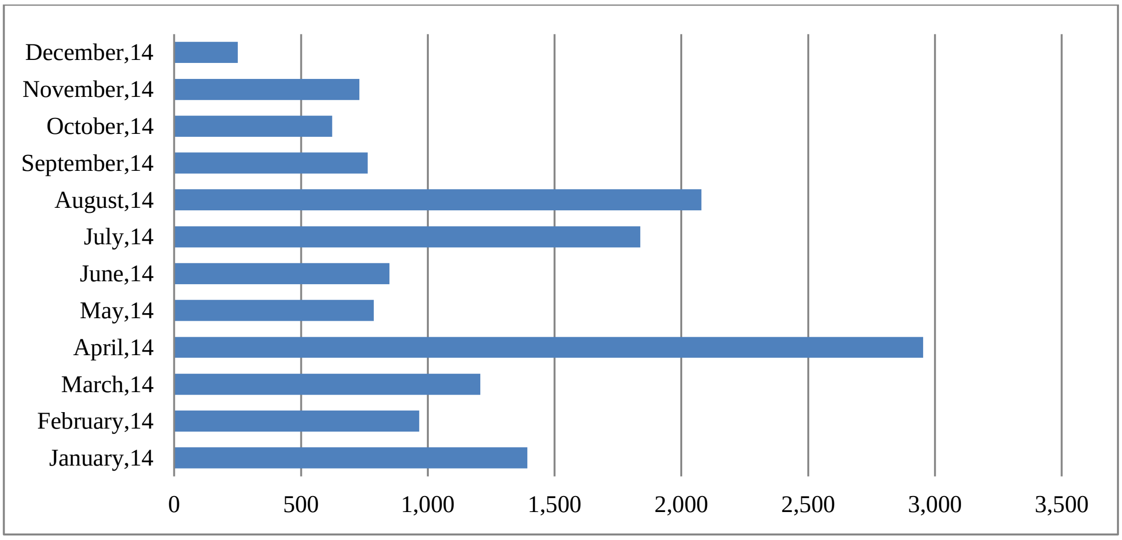

Figure.8-7. Quantity of traditional fuel and raw materials replaced by AFRs in the year 2014

The co-processing of AFRs doesn’t only have an environmental benefit as a low carbon manufacturing process but also has a benefit in term of monitory gain with respect to substitution benefits which runs to millions of USD with highest substitution benefit of over

1.39 million USD, achieved during the month of December (figure.8-8). The fluctuation in the values is contributed to the feeding rate which is directly proportional to the production fluctuation. The stack emission of the cement kiln was monitored during the year 2014 for each of the month in both online and offline mode based on the different parameters. The average value indicates no increment in the emission during the co-processing of different AFRs (table.8-3).

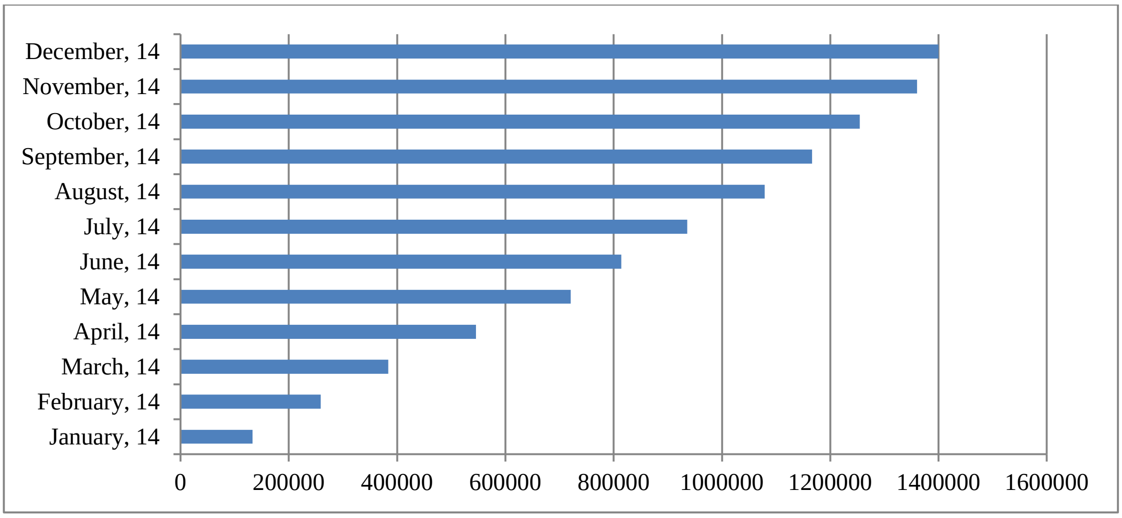

Figure.8-8. Substitution benefit of AFRs obtained in USD month wise for the year 2014

Parameter	Unit	Method Used	Norms for Cement Plant Co-processing Waste	2014
SPM	mg/Nm^3	USEPA 17	30	27.81
SO_2	mg/Nm^3	USEPA 6B	100	36.7
NOx	mg/Nm^3	USEPA 29	800	318
Hg	mg/Nm^3	USEPA 7E	0.05	0.0003
Cd & Tl	mg/Nm^3	USEPA 29	0.05	0.0005
Sb+As+Pb+Co+Cr+Cu+ Mn+Ni+V	mg/Nm^3	USEPA 29	0.5	0.018
HF	mg/Nm^3	USEPA 26	1	0.15
HCL	mg/Nm^3	USEPA 26	10	4.56
TOC	mg/Nm^3	USEPA 25A	10	6.06
Dioxin/ Furan	ng TEQ/Nm^3	USEPA 23A	0.1	0.0041

Table.8-3. Average stack emissions for each of the parameters during trial

The clinker quality was monitored regularly during the production process. The analysis of the data of the clinker analysis showed marginal deviation from the pre co-processing period to post co-processing period. There were minimal changes as revealed during the overall study period. All the parameters were well below the production tolerance limit of the cement plant (table.8-4).

Parameter [%]	Pre Co processing Month Average Value	During Co- Processing Average Value Every Quarter for the Year 2014				Post Co processing Month Average Value
		1st Quarter	2nd Quarter	3rd Quarter	4th Quarter	
SiO_2	24.15	23.54	22.85	24.08	23.95	23.48
Al_2O_3	7.59	7.25	7.18	7.45	6.99	7.25
Fe_2O_3	3.98	3.86	3.58	3.28	3.68	3.05
CaO	65.48	63.58	64	64.54	65.12	65.28
MgO	2.85	2.66	2.81	2.46	2.78	2.65
SO_3	0.36	0.32	0.40	0.38	0.31	0.35
Na_2O	0.28	0.27	0.24	0.23	0.26	0.29
K_2O	1.58	1.48	1.55	1.61	1.44	1.51
Cl	0.00	0.00	0.00	0.00	0.00	0.00
TiO_2	0.36	0.37	0.32	0.35	00.38	0.32
Mn_2O_3	0.08	0.09	0.06	0.07	0.09	0.09
Free CaO	2.98	2.88	2.50	2.81	2.95	2.75
LSF	0.98	0.91	0.94	0.89	0.83	0.92
SM	2.76	2.65	2.56	2.61	2.70	2.68
AM	2.82	2.75	2.86	2.72	2.75	2.83
Liter Weight	1350	1340	1338	1328	1336	1340

Table.8-4. Clinker quality analysis during the trial

8.4. Findings

The study reveals effectiveness of co-processing as a low carbon cement manufacturing process based on the case studies in the cement plant. The case studies reveal enormous saving in term of monetary values, by co-processing of industrial waste and by-products as an alternative fuel and raw materials. The gain is derived from both the tipping fees provided by the waste producer and by reduction in the consumption of conventional resources. The delivery of the wastes to the plant site by the waste producer further reduces the logistic cost.

The co-processing of waste in cement plants helps in complete thermal and material recovery of waste with no secondary products (slag, ashes) as the co-processed waste becomes an integral part of the clinker. Co-processing of AFRs in cement plants reduces greenhouse gas (GHG) emission by reducing the use of conventional resources which would have otherwise added to carbon foot print of the clinker. The process also reduces the waste going to the landfill and thus indirectly reducing the GHG emission. The study also reveals the economic and environmental potential achieved in an existing cement plants in term of utilizing AFRs in cement kiln. India being the second largest producer of cement in the world the potential of co-processing waste as AFRs is enormous.

The co-processing of waste not only reduces the carbon emission which would have otherwise taken place if the waste were land filled but it also reduces the carbon foot print of the cement plant and the industry disposing of their waste. The analysis of the two cement plants revealed high rate of TSR%, indicating substitution of high amount of conventional resources. The technology requirement for feeding arrangement is less thus reducing the setup cost for a cement plant. The emission controlling equipment already present in cement plants are substantial in-term of the feeding rate practiced currently, feeding rate is a very important deciding factor for emission and quality of the clinker and it is strictly controlled during co-processing based on the waste composition and characteristics as analysed by the in-house laboratory for each batch of waste received by the cement plant. Also with controlled feeding rate co-processing, has a proven zero emission problem as coined by number of literature and in the other chapters.

The mixed fuel i.e. co-processing of AF and TF can be 20-25% less carbon intensive than coal. These less carbon-intensive fuels could reduce overall cement emissions by 18-24% from 2006 levels by 2050 (WBCSD, 2009). The use of AF restricts emission of 2.79 tonne of CO_2 equivalent for each tonne of waste recycled at cement plant instead of land filled (US EPA). Thus co-processing methodology is reducing the carbon foot print and making the process much more greener and low carbon process. Indian cement industries effort towards reduction of carbon emission by adopting the best available practices are reflected in the achievement that is in reduction of total CO_2 emissions to an industrial average of 0.719 tonne CO_2 per tonnes of cement in 2010 from a substantially higher level of 1.12 tonne CO_2 per tonne of cement in 1996 (Technology Roadmap – Low Carbon Technology for the Indian Cement Industry 2012). Although the co-processing of waste in cement plant is a holistic process as can be gauged from the literature and cases studies, number of constraints exists which need to be addressed effectively to stream line the low carbon cement manufacturing process in India. The increased use of AFRs in cement production is thus a core element of carbon mitigation strategy.

8.5. Conclusion

The study analysis the low carbon cement manufacturing potential based on two case studies at cement plants in India. The cement plants under study are co-processing industrial waste and by-products as alternative fuel and raw materials. The study showed the potential based on the critical constructs as identified from literature and case studies. The study analysed a one year statistical data obtained from the plant production process monitored during the co-processing period. The four constructs considered for the analysis were TSR%, AFRs utilized, traditional fuel (TF) and traditional raw material (TR) replaced by AFRs and substitution benefit obtained in term of monetary gain. The sustainability of the co-processing was gauged in term of environmental implication through monitoring of the average stack emission. The emission result indicated negative deviation as all parameters were well below the norms. The economical analysis revealed enormous monetary gain. There was no reported effect of co-processing on the quality of the clinker during the one year period of analysis. Thus waste utilization as AFRs can solve the waste disposal problem plaguing the waste management system of the country. India being the second highest cement producing country, using of AFRs to its full potential can impact positively to global carbon mitigation efforts.

Chapter 9

Co-processing of Blast Furnace Flue Dust as AFRs in Cement Plant (Addressing Objective – 3)

9.1. Introduction

A steel plant produces 2–4 tonnes of waste for each tonne of steel produced. The various wastes produced during the process are blast furnace slag, blast furnace flue dust and sludge. The composition of these materials vary widely but usually contains number of useful resources including iron, carbon, calcium, zinc, lead, etc., which can be recovered and recycled. An integrated steel plants produces BF flue dust of around 18-22 kg/tonnes of hot metal (Nibedita, 2002; Roudier et al., 2013). The direct recycling of BF flue dust is not possible due to presence of undesirable elements (like zinc, lead and alkali metals) which may cause operational difficulties in the blast furnace. Therefore, it is desirable to recover the valuables and utilize these industrial wastes holistically (Das et al., 2007). Yehia and El-Rahiem,(2005) have reported that BF flue dust can be recycled based on magnetic and carbon content for sintering, re-burning, waste water treatment, production of carbon block, bricks and as inert filler for plastic. The BF flue dust has also been used as a source of solid reductant while production of cold bonded pellets (Robinson, 2005). It has also been used as an additive for building industries (Škvára et al., 2002). Shen et al.,(2010) utilized BF flue dust to prepare nanometer-sized black iron oxide pigment (Fe_3O_4, magnetite) with NaOH as precipitant. El-Hussiny and Shalabi, (2010) investigated the production of pellets with BF flue dust, using molasses as organic binder and its application in sintering of iron ore. El-Hussiny and Shalabi,(2011) investigated the potential utilization of BF flue dust and mill scale as a self-reducing briquette with different mass ratios in electric arc furnace to produce steel. da Rocha et al.,(2014) proposed a simple characterization route to produce self-reducing pellets to be used in the blast furnace process in order to minimize the incorrect disposal of dust generated in the basic oxygen furnace (BOF) converter. Zhang et al.,(2017) recycled the carbonaceous iron-bearing dusts generated from the iron & steel companies as pellets and used it as agglomeration feeds. Mombelli et al.,(2016) analysed the feasibility of the use of blast furnace sludge as a reducing agent to produce direct reduced iron from BOF-dust, further self-reducing briquettes containing a mixture of BOF-dust, BOF-sludge and BF-sludge were also produced. The BF flue dust has been utilized in number of ways as coined by different literature, but utilization of it as AFRs in the cement manufacturing process is still illusive in literature. Thus the present study deals with the evaluation of the use blast furnace (BF) flue dust in the cement manufacturing process. Cement manufacturing consists of raw meal grinding, blending, pre-calcining, clinker burning and cement grinding (Alsop, 2007). The raw material for cement manufacture is a rock mixture of about 80% limestone ($CaCO_3$) and about 20% balance material consisting of silica (SiO_2), alumina (Al_2O_3) and ferric oxide (Fe_2O_3). India is the second largest producer of cement in the world with capacity of 460 Million tonnes. Cement manufacturing is an energy and carbon-intensive industry. Each tonne of cement generates approximately 0.7 – 0.93 tonne of CO_2 depending on the kiln technology used. The cement industry contributes approximately 5% of the global man-made carbon dioxide (CO_2) emissions (Ishak and Hashim, 2015; Kajaste and Hurme, 2016). A wide range of options are available to considerably reduce this CO_2 emissions (Ishak and Hashim, 2015). And one of the predominant options is co-processing of different waste in cement kiln (Boesch et al., 2009; Boesch and Hellweg, 2010; Reijnders, 2007). The objective of the present work is to gauge the potential of co-processing BF flue dust in cement kiln. The study also analyses the cost benefit of co-processing blast furnace flue dust in cement kiln. The study, carried out over a month in one of the cement plant in central part of India, evaluates blast furnace flue dust as a substitute for iron and coal in cement manufacturing as AFRs.

9.2. Materials and Method

The study follows a cases study approach with a qualitative and quantitative analysis of the cement plant, co-processing BF flue dust as AFRs. The gap in the literature was analysed with specific emphasis on BF flue dust utilization. The chemical and proximate analysis of the BF flue dust samples were carried out. The study then analysed the economical potential of co-processing BF flue dust. And finally the study was concluded with emphasizes on BF flue dust utilisation in cement kiln.

9.2.1 Case study-trial

The case study was carried out in one of the oldest cement plant in central part of India with a capacity of approximately 1200t/day. It has a dry process type kiln with a modern cyclone pre-heater. The co-processing of blast furnace flue dust was carried out in the kiln. The kiln has a five stage pre heater tower with kiln diameter of 3.75m and length of 54m. The kiln rotates with a speed of 1.6 rounds per minute. This plant also has been co-processing different kinds of industrial wastes such as effluent treatment plant (ETP) sludge, bio sludge, carbon black, water treatment plant (WTP) sludge and expired fast moving consumer goods (FMCG) as AFRs. The capacity of feeding system was 4t/hr. The plant also has been using certain biomass like rice husk and saw dust, although their quantity was low. Approximately 12,054 tonnes of AFRs were utilised in the year 2014 in the cement kiln out of which 7,976 tonnes was alternative raw materials and 4079 tonnes was alternative fuel, due to which 8859 tonnes of traditional fuel and raw materials was replaced. Traditional Portland cement is produced in this plant using the raw meal having the chemical composition as shown in table.9-1.

Chemical Composition	**(%Mass)**
SiO_2	13.09
Al_2O_3	3.49
Fe_2O_3	2.32
CaO	42.04
MgO	2.26
SO_3	0.13
Na_2O	0.12
K_2O	0.95
TiO_2	0.14
P_2O_5	0.03
Mn_2O_3	0.05
BaO	0.01
LOI	35.49

Table.9-1. Average raw meal chemical composition for the trial month

It may be observed that the iron content in the raw meal is already there in reasonable proportion. The co-processing of the BF flue dust was carried out for one month to analyse the techno-economical benefit in term of substitution of conventional iron ore and conventional fuel with BF flue dust. Approximately 1305 tonnes of BF flue dust was co-processed during the one month study period, due to co-processing 870 tonnes of traditional raw materials (TRs) was saved. The assessment of the net calorific value of the BF flue dust over the period of the study revealed a range of 2092 – 2644 kcal/kg. The flue dust composition was studied by chemical and proximate analysis and the different constituent quantity is gauged. The flue dust which was obtained from the state owned steel plant was evaluated to see weather BF flue dust can be segregated in to iron rich and energy rich fractions so that more quantum of BF Flue dust can be co-processed in this plant, having limitation in utilising higher quantum of iron oxide. To evaluate this segregation, a drum type magnetic separator was used to separate out magnetic and non magnetic part of the BF Flue dust. The magnetic separator has a drum diameter of 400 mm and length of 600mm. The drum had motor power ratings of 1kW, with rated 15rpm speed. The drum separator could handle 0.5t/hr of raw feed (BF flue dust) (figure.9-1).

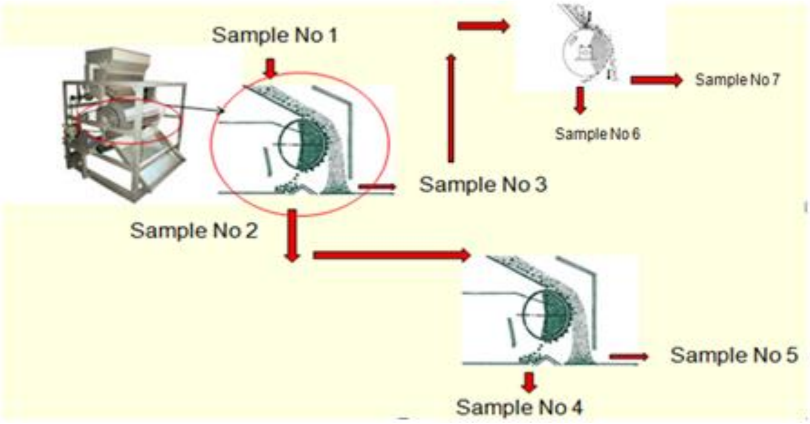

Figure.9-1. Drum type magnetic separator

The magnetic separation of the iron fraction was attempted through a three stage approach in which the non-magnetic fraction from the earlier stage was used as the input material in the magnetic separator twice. The drum type magnetic separator separated the raw feed in to six samples as is depicted in figure.9-1. Hence, in total 7 samples were generated through these processes which are depicted in figure.9-2 and their identity are provided in table.9-2.

Sample Number	**Details of the sample**
Sample No. 1	Original BF Flue Dust from steel plant
Sample No. 2	Magnetic fraction after first separation
Sample No. 3	Non Magnetic fraction after first separation
Sample No. 4	Magnetic fraction after Second separation
Sample No. 5	Non Magnetic fraction after Second separation
Sample No. 6	Magnetic fraction after third separation
Sample No. 7	Non Magnetic fraction after third separation

Table.9-2. Sample Identification

The percentage of iron and its oxide which can be co-processed is limited by the process requirement. Lime stone and other raw materials also have iron content. Iron oxide required to be added therefore is the difference of iron oxide required minus the existing one from the traditional raw materials. The raw materials used in the plant already has a reasonable quantum of iron oxide thus the required amount to be added through flue dust is very small - in the range of about 0.12% to 0.18% of the raw material. In some other cases, where the iron content in raw materials is low, the same amount can be higher.

Sample No.1: Original BF Flue Dust from steel plant

Sample No.2: Magnetic Fraction Sample No.4: Magnetic Fraction Sample No.6: Magnetic Fraction

Sample No.3: Non Magnetic Fraction Sample No.5: Non Magnetic Fraction Sample No.7: Non Magnetic Fraction

Figure.9-2. Sample of blast furnace flue dust (Scaled to 25:1)

9.3. Results and Discussion

9.3.1. Analysis of the samples

During the first round of separation 117 tonnes was separated in to magnetic and non-magnetic fraction via a magnetic separator. After first round of separation 49.3 tonnes were separated as magnetic (sample 2) and 67.7 tonnes as non magnetic (sample 3). The second stage followed, the sample 2 was further processed and magnetic portion accounted for 39.4 tonnes (sample 4) and non magnetic accounted for 9.9 tonnes (sample 5). The sample 3 was then processed in to 2.3 tonnes of magnetic fraction (sample 6) and 65.4 tonnes of non magnetic fraction (sample 7). Thus after two stage separation process total magnetic fraction was 41.7 tonnes and total non magnetic fraction was 75.3 tonnes (table.9-3).

1st round of separation		2nd Round of Separation		% age
49.3	Magnetic (Sample 2)	39.4	Magnetic (Sample 4)	33.68
		9.9	Non-Magnetic (Sample 5)	8.46
67.7	Non-Magnetic (Sample 3)	2.3	Magnetic (Sample 6)	1.97
		65.4	Non-Magnetic (Sample 7)	55.90
		41.7	Total Magnetic	35.64
		75.3	Total Non Magnetic	64.36

Table.9-3. Sampling of blast furnace flue dust

9.3.2. Proximate and chemical analysis

Proximate analysis and chemical analysis of each of these 7 samples were carried out using different ASTM methods (table.9-4), so as to gauge the feeding rate potential and other detrimental factor of co-processing. The analysis of sulphur was carried out as per the ASTM D4239-17 standard and the thermo gravimetric analysis (TGA) i.e. proximate analysis was carried out as per ASTM D 7582-15 standard. The calorific value was analysed using ASTM D 5865-13 standards. The BF flue dust samples for analysis was prepared using fusion technique following ISO 29581-2 standards and the glass bead was dissolved in nitric acid and then aspirated in inductive coupled plasma atomic emission spectroscopy (ICP-AES). AFRs feeding in the cement plant requires in depth analysis and controlling of the raw material constituents, so as not to disturb the final product in anyway. The iron requirement has a fixed tolerance level and it is needed to be controlled strictly while co-processing. The proximate and chemical analysis reveals the percentage of volatile matters (VM), ash contents, moisture contents, fixed carbon content, calorific value, useful heat obtainable, sulphur, chlorine, iron oxide and oxides of different trace material. The proximate analysis reveals that BF flue dust is not only used as a corrective for iron in the raw materials but also as a fuel (table.9-4) The calorific value of the blast furnace flue dust sample was in the range of 2340 - 2944 kcal/kg and percentage of iron oxide in the sample ranges in between 50.2% - 60.4%, based on the sample type magnetic or non magnetic as revealed by the chemical analysis of the samples. The loss of ignition (LOI) value indicates high quantity of unburned carbon content; it ranges from 24.5 to 36.5% of the sample it was analysed using IS 4032 standards. The oxide of trace elements also makes the controlling critical as co-processing process is highly critical of the constituents going in to the kiln. The sum up of each sample shows a percentage more than 100, due to the presence of iron in its metallic or reduced oxide form (table.9-5). The volatile matter presents in the raw material further increases the criticality of co-processing process.

Sample Detail	Proximate Analysis				Calorific Value kcal/kg	Useful Heat kcal/kg	% S	% Cl
	% Moisture	% VM	% Ash	% Fixed Carbon				
Sample - 1	0.1	8.1	64.5	27.4	2810	2531	0.5	0.16
Sample - 2	0.3	8.4	72.7	18.6	2686	2437	0.25	0.16
Sample - 3	0.5	7.3	78.5	14.8	2340	2092	0.2	0.15
Sample - 4	0.2	5.7	71.2	23.2	2673	2422	0.4	0.16
Sample - 5	0.1	6.4	68.8	25.4	2944	2664	0.5	0.16
Sample - 6	0.7	10.1	71.2	19.1	2452	2185	0.5	0.15
Sample - 7	0.6	6.2	66.3	28.1	2601	2333	0.4	0.15

Table.9-4. Proximate analysis of the samples

Sample Details	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**LOI**	**Na_2O**	**K_2O**	**SO_3**	**TiO_2**	**Mn_2O_3**	**P_2O_5**	**Total**
Sample-1	7.3	3.6	50.2	5.5	2.9	36.5	1.06	0.63	1.5	0.2	0.16	0.18	109.73
Sample-2	4.7	2.4	59.4	5.6	3.2	28.3	1.25	0.32	0.8	0.1	0.14	0.16	106.37
Sample-3	4.4	2.3	60.4	5.7	3.2	24.5	1.25	0.28	0.6	0.1	0.14	0.15	103.02
Sample-4	6.1	3	55.1	5.3	3	30.5	1.14	0.46	1.1	0.2	0.17	0.17	106.24
Sample-5	7.3	3.4	51.7	4.2	2.5	30.3	1.06	0.51	1.5	0.2	0.18	0.16	103.01
Sample-6	6.6	3.2	53.6	3.8	2.6	28.8	1.1	0.51	1.3	0.2	0.2	0.2	102.11
Sample-7	7.6	3.5	53.9	3.8	2.6	33.5	1.1	0.51	1.3	0.2	0.17	0.16	108.34

Table.9-5. Chemical analysis of the samples

The results of the proximate and chemical analysis of these 7 samples indicated that the magnetic separation could not segregate the BF flue dust material into iron rich and energy rich materials and hence, the co-processing of BF flue dust had to be carried out using the as received material only. Although the magnetic separation of BF flue dust was carried out to increase the feeding rate by reducing the iron content but even after magnetic separation, different sample had Fe_2O_3 in the range of 50 – 61% by mass, thus magnetic separation doesn't effectively reduce the iron content. Thus the methodology of magnetic separation to increase the feeding rate was not possible thus co-processing was carried out without separation.

9.3.3. Cost benefit analysis

The economical feasibility of utilising flue dust in the cement process is evaluated based on the mass and energy data generated during the trial by considering (1) raw material substitution rate achieved and (2) calorific value substitution rate achieved. Based on the laboratory analysis, the iron content in the flue dust was found to be approximately 60%. The natural iron oxide is having around 65% purity & its price ranges at around USD 43.79/t. Hence for iron ore, the iron cost works out to be USD 67.36/t on 100% iron basis (USD 43.79/0.65). While based on the iron content in flue dust, the feasible price of iron content at 60% workout to be USD 40.43/t. Considering allowance of about 50% of the cost of iron to account for the impurities present in the flue dust and its pre-processing, logistics etc., a price of USD 20.21/t seems reasonable for the flue dust to get utilised cost effectively in the cement kiln.

In term of calorific value (CV) available in the flue dust, which ranges from 2092 - 2664kcal/kg, the feasible cost for its utilisation, works out to about following two cases. 1) Flue dust with CV of 2092 kcal/kg: considering the cost of coal at about USD 0.015 per 1000 kcal, the substitution benefit available from the CV present in the flue dust works out to be USD 0.031/ kg or USD 30.53/t of flue dust. 2) Flue dust with CV of 2664 kcal/kg: again considering the cost of coal at about USD 0.015 per 1000kcal, the substitution benefit available from the CV present in the flue dust works out to be USD 0.039/kg or Rs. 38.88/t of flue dust. Giving an allowance of about 50% of this cost for impact of impurities etc present in flue dust, a net benefit of USD 15.27 to USD 19.44 is feasible for using flue dust in cement kiln. Overall therefore from iron content and CV content, the flue dust becomes attractive for use in cement plants at a cost ranging from about USD 35.48/t (20.21+15.27) to USD 39.66/t (20.21+19.44). Hence, the flue dust could be utilised cost effectively by the cement industry in the range of about USD 35 - 39/t (table.9-6).

The BF flue dust is not a hazardous waste as per the legislation of India, thus requirement of co-processing trial with emission monitoring was not mandatory, the plant only need to measure the dust (solid particulate matter) emission from kiln stack and it must be complied within 100µg/m^3 as per national ambient air quality standard 2009 and it was well below the level during the trial period. However, the stack emission of the cement kiln for different elements were monitored as normal plant procedure, both in online and offline mode and all the emission parameters were within the co-processing guidelines of Ministry of Environment, Forest and Climate Change (MOEF&CC), India.

<table>
<tr><td colspan="6">Based on the Raw Material Substitution</td></tr>
<tr><td>Iron Content In BF Flue Dust</td><td>Natural Iron Oxide Purity</td><td>Price Range of Natural Iron Oxide (USD/t)</td><td>On iron basis natural iron ore cost (USD/t)</td><td>On basis of iron content BF flue dust feasible costs (USD/t)</td><td>Assuming allowance of 50% of the cost on account of impurity an pre-processing (USD/t)</td></tr>
<tr><td>60%</td><td>65%</td><td>43.79</td><td>67.36</td><td>40.43</td><td>20.21</td></tr>
<tr><td colspan="6">Based on the Calorific Value</td></tr>
<tr><td colspan="3"></td><td colspan="3">Substitution benefit works out for flue dust (USD/t)</td></tr>
<tr><td colspan="3">Coal Cost in term of Calorific Value (CV) (USD/1000kcal)</td><td colspan="2">Considering lowest case of CV = 2092kcal/kg</td><td>Considering highest case of CV= 2664 kcal/kg</td></tr>
<tr><td colspan="3">0.015</td><td colspan="2">30.53</td><td>38.88</td></tr>
<tr><td colspan="3">Giving the allowance of 50% of this cost on account of impurity and pre-processing</td><td colspan="2">15.27</td><td>19.44</td></tr>
<tr><td colspan="3">Overall cost benefit from CV and Iron ore Substitution</td><td colspan="2">35.48</td><td>39.66</td></tr>
</table>

Table.9-6. Cost benefit analysis considering iron ore substitution and CV benefits of flue dust

The co-processing of BF flue dust in cement plant is highly sustainable methodology for utilization of this particular industrial waste, generated by the steel plant. Co-processing of this waste not only reduces conventional iron ore consumption but also reduces conventional fuel consumption due to its calorific value potential, thus BF flue dust acts as an AFRs and shows huge economical benefit as revealed by the trial of one month. The environmental sustainability was also revealed as no effect on emission was gauged during the trial as all the parameters were normal, further waste is re-circulated as a resource enabling a circular economy, reducing the carbon foot print of both the steel plant and cement plant as it manages to reduce the waste going to the landfill and saving tons of traditional fuel and raw materials.

9.4. Conclusion

The work presents a study based on BF flue dust, co-processing, as an experimental trial in one of the cement plant in India. The study is carried out for one month duration. The segregation of BF flue dust into iron rich and energy rich materials using magnetic separator was not effective as evaluated during process, and also the percentage substitution is very small ranging in between 0.12 – 0.18% of raw materials. The techno-economical potential of co-processing BF flue dust was analysed and was found to be attractive, as the flue dust could be utilised effectively by the cement industry at the range of about USD 35 - 39/t. Co-processing of BF flue dust lead to the reduction of carbon footprint of both steel plant and cement plant as 870t of conventional resource was saved. All the stack emissions were well below the guidelines of MOEF&CC, India. The low feeding rate as practised during the trial also reduces the chances of any impact on normal clinkering process and clinker quality. This process is adaptable for other cement plant also and the business case is highly profitable as shown in the calculation, both in terms of CV and iron substitution. The findings of the study revealed that the BF flue dust, waste from steel plant can be gainfully co-processed in the cement plant as AFRs and there exists a techno-economic potential for the same. The study thus shows the effectiveness of industrial waste co-processing in cement kiln as a way of resource recovery from waste leading to resource circulation.

Chapter 10

Utilization of Marble Slurry as a Sustainable Substitution for Conventional Resource in Cement Kiln

(Addressing Objective – 3)

10.1. Introduction

India is the largest producer of marble stones, with Rajasthan contributing to 95% of the overall production (MSME, 'Status report on commercial utilization of marble slurry in Rajasthan.'). Around 4000 marble mines and 1100 marble processing units are spread over 16 districts of Rajasthan (CPCB- Report on "Disposal Options Of Marble Slurry In Rajasthan). Marble sludge is generated as by-products during the cutting and polishing processes of the marble blocks. The marble blocks processing results in 30% waste generation. This contains 20-25% marble dust slurry and 5-10% of broken edges/slabs. The quantity of slurry generation during marble processing is directly related to the thickness of gang saw blades. This slurry waste has 70% of water content and rest is marble dust and edges/slabs. The water is recycled through settling tank and the settled moist marble dust is transported for disposal, the water is reused in the process again. Marble dust is a very fine powder has approximately 40% particles below 75μm diameter of which approximately 30% are having a size less than 25μm. Specific gravity of marble slurry is in the range of 2.70-3.00 gm/cm^3 with 5-20% water content (CPCB- Report on "Disposal Options Of Marble Slurry In Rajasthan). The residue marble slurry/powder was disposed of in to the nearby pit or vacant spaces. This leads to serious environmental pollution creating dust, which caused occupational health hazard in the vast area of land especially after the powder dries up (Vijayalakshmi et al., 2001). This unscientific disposal also lead to contamination of the underground water reserves and in some cases reduces porosity of soil thus reducing percolation rate of rain water (Almeida et al., 2007; CPCB- Report on Disposal Options Of Marble Slurry In Rajasthan; Vijayalakshmi et al., 2001).

The marble slurry can be utilized or disposed of in a number of ways. It can be utilized in number of industrial waste to name a few, making bricks, manufacturing of cement, production of ceramics tiles, cement concrete as an replacement materials, manufacturing of resins composites and as filler materials for road. Cement is produced by heating raw materials like oxides of silicon, calcium, aluminium and iron to temperatures of around 1450°C. The raw material for cement manufacture is a rock mixture which is about 80% limestone (which is rich in $CaCO_3$) and about 20% balance materials consisting of silica (SiO_2), alumina (Al_2O_3) and ferric oxide (Fe_2O_3). As 80% of the constituent going into the kiln is limestone, thus there lies huge potential for utilization of marble slurry in cement kiln as a substitute for conventional resource.

The objective of the current work is to gauge the potential and effects of co-processing of marble slurry on the cement manufacturing. The study evaluate marble slurry as an alternative raw material in cement kiln based on a case study analysis, which had been carried out over four years in a western part of India.

10.2. Materials and Methods

The study follows a two stage case study analysis consisting of qualitative and quantitative stages. Firstly a literature review has been carried out to find the present practices on disposal of marble slurry in cement kiln and its effect on the environment. Secondly, the co-processing potential was gauged based on the existing practises in cement plant for different waste stream. Thirdly, a case study - trial analysis was carried out at one of the cement plant in Rajasthan based on co-processing trial data of four years. The data was analysed to gauge the effect of marble slurry on the cement production process. Number of key parameter were analysed so as to reveal the sustainability of co-processing marble slurry. The parameters like emission (including heavy metals), quality of the clinker, TSR% achieved, quantity of traditional fuel and raw materials replaced, AFRs co-processed, economical gains obtained and leachate behaviour of the clinker were analysed. Finally the study concludes with emphasising the benefits of co-processing marble slurry in cement kiln. The process not only disposes the industrial waste generated in marble plants but also reduces the carbon footprint of the cement plant as conventional raw materials is saved, with gain in both economical and environmental aspect.

10.3. Case Study-Trial

The case study was carried out in a cement plant situated in the state of Rajasthan. The plant has an annual capacity of approximately 2.24 million tonnes. The plant has 2 working kiln in operation with a modern type five-stage cyclone pre-heater with in-line pre-calciner. The line-2 has AFRs feeding system, with a capacity of 4t/hr. The plant handles different industrial waste as AFRs. The plant is also using biomass, mainly saw dust and rice husk for impregnation in industrial waste to reduce the moisture content. The co-processing capacity is limited as the feeding system is not fully mechanised also the absence of pre-processing platform hinders feeding of large size materials. The plant has conglomeration with number of industries for supplying of waste; the transportation of waste to the cement plant is the responsibility of the waste generator. Tipping fee on a per tonne basis is provided by the waste producer for disposal of the same. As per the Solid Waste Management Rules - 2016, the waste generators have to dispose of the production process waste in a sustainable and environmentally sound way; co-processing being listed as one of the most effective way of disposal. Further, cement plants are able to reduce their carbon footprint by using AFRs by disposing the waste in kiln, making a sustainable business model. The industrial waste constitutes FMCG trade rejects, coagulation sludge, paint sludge, ETP bio sludge, spent carbon and carbon black. The assessment of the net calorific value over the period of the study revealed a range of 1700 – 6000 kcal/kg. The waste usually differ in their nature, physical consistency, packaging types and sizes, thus a pre-processing and characterization is required to gauge the feeding rate and with it the amount of impregnation required is also needed to be gauged so that the quality of the clinker and emission is not effected by co-processing the waste.

The plant is co-processing very small quantity of alternative fuel (AF) and thus pre-processing platform is not required. The bulk of the AFRs co-processed are marble slurry.

The waste generated at the waste generator's site is suitably packed by the waste generators and then the same is transported to the cement plant in trucks. Manifests and Transport Emergency Cards (TREM) are generated by the waste generator as per the co-processing guidelines before the commencement of the journey to the cement plant. The transportation of the waste to the cement plant is taken care by the waste generators, in the case of biomass, by the plant authorities. The waste is received at the plant gate by ensuring full compliance to the regulatory and other norms. The waste sampling and fingerprinting is carried out by the laboratory subsequently. Once the laboratory report gives positive result, the waste receipt conformation is given and the waste unloading in a permanent storage area is carried out. If the waste characteristic does not conform to the requirement then a negotiation and discussion starts with the waste generators for the way forward and final decision taken on the fate of the waste received. The waste is then fired as per the feeding rate decided by the sampling results of that particular batch of waste. The feeding rate is one of the primary deciding factors in co-processing of AFRs.

10.4. Results and Discussion

The four year plant data revealed the sustainability aspect in co-processing of industrial waste in cement plant specifically marble slurry as AR. The analysis showed that a high quantity of AFRs was processed during each month of the year 2014. The quantity is enormous, amounting to 98693 tonnes (figure.10-1). The AFRs co-processing analysis revealed that the bulk of the co-processed waste was AR, in total 92730 tonnes has been utilized in the year 2014 (figure.10-2). The traditional fuel (TF) and traditional raw materials (TR) replaced by co-processing AFRs is a staggering amount of 91957 tonnes during the year 2014 (Figure.10-3). The co-processing economical gain also runs to thousands of USD during the year 2014. The month wise gain for the year 2014 has been gauged (figure.10-4). Highest economical gain was achieved during the month of March.

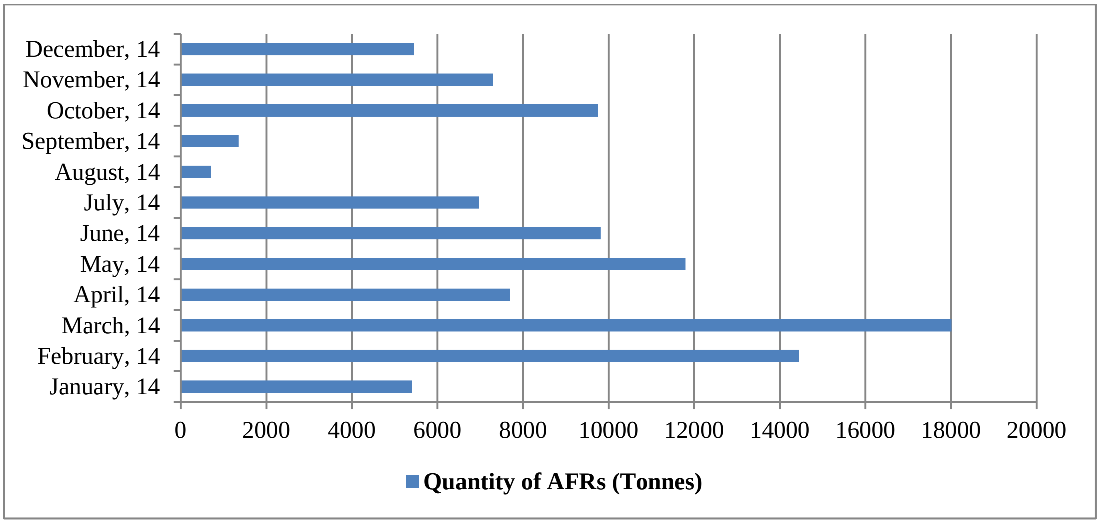

Figure.10-1. Quantity of AFRs used month wise in tonnes for the year 2014

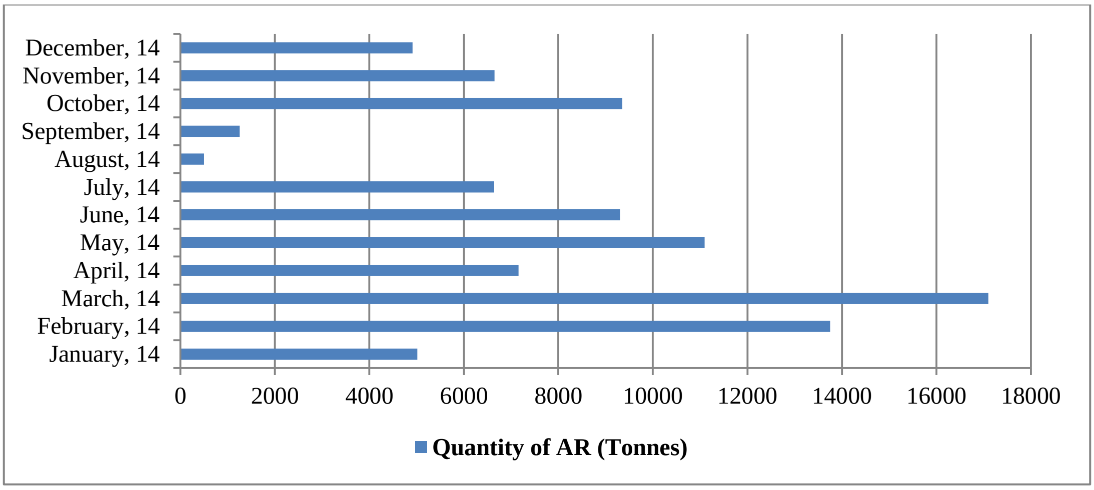

Figure.10-2. Quantity of alternative raw materials (AR) used month wise for the year 2014

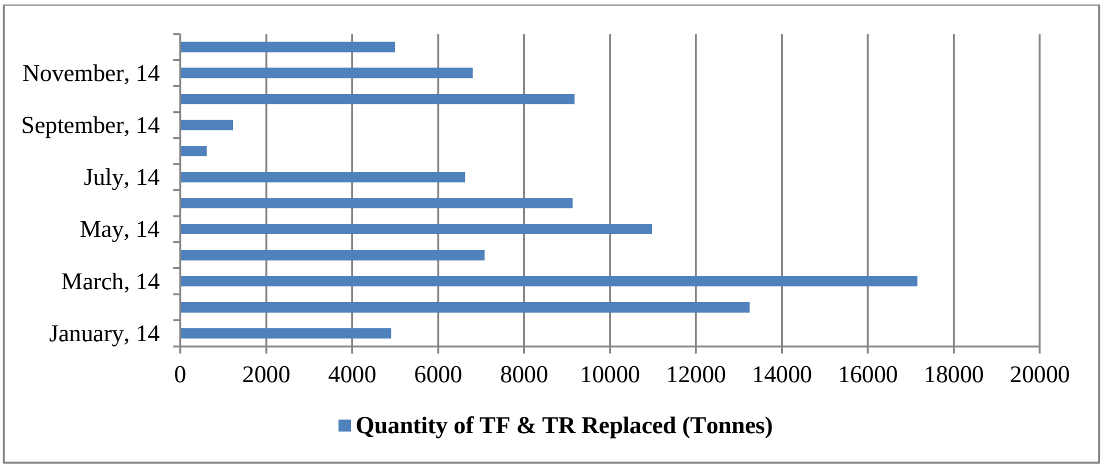

Figure.10-3. Quantity of traditional fuel and raw materials replaced by AFRs month wise for the year 2014

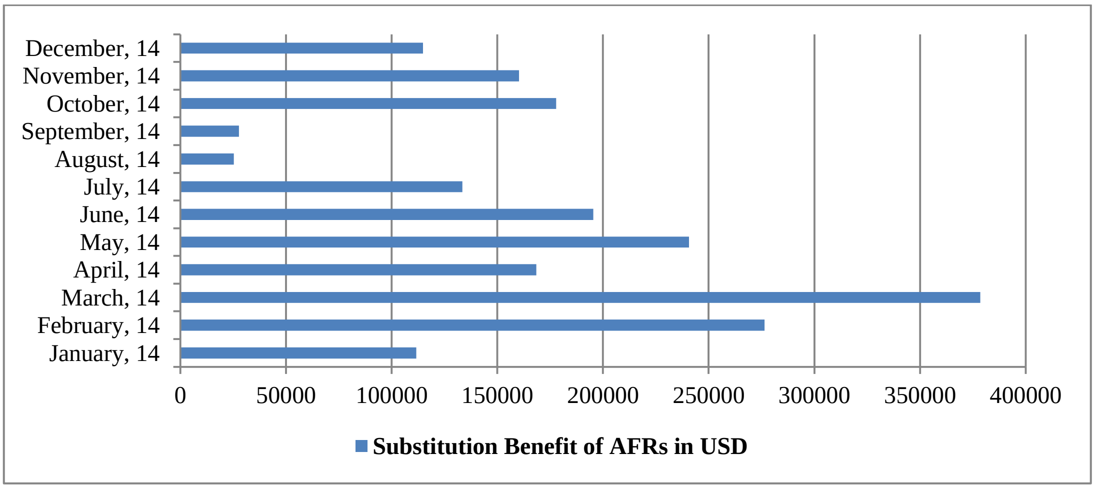

Figure.10-4. Trends in economical savings on the basis of AFRs substitution

The waste co-processed for each month of the year 2014, revealed that, the waste co-processing varied according to the kiln running hours and production process requirements. The quantity of waste which can be co-processed is directly related to the different process parameter of the cement plant. Strict controlling of AFRs firing is required for keeping the quality of the clinker intact and not to increases the emissions from kiln. The operational ease and economic effectiveness can be also gauged from the thermal substitution rate percentage (TSR%) in comparison to conventional fuel, as shown in figure.10-5.

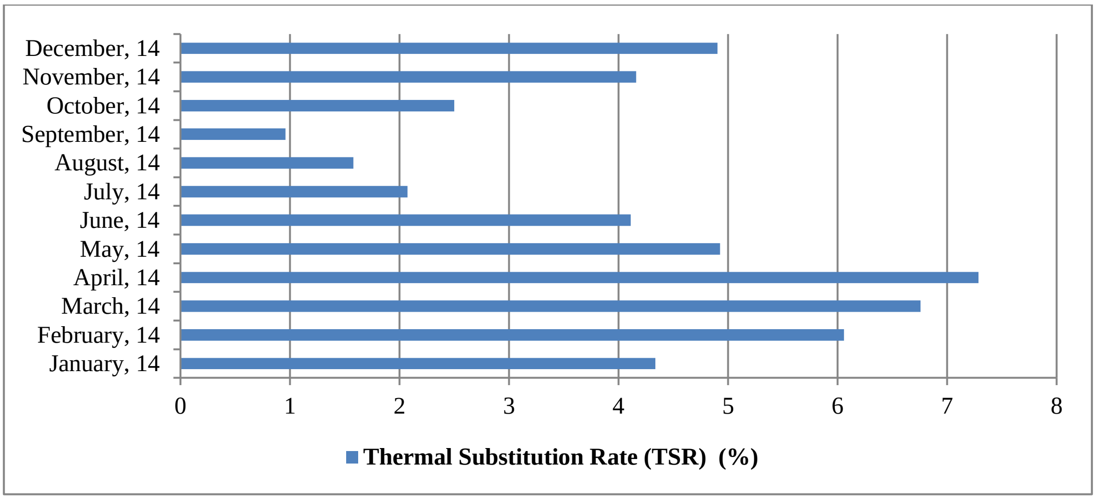

Figure.10-5. Thermal Substitution Rate % achieved month wise during the year 2014

The plant was primarily utilizing marble slurry as alternative raw materials as can be seen in the year 2014, out of 92730 tonnes, 92217 tonnes is marble slurry. The cement plant was co-processing marble slurry produced from mines of Makrana as the replacement of limestone. Marble slurry of Makrana region has calcined nature and low moisture percentage. Marble is recrystallised limestone and its main constituent is calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), lime (CaO) and magnesium oxide (MgO). High percentage of magnesium hinders the co-processing of the marble slurry. The typical analysis of the marble slurry received from this region was measured (table.10-1).

CaO	**MgO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**Na_2O**	**K_2O**
50.2	3.5	1.1	0.2	0.3	0.03	0.07
SO_3	**Cl**	**TiO_2**	**Mn_2O_3**	**P_2O_5**	**LOI**	**Moisture**
0.3	0.07	<0.01	0.008	0.3	44	1.40

Table.10-1.Typical compositional analysis of marble slurry during raw meal preparation

The acceptable percentage of MgO in cement manufacturing is in the range of 1-5%. The increased percentage of MgO in raw mix delays the hydration process as well as produce cracks in the clinker, thus impairing the soundness of the cement (Liu and Li, 2005) The percentage of moisture in raw mix required by cement plants is below 0.5-1% whereas in marble slurry it is of the order of 25%. The marble slurry generated during the process and available in the dumpsites is transported in the semi dried state to the cement plant and is used during the raw meal preparation. The cement plant has co-processed, in total 3, 50, 934 tonnes of marble slurry during the period 2012 - 2015 (figure.10-6).

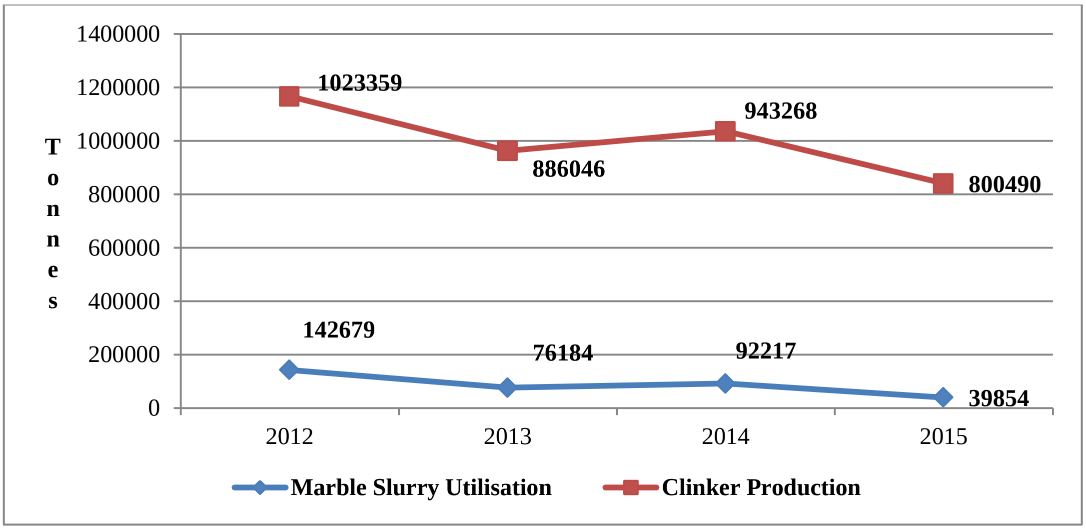

Figure.10-6. Marble slurry utilisation and clinker production in tonnes

The fluctuation was contributed due the production process, availability and as per the quality of the marble slurry. The total clinker productions during the periods were 3,653,163 tonnes with normal production fluctuation (figure.10-6). Thus a large quantity of conventional material has been substituted by co-processing the marble slurry/powder. The substitution rate achieved considering marble slurry in kg per tonne of clinker produced indicates high sustainability of the process as annual average of 139kg/tonne of clinker has been achieved during 2012 and with waste quality and availability there was fluctuation of the value with minimum substitution at 50kg/tonne in the year 2015 (figure.10-7).

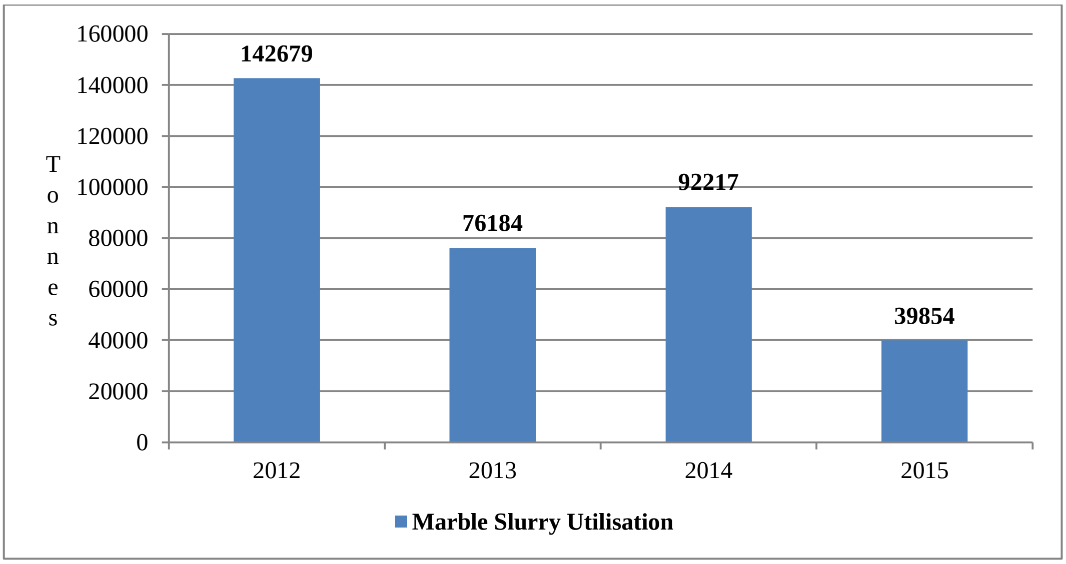

Figure.10-7. Marble slurry utilisation (Kg/Tonne of clinker)

The stack emission was monitored during the period in both online and offline mode based on the requirements of different parameters. None of the emission measured was above the co-processing guidelines (table.10-2). The analysis shows the effectiveness of co-processing marble slurry/powder in cement plant without any effect on emissions.

Parameter	**Unit**	**2012**	**2013**	**2014**	**2015**	**Norms**
SPM	mg/Nm^3	6.6	25.9	26.6	22.9	30
SO_2	mg/Nm^3	8.3	22	36.6	27.6	200
NO_X	mg/Nm^3	580	550	590	570	800
Hg	mg/Nm^3	0.0005	0.0005	0.0003	0.0005	0.05
Cd	mg/Nm^3	0.0005	0.0005	0.0005	0.0005	0.05
Tl	mg/Nm^3	0.0005	0.0005	0.0005	0.0005	0.05
As	mg/Nm^3	0.0005	0.0005	0.0003	0.0005	0.5
Co	mg/Nm^3	0.0005	0.0005	0.0005	0.0005	0.5
Ni	mg/Nm^3	0.0005	0.0005	0.0005	0.0005	0.5
Cu	mg/Nm^3	0.015	0.0005	0.0005	0.0005	0.5
Cr	mg/Nm^3	0.0005	0.0005	0.0005	0.0005	0.5
Pb	mg/Nm^3	0.0005	0.0005	0.0005	0.0005	0.5
Mn	mg/Nm^3	0.023	0.018	0.02	0.0179	0.5
Sb	mg/Nm^3	0.0005	0.0025	0.0025	0.0025	0.5
V	mg/Nm^3	0.0005	0.0005	0.0005	0.0005	0.5
Dioxin/ Furan	ng TEQ/Nm^3	0.014	0.0045	0.0045	0.0055	0.1

Table.10-2. Average stack emissions for each of the years

Clinker quality is the defining property of the final finished product of the production process; it was monitored extensively during the trial from collected samples across the years. It is required to be measured and analysed daily during each shift of production as per the company policy and to gauge any deviation in production process. The quality of the clinker largely depends upon the quantity and characteristics of the elements and their combined molecular properties. These parameters are usually kept fixed with in a tolerance level. There were hardly any reported changes during the co-processing; all the deciding parameters were well below the company production tolerance limit across the year (table.10-3).

Parameter [%]	**Average Value for the Year**	**During Co-processing Average Value for Each of the Year**				**Average Value for the Year**
	2011	**2012**	**2013**	**2014**	**2015**	**2016**
SiO_2	23.14	22.54	23.07	22.80	22.95	22.95
Al_2O_3	7.18	6.23	7.25	6.94	6.85	6.69
Fe_2O_3	3.16	2.82	3.03	3.05	2.99	3.00
CaO	62.35	61.91	61	61.20	60.20	60.10
MgO	2.64	2.55	2.91	2.68	2.75	2.74
SO_3	0.33	0.32	0.35	0.33	0.34	0.0.37
Na_2O	0.24	0.24	0.24	0.24	0.24	0.25
K_2O	1.31	1.42	1.36	1.18	1.25	1.43
Cl	0.00	0.00	0.00	0.00	0.00	0.00
TiO_2	0.38	0.34	0.39	0.30	0.35	0.38
Mn_2O_3	0.09	0.09	0.08	0.08	0.09	0.09
Free CaO	2.87	2.12	1.84	3.88	2.99	2.51
LSF	0.82	0.84	0.81	0.84	0.83	0.83
SM	2.23	2.49	2.26	2.27	2.28	2.37
AM	2.27	2.20	2.37	2.27	2.28	2.24
Liter Wt.	1300	1320	1334	1317	1325	1314

Table.10-3. Parameter percentage in clinker

The quality of the clinker was also analysed by carrying out a leach test during the study period and no deviations were noted (table.10-4). The analysis of data of four years thus demonstrated the waste marble slurry potential as a resource material, facilitating the circular economy.

Parameter	**Unit**	**Average Value for the Year**	**During Co-processing Average Value for Each of the Year**				**Average Value for the Year**
		2011	**2012**	**2013**	**2014**	**2015**	**2016**
Antimony	mg/kg	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00
Arsenic	mg/kg	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cadmium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Chromium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Cobalt	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Copper	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Lead	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Manganese	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Nickel	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Thallium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Vanadium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Mercury	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Zinc	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Tin	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Selenium	mg/kg	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Aluminium	mg/kg	7.00	4.00	11.2	4.4	<1.00	<1.00
Iron	mg/kg	1.40	3.00	1.40	1.00	1.50	2.20

Table.10-4. Clinker leach analysis during the co-processing period

The analysis of different property of cement was also carried out. The parameters analysed include blaine, setting time, soundness and compressive strength. The analysis of the pre co-processing year (2011 was taken as a benchmarked value for the cement produced in the plant. The blaine parameter of the cement was near the normal range; it changed marginally during the co processing period from 2012 – 2015. Similarly the soundness and compressive strength show marginal variation from their normal value. All the parameter changes as analysed during the six year period were within the tolerance limit of the product as practised by the plant (table.10-5).

Parameters		**Average Value for the Year**	**During Co-processing Average Value for Each of the Year**				**Average Value for the Year**
		2011	**2012**	**2013**	**2014**	**2015**	**2016**
Blaine (m^2 / kg)		327	326	325	323	328	327
Setting Time	Initial setting time	141	136	138	135	139	140
(Minutes)	Final setting time	192	189	191	187	190	189
Soundness	Le – Chat (mm)	1.0	1.0	0.5	1.0	0.5	0.5
	Autoclave (%)	0.04	0.04	0.03	0.05	0.04	0.05
Compressive	3 days	21.6	20.4	22.8	21.5	22.3	23.4
Strength	7 days	35.2	35	33.1	34.2	34	35.1
(in MPa)	28 days	47.2	45.5	46	45.8	46.7	45.9

Table.10-5. Analysis of different parameter of cement

The case analysis revealed that utilizing the industrial waste specifically marble slurry in cement plant is a favourable option, as AFRs reduces the waste going to the landfill site and reduces the use of TF and TR in the cement production process. Economically co-processing of AFRs is sustainable as high substitution benefit is achieved. The emission measurement during the study period also indicates environmental sustainability as there was no incremental variation in the deferent emission parameters during the consecutive years. The process also plays a role in reduction of carbon footprint of the cement plant and the waste producing plants by disposing of the waste and reducing the use of traditional fuel. A typical Portland cement contains around 67% calcium expressed as oxide (CaO). Assuming that all the calcium comes from limestone ($CaCO_3$), it can be estimated that one tonne of clinker requires roughly 1.2 tons of limestone which releases about 526 kg of CO_2 (Barcelo et al., 2014). The finding thus shows the sustainability of co-processing of marble slurry in Indian cement kiln. India being the largest producer of marble and a second largest producer of cement, a sustainable disposal methodology will help in resource circulation economy.

10.5. Conclusion

The study, based on analysis of four years of data, spread over 2012-2015, reveals the sustainability of marble slurry/powder co-processing in the cement kiln. The findings point to the fact that marble slurry can be used as an alternative raw material in the cement kiln at an extensive rate. The monitoring of stack emission during the observation period offered no pointers as to any adverse effect of co-processing - high economic gain that can be attributed to substitution of traditional fuel and raw materials was noted. The co-processing also had no impact on the product quality; a fact confirmed by the clinker quality analysis. The leach test also showed negative deviation of the clinker leach behaviour. The cement property analysis reported marginal fluctuation over the years; changes, which were well below the allowable limit laid down by the company. The fluctuations could be attributed to minor variations in production process parameters. Marble slurry, which has long been considered to be process waste, provides for a viable means of waste management that leads to substantive economic gains.

Chapter 11

Acid Tar Sludge Disposal in Cement Plant
(Addressing Objective – 4)

11.1. Introduction

Acid tar sludge (ATS) is a by-product of the steel production process which needs to be disposed of safely owing to its highly hazardous nature as defined by number of countries in their respective rules; in India, it is defined under the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016. The best possible disposal technique is thermal decomposition but most developing countries do not have dedicated hazardous waste incinerators or non-combustion technologies available for treatment of hazardous waste as such and can usually not afford exporting due to high costs (Karstensen et al., 2010). India alone generates 7234259 tonnes of hazardous wastes every year, out of which land fillable hazardous waste is 3509513 tonnes, incinerable 873405 tonnes and recyclable 2851341 tonnes as per CPCB. On the other hand, cement kilns are present in large number in developing countries and India, being the second largest producer of cement, provides ample scope for disposal. Cement kilns possess many inherent features which makes them suited for hazardous waste treatment; such as high temperatures, long residence time, surplus oxygen during and after combustion, good turbulence and mixing conditions, no generation of by-products such as slag, ashes or liquid residues and complete recovery of energy and raw material components in the waste (Karstensen et al., 2006; Strazza et al., 2011; Tiwary et al., 2014; Yang et al., 2014). Moreover, the alkaline environment leads to, sulphur and chlorine neutralization, and thus, the cement kiln can be described as a ‘‘huge scrubber’’ (Cong et al., 2015; Lemarchand, 2000). Although the cement manufacturing process is ideally suited for the incineration of waste-derived fuel and hazardous waste (Baidya et al., 2017; Liu et al., 2015; Mokrzycki et al., 2003; Mokrzycki and Uliasz-Bocheńczyk, 2003), the heavy metal accumulation and emission are area of concern when co-processing hazardous waste (Cong et al., 2015; Huang et al., 2012) and needed to be looked upon. Cement kiln requires appropriate installations for co-processing of wastes. Due to the inherent characteristics of the cement plants, the use of alternative fuels and disposal of hazardous waste in the cement industry is increasingly becoming an attractive option and it is estimated that approximately 10 to 15 % of substitution of conventional fuel in the kiln are carried out with hazardous waste in US (IFC, 2017). Different trial run identified wastes suitable for co-processing; source emission monitoring assessed environmental impacts and quantified the reduced environmental impacts to give a clear picture of actual benefits of co-processing (Tiwary et al., 2014).

A broad spectrum of study with different waste stream are available in literature like oil-based mud (OBM), an oil well drilling waste, as a partial replacement for the limestone in the kiln feed was studied for its effect on CO_2 emissions. The study revealed positive impact on reduction of CO_2 (Abdul-Wahab et al., 2016). Li et al., (2015) analysed the environmental impact caused by blast furnace slag co-processing on cement production. Rodríguez et al., (2016) explored the feasibility of co-processing spent activated carbon a by-product of potabilization plants, as an alternative fuel, and showed clinker quality comparable to the common industrial clinker. A cement plant in Sri Lanka carried out a three day test burn to study the disposal potential of PCB – oil in cement kiln. The test revealed environmental sustainability without causing any new formation of PCDD/PCDF or HCB (Karstensen et al., 2010). Similar test burn was carried out with two obsolete insecticides in a cement kiln in Vietnam. The destruction efficiency was measured to be better than 99.9999969% for Fenobucarb and better than 99.9999832% for Fipronil (Karstensen et al., 2006). Li et al., (2012) studied co-processing of 350 tons of obsolete pesticides including 160 tons of DDT as a successful disposable business case in China.

Different waste streams, some hazardous, have been studied, as mentioned by several articles but till date a specific study on co-processing of acid tar sludge a by-product of steel industry hasn’t been reported in literature. The study not only shows the potential but also provides a basis to develop standards for Indian co-processing guidelines based on the results of the trial. The objective of the work is to study the sustainability and potential of ATS disposal as AFRs in cement kiln by carrying out five trials of five days each as a pilot study and to show the potential of cement kiln as a sink for hazardous waste. The co-processing trials will demonstrate that the cement kilns are highly capable of co-processing hazardous waste like ATS. The emission monitoring, clinker and cement quality result of the trials will form a basis to gauge co-processing as an environmentally sound and effective hazardous waste disposal methodology.

11.2. Materials and Methods

The cement plant is located near a state owned steel plant in central part of India, generating ATS as a by-product from the process. The plant needs to dispose of the hazardous waste in environmentally sustainable way, in accordance with Hazardous Wastes (Management, Handling and Trans-Boundary Movement) Rule 2016 of India. Thus five trial runs were carried out in the cement plant for the disposal of generated ATS, each trial were of five days. The cement plant has two kilns; one is a semi dry process type and another modern cyclone preheated dry process type. The capacity of kiln-1 is 600 tonnes/day and that of the kiln-2, in which the trial was conducted, is 1200 tonnes/day. The kiln-2 is equipped with a feeding system for solid alternative fuel and the experimental ATS feeding system. The kiln-2 has a five stage pre heater tower with diameter of 3.75 m and is 54 m long. The kiln rotates with a speed of 1.6 rounds per minute. The study specifically discusses the results of trials and presents it potential as a sink for ATS. The study also presents an impact analysis of ATS trials on the environment and quality of the final product.

11.2.1. ATS generation

In the coke oven of a steel plant, when coke is made from coal, the volatile matter leaves coke oven chambers as raw coke oven gas, these gases are condensed. The liquid fraction of the condensate is used for recovery of chemicals and the gas fraction is used as fuel; a by-product ATS is generated in the process of purification. This by-product constitutes a mixture of sulphuric acid & heavy polymers, which are formed because of the reaction of concentrated sulphuric acid & unsaturated hydrocarbons during the process.

The detail process of ATS formation is explained using a step by step approach; firstly, tar is separated by cooling the coke oven gases at about 170°C. Tar gets condensed and separated. Gases are then sent for further operation. Secondly, ammonia is separated by water wash process; in this the coke oven gas is scrubbed by water, which dissolves the ammonia, along with some hydrogen sulphide and hydrogen cyanide. The resulting scrubbing solution is pumped to ammonia still, where steam is used to strip out the ammonia. The ammonia vapours from the still are processed to form ammonium sulphate. Thirdly, the coke oven gas from ammonium sulphate plant enters the final gas cooler where the coke oven gas is directly cooled with the water. The water carries the naphthalene to the bottom section of final gas cooler, where water containing naphthalene comes in direct contact with crude tar. The crude tar dissolves naphthalene & carries it to the tar tank & naphthalene free water goes to settling tank. The crude tar containing naphthalene is pumped to tar distillation plant for further processing and water after settling goes to cooling tower. Fourthly, the gas after final cooling is scrubbed with wash oil to make it free from crude benzol. The crude benzol dissolved in wash oil is distilled to separate wash oil, which after cooling is recycled for scrubbing crude benzol. The crude benzol is separated in to light crude benzol (LCB) & heavy crude benzol in distillation column. Heavy crude benzol is sold & LCB is processed in benzol rectification plant. Fifthly, LCB is received from benzol recovery plant in storage tanks. LCB is processed in CS2 column for removal of CS2 fraction from top of the column whereas the bottom material from CS2 column goes to tanks after cooling. CS2 bottom material is called unwashed BTX which is charged into batch agitators for sulphuric acid (93-98%) washing, for removal of unsaturated hydrocarbons & sulphur compounds. In this reaction the unsaturated hydrocarbons & sulphur compounds form polymers with H_2SO_4. These polymers and acid mixture form a dense layer at bottom and it is then drained out. This drained material is known as acid tar sludge. Acidic unwashed BTX is then neutralized with 15-18% caustic soda. This BTX is then distilled to form benzene, toluene, and xylene (figure11-1). The generated ATS is then transported by a specifically designed tanker to the cement plant for co-processing or final disposal.

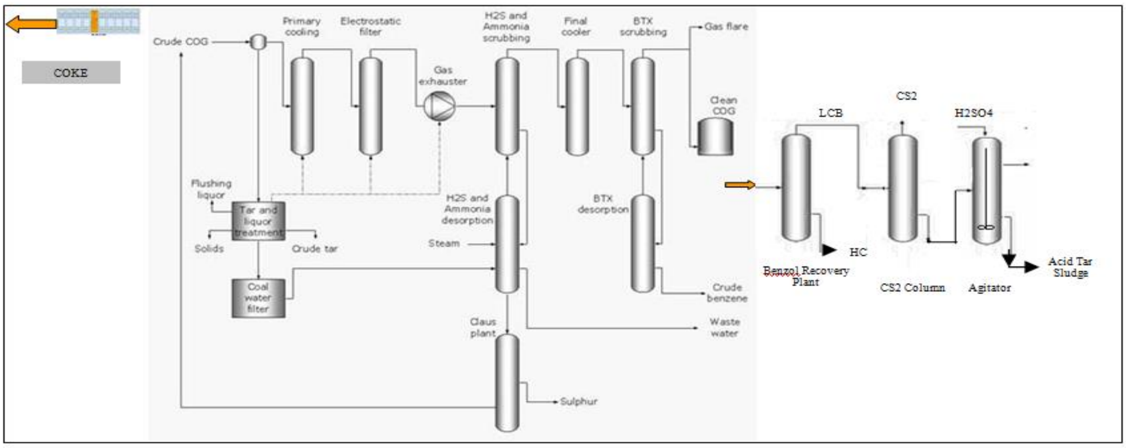

Figure.11-1. Generation of acid tar sludge

11.2.2. Storage and feeding arrangement of ATS at cement plant

The storage capacity of the tank is 10.2 m^3 and it has a lining of lead, to avoid corrosion. The tank is installed on the concrete floor, having a dyke to collect spilled ATS in the event of spillage as a safety measures. ATS is unloaded from tanker to the storage tank by a hose connected through a double diaphragm pump. The feeding system installed for co-processing consists of compressed air source, pressure gauge, double diaphragm pump and flow control valves along with stainless steel pipeline of 0.0508 m internal diameter. The feed rate of ATS is maintained by adjusting re-circulating and feeding valve. All the flanges in the feeding system were covered with flange guard. Both unloading & feeding is done with the help of same pump. Air flushing arrangement is made an integral part of the system to avoid jamming problem in pipe line (figure.11-2).

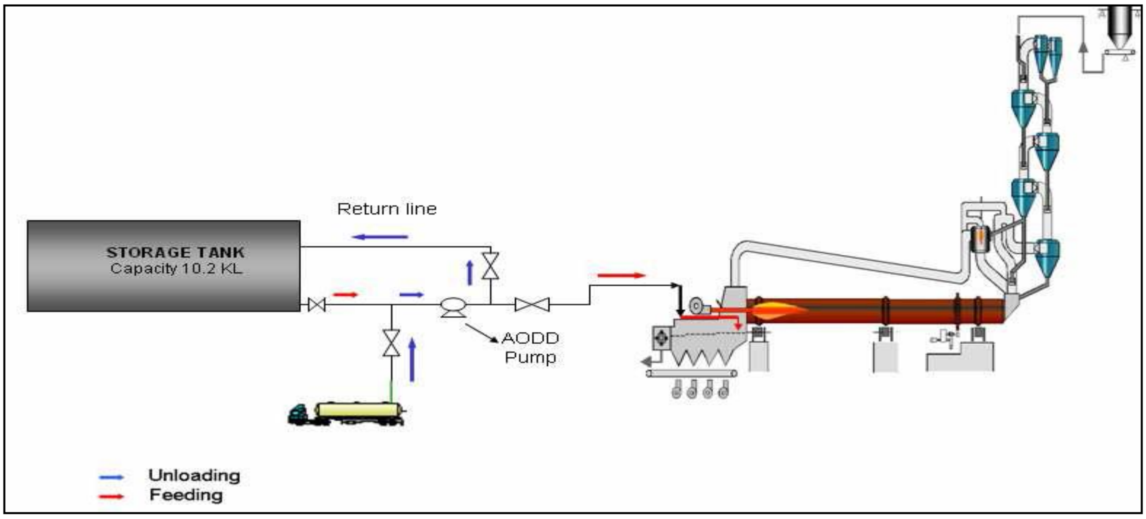

Figure.11-2. Acid tar sludge feeding system arrangement

11.2.3. Co-processing trials monitoring

The co-processing trials were carried out in three phases - pre-co-processing (Day-1), co-processing (Day 2-4) and post-co-processing (Day-5). Before the co-processing trials a kiln stabilization period with conventional fuel for a span of 24 hours was carried out. The emission measurement of various parameters was carried out during the trials, with sampling range, varying from one to four samples per day. The sampling methods used for each of the parameters are given in table.11-1.

Sl. No.	Parameter	Method	No. of samples per trial	Frequency
1	Particulate matter	USEPA 17	20	4 samples each day
2	SO_2	USEPA 6B	20	4 samples each day
3	HCl	USEPA 26	20	4 samples each day
4	HF	USEPA 26	20	4 samples each day
5	HBr	USEPA 26	15	3 samples each day
6	CO_2+CO+O_2+Moisture	USEPA 3B, 4	20	4 samples each day
7	NO_X	USEPA 7E	20	4 samples each day
8	Total Organic Carbon	USEPA 25A	5	1 samples each day
9	VOC	USEPA 31	10	2 samples each day
10	Total Hydro Carbon	USEPA 18	10	2 samples each day
11	PAH	CEPA 429	10	2 samples each day

Sl. No.	Parameter	Method	No. of samples per trial	Frequency
12	Metal (both particulate and vapour phase) Cd, Tl, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Zn, Sn, Se, Al	USEPA 29	5	1 samples each day
13	Mercury (Particulate and Vapour phase)	USEPA 29	5	1 samples each day
14	Dioxin & Furan	USEPA 23A	5	1 samples each day
15	Cyanide	CARB 426	5	1 samples each day
16	Ammonia	USEPA 6A/B modified	15	3 samples each day
17	Benzene	NIOSH 1501	15	3 samples each day

Table.11-1.Typical analysis method during each phase of co-processing Trial-1(T1)

During the five co-processing trials hourly samples of all raw materials (lime stone, bauxite & iron ore), raw meal, kiln coal, calciner coal, clinker and ATS were collected and one composite sample on daily basis was made. Particular parameters of the prepared sample was analysed and the methods used are mentioned in the table.11-2 to 11-5. The composite sample of ATS was analysed for gauging the different constituents in it. The sampling was done on daily basis during the trial period and similar data table was obtained during each trials (table.11-6). Negligible deviation of the parameter percentage was noticed during other four trials.

Sl.No.	Parameter	Method	No. of sample
1	Chlorine, Fluorine, Sulphur & Cyanide	USEPA 5050 / 9212/ 9214 / 9010C	5
2	Metal i.e. Cd, Tl, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Zn, Sn, Se, Al	USEPA 3050B / 3051A / 3052	5
3	Leachablity study for clinker including metal i.e. Cd, Tl, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Zn, Sn, Se, Al	USEPA 1311	5
4	Total Organic Carbon (TOC)	USEPA 9060	5

Table.11-2. Typical analysis method for clinker sample for Trial-1(T1)

Sl. No.	Parameter	Method	No. of sample
1	Calorific Value (Kcal/kg) Gross and Net	ASTM E711	1
2	Proximate Analysis (Moisture content, Ash content, Volatile Matter content, Fixed Carbon Content)	By Thermo gravimetric analyser	1
3	Ultimate analysis (Carbon content, Hydrogen content, Sulphur content, Nitrogen content, Oxygen content)	By CHNSO analyser	1
4	Characteristic of fuel (Chlorine, Fluorine& Heavy Metals -lead, zinc, tin, cadmium, arsenic, mercury, cobalt, nickel, thallium, copper, vanadium, antimony, chromium, manganese, selenium, iron)	USEPA 5050 / 9212 / 9214 / 3050B / 3051A / 3052	1
5	Total Organic Carbon	USEPA 9060A	1

Table.11-3. Typical analysis method for coal sample for Trial-1(T1)

Sl. No.	Parameter	Method	No. of sample
1	Calorific Value of the Waste (Kcal/kg) Gross and Net	ASTM E711	1
2	Proximate Analysis (Moisture content, Ash content, Volatile Matter content, Fixed Carbon Content)	By Thermo gravimetric analyser	1
3	Ultimate analysis (Carbon content, Hydrogen content, Sulphur content, Nitrogen content, Oxygen content)	By CHNSO analyser	1
4	Characteristics of waste (Chlorine, Fluorine& Heavy Metals lead, zinc, tin, cadmium, arsenic, mercury, cobalt, nickel, thallium, copper, vanadium, antimony, chromium, manganese, selenium, iron)	USEPA 5050 / 9212 / 9214 / 3050B / 3051A / 3052	1
5	Total Organic Carbon	USEPA 9060A	1
6	Total Petroleum Hydrocarbon	USEPA 8015B	1
7	Organo - chloride compounds	USEPA 8081B	1
8	VOC's and Semi VOCs	USEPA 8260B /8270D	1
9	Poly Chloro Biphenyl (PCBs)	USEPA 8082	1
10	Poly Chloro Phenols (PCPs)	EPA 8270D	1
11	TCLP	EPA 1311	1
12	Viscosity	ASTM D 445 2006	1
13	Water Content	ASTM D 5530	1
14	Solid Content	ASTM D 6050	1

Table. 11-4. Typical analysis method for acid tar sludge sample for Trial-1(T1)

Sl. No.	Parameter	Method	No. of sample
1	Fluoride as F, Sulphate as SO4, Aluminium as Al_2O_3, Silica as SiO_2, Iron as Fe_2O_3 Metals i.e. Cd, Th, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, V, Zn, Sn, Se, Ni, Fe	USEPA 5050 / 9212 / 9214 / 3050B / 3051A / 3052	1
2	Total Organic Carbon	USEPA 9060A	1

Table.11-5. Typical analysis method for raw meal sample for Trial-1(T1)

Sl. No	Parameter	Unit	Result
1	Antimony	mg/Kg	1.63
2	Arsenic	mg/Kg	2.07
3	Cadmium	mg/Kg	<1.0
4	Chromium	mg/Kg	3.33
5	Cobalt	mg/Kg	<1.0
6	Copper	mg/Kg	<1.0
7	Lead	mg/Kg	<1.0
8	Manganese	mg/Kg	<1.0
9	Nickel	mg/Kg	<1.0
10	Thallium	mg/Kg	<1.0
11	Vanadium	%	<1.0
12	Mercury	mg/Kg	<0.5
13	Zinc	mg/Kg	<1.0
14	Tin	mg/Kg	<1.0
15	Selenium	mg/Kg	1.63
16	Iron	mg/Kg	1.90
17	Chloride	mg/Kg	108.42

Sl. No	Parameter	Unit	Result
18	Fluoride	mg/Kg	<1.0
19	Carbon	%	25.29
20	Hydrogen	%	4.23
21	Sulphur	%	22.0
22	Nitrogen	%	1.94
23	Oxygen	%	46.33
24	Moisture	%	25.45
25	Ash	%	4.64
26	Volatile Matter	%	52.35
27	Fixed Carbon	%	17.74
28	TPH	mg/Kg	<0.03
29	PCB	mg/Kg	<0.1
30	PCP	mg/Kg	<0.1

Table.11-6. Analysis of composite ATS sample during Trial-1(T1)

11.3. Results and Discussion

During the five trials, an hourly process monitoring of 22 parameters were carried out. The details of each of the parameters were analysed; trial-1 data has been presented as a representation of the other four trials as there were negligible deviations. The average kiln feed rate during co-processing trial-1 were 76.79, 75.74, 73.95, 73.47 and 74.84 tph for each of the five days, with approximately similar feed rate during the other four trials. The monitoring of the trials revealed negligible operational deviation. Similar trends were also noticed for the clinker production. The coal feed rate to the kiln during the trial-1 period were on average 5.6, 5.71, 5.71, 5.67 and 5.68 tph, the fluctuation was attributed to the process demand and overall feeding requirement. The coal feed rate to the calciner showed similar fluctuation due to production process requirement. The fifth cyclone preheater bottom temperature revealed marginal fluctuation with average temperatures of 826.5°C, 825.9°C, 826°C, 821°C and 817°C during five day of trial-1.

The kiln speed during the trial-1 was 1.48, 1.44, 1.36, 1.37 and 1.46 rpm. The kiln speed deviation is attributed to the feed rate of coal in kiln and calciner as the kiln speed is directly proportional to the rate of feeding. Similar trends were reported for kiln torque percentage. The pre-heater outlet average temperature during the trial-1 were 412.53°C, 411.11°C, 415.89°C, 424.68°C and 420.79°C, the deviation is negligible. The average pre heater outlet draft was 634.12, 639.32, 626.63, 608.68 and 600.12 mmWG. The pre-heater outlet gas was sampled for possible increment in emission percentage of carbon monoxide (CO) due to the trials. The average CO percentage emissions during trial-1 were 0.26 %, 0.155%, 0.14%, 0.21% and 0.12% (figure.11-3), similar trends were reported for other four trials. Monitoring of the result indicates no incremental effect due to ATS feeding. The average tertiary air temperature was 652°C, 647.74°C, 658.42°C, 634.05 °C and 619.37°C during the trial-1, without major fluctuation.

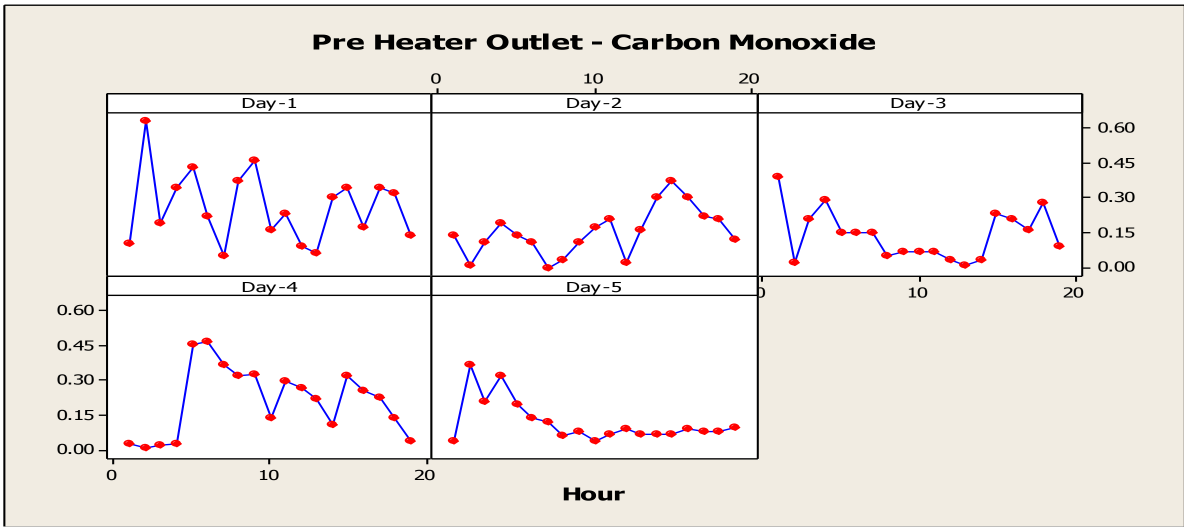

Figure.11-3. Pre-heater outlet carbon monoxide percentage (CO%)

The opacity meter reading was below the normal level, the average reading obtained during the five day of the trial-1 were 2.76, 2.49, 2.6, 2.48 and 2.51 mg/m^3. The coal mill draft was analysed for 16 hours for each day of the five trials. The coal mill draft average value showed small deviation during all the trials. The deviation of both the parameters can be contributed to the deviation in the production process and not due to ATS co-processing. The coal mill outlet and coal mill bag filter inlet temperature analysis revealed minimal deviation from the normal temperature. The average pressure of six cooler compartments - 1A, 1B, 2, 3, 4 and 5 showed similar production fluctuation during the monitoring. The average cooler ID fan temperatures during the five day of trial-1 were 257.63°C, 226.38°C, 242.06°C, 230.38°C and 227°C, similar process variation was noticed for the cooler stroke rpm. All the 22 parameters analysed during the co-processing trials revealed normal process fluctuation as discussed and this fluctuation are due to normal process deviation rather than due to co-processing of ATS.

11.3.1. Results of emission monitoring during co-processing trials

The results shown are the average values for number of samples, collected at the time of monitoring during the trials. Some of the data presented are of trial-1 and can be taken as an approximate representation of the trends of other four trials as there were minimal reported changes in the other trials. The particulate matter (PM) was sampled using protocol USEPA method no.17, with 4 samples each day. The CPCB norm for common hazardous waste incinerator for particulate matters (PM) is 50mg/Nm^3 (for cement plant co-processing hazardous waste is not defined) but emission during the trial-1 were 5.96, 6.08 and 6.4mg/Nm^3 respectively for day-2, day-3 and day-4 (table.11-7). The analysis revealed that the PM in flue gas increased by only 0.46 mg/Nm^3 from day-1 to 5, the other four trials (T2, T3, T4 and T5) reporting similar fluctuations (figure.11-4). The total organic compounds (TOC) were sampled using USEPA method no. 25A. The norm for cement plant co-processing hazardous waste is 10mg/Nm^3, and the maximum emissions recorded during the trial-1 were 4.56mg/Nm^3, an increase of 0.86mg/Nm^3 from the pre co-processing value (table.11-6). The total hydro-carbon was sampled using USEPA method no.18. There were no predefined norm for cement plants and also hazardous waste incinerator guidelines don't define the limits. During the trial-1, on day-1 emission level showed 4.7 mg/Nm^3 and on day-2 it went up to 20.99 mg/Nm^3 but went down to 2.72 mg/Nm^3 on day-3. The fluctuation is attributed to the production process deviations and effect of ATS feeding was marginal (figure.11-4).

Hydrogen Chloride, Hydrogen Fluorides & Hydrogen Bromide were sampled using USEPA Method No.26, emission of these halides had not been observed in any stage of the five trials (table.11-7). Gases like carbon monoxide, nitrogen, sulphur oxides were sampled using procedure – NO_X (USEPA Method No. 7E), O_2 & CO_2 (USEPA Method No. 3B) and SO_2 (USEPA Method No. 6 B). The base limit for CO emission is 100 mg/Nm^3 for common hazardous waste incinerator but for a cement kiln the CO emission falls under the co-processing emission guidelines which are not defined in the guidelines. So for the purpose of analysis, the pre co-processing stage is used as a benchmarked value for comparison, the CO emission was observed at 1140 mg/Nm^3 level before co-processing and maximum CO emission during the trial-1 were 1175 mg/Nm^3 with increment value of only 35 mg/Nm^3 considering the pre-co-processing stage. The SO_2 and NOx had norms for cement plant co-processing hazardous waste at 100 mg/Nm^3 and 800 mg/Nm^3 respectively and maximum observed emission were 87 mg/Nm^3 and 396 mg/Nm^3 respectively (table.11-7). The emission of heavy metal was sampled using USEPA method no. 29 and detail measurement was given in table.11-7. There wasn't any mercury emission observed during the trial period. The norms for zinc and aluminium are not defined in the norms. The measurement of zinc revealed fluctuation during the co-processing days. The values were marginally on the higher side which may be contributed to the ATS co-processing and production process fluctuation. The aluminium measurement showed negligible fluctuation during the trial period (figure.11-5). The norms for dioxin / furan limit is 0.1ng TEQ/Nm^3 but during the trial-1 the maximum dioxin emission reached was 0.005ngTEQ/Nm^3 (figure.11-6) and due to feeding of ATS there was only incremental change of 0.001ngTEQ/Nm^3 (table.11-7). The USEPA method no. 23A protocol was used to measure the dioxin/furan emission (figure.11-6). All the emissions of different parameters during each of the five trials (T1, T2, T3, T4 & T5) as measured were within the specified norms as represented in figures.11-4 to 11-6.

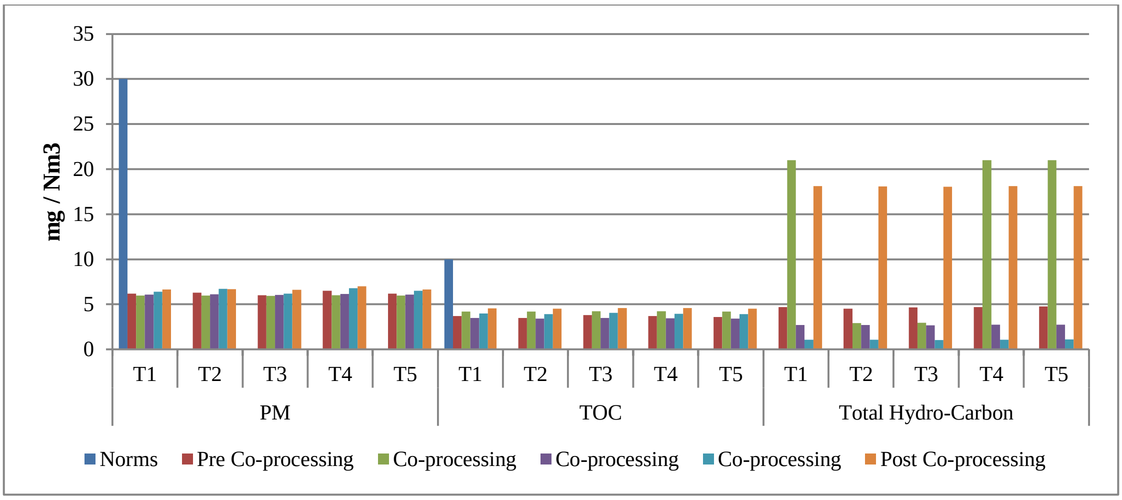

Figure.11-4. Emission of PM, TOC and Total hydro carbon during the five trials

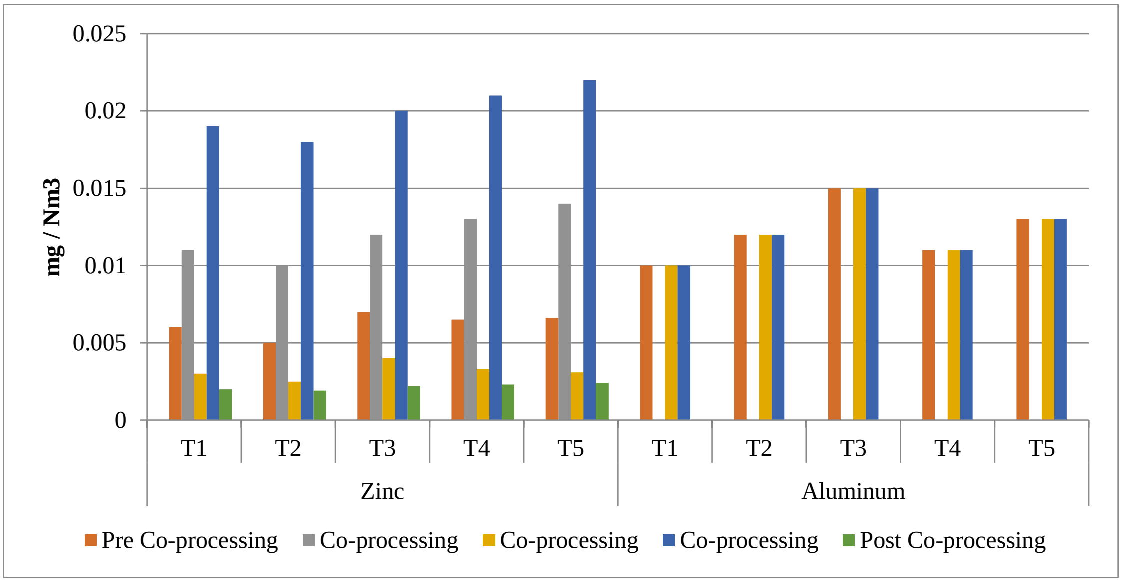

Figure.11-5. Emission of metals during the five trials

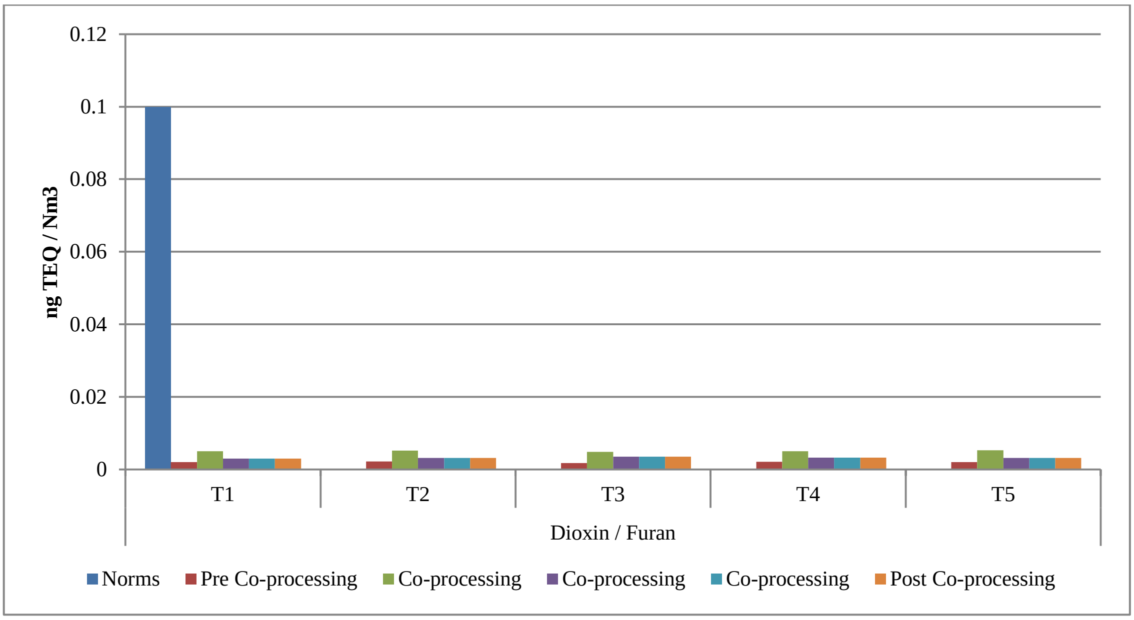

Figure.11-6. Emission of dioxin/furan during the five trials

11.3.2. Clinker quality monitoring during trails

Clinker quality is a defining property of the final finished products; it was monitored extensively during the trial via the collected samples. The quality of the clinker largely depends upon the quantity of the elements and their combined molecular properties. These parameters are usually kept fixed with in a tolerance level as per the industry standards. There were marginal deviation during the five trial run; all the critical parameters of clinker were almost near to the benchmarked value of pre co-processing stage (table.11-8).

Parameter	**Unit**	**Norm for Common Hazardous waste incinerator**	**Norms for Cement Plant co-processing Hazardous Waste**	**Pre Co-processing**	**Co-processing**	**Co-processing**	**Co-processing**	**Post Co-processing**	**Change in Emission during Co-processing of waste**			**Change in Emission after Co-processing of waste**
				A	**B**	**C**	**D**	**E**	**(B-A)**	**(C-A)**	**(D-A)**	**(E-A)**
PM	mg / Nm^3	50	30	6.2	5.96	6.08	6.4	6.66	0.24	0.12	0.2	0.46
Carbon Monoxide	mg / Nm^3	100	NA	1140	1157	1002	1225	1175	17	138	85	35
NOx	mg / Nm^3	400	800	270	277	316	267	396	7	47	3	127
SO_2	mg / Nm^3	200	100	34	69	80	87	19	34	45	53	15
HCL	mg / Nm^3	50	10	-	-	-	-	-	-	-	-	-
HF	mg / Nm^3	4	1	-	-	-	-	-	-	-	-	-
HBr	mg / Nm^3	N.A	NA	-	-	-	-	-	-	-	-	-
TOC	mg / Nm^3	20	10	3.7	4.21	3.47	3.99	4.56	0.51	0.23	0.29	0.86
Mercury	mg / Nm^3	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01
Cd + Tl	mg / Nm^3	0.05	0.05	-	-	-	-	-	-	-	-	-
Sb+As+Pb+Co+Cr+ Cu+Mn+Ni+V	mg / Nm^3	0.5	0.5	0.06	0.03	0.05	0.02	0.03	0.023	0.007	0.039	0.026
Zinc	mg / Nm^3	N.A	N.A	0.006	0.011	0.003	0.019	0.002	0.005	0.003	0.013	0.004
Tin	mg / Nm^3	N.A	N.A	-	-	-	-	-	-	-	-	-
Selenium	mg / Nm^3	N.A	N.A	-	-	-	-	-	-	-	-	-
Aluminium	mg / Nm^3	N.A	N.A	0.01	0.00	0.01	0.01	0.00	0.004	0.000	0.008	0.003
Dioxin / furan	ngTEQ / Nm^3	0.1	0.1	0.002	0.005	0.003	0.003	0.003	0.003	0.001	0.001	0.001
NH_3	mg / Nm^3	N.A	N.A	-	-	-	-	-	-	-	-	-
C_6H_6	mg / Nm^3	N.A	N.A	-	-	-	-	-	-	-	-	-
Cyanide	mg / Nm^3	N.A	N.A	-	-	-	-	-	-	-	-	-
Total Hydro-Carbon	mg / Nm^3	N.A	N.A	4.7	20.99	2.72	1.08	18.12	16.30	1.98	3.62	13.43

Table.11-7. Typical Emissions during the five day of Trial-1(T1)

Parameter [%]	**Pre Co processing**					**During Co processing**															**Post Co processing**				
	Day 1					**Day 2**					**Day 3**					**Day 4**					**Day 5**				
Trial	**T1**	**T-2**	**T3**	**T4**	**T5**	**T1**	**T2**	**T3**	**T4**	**T5**	**T1**	**T2**	**T3**	**T4**	**T5**	**T1**	**T2**	**T3**	**T4**	**T5**	**T1**	**T2**	**T3**	**T4**	**T5**
SiO_2	23.14	23.10	23.18	23.12	22.9	22.54	22.92	23.05	23.01	22.60	23.07	23.45	23.58	23.54	23.13	22.80	23.18	23.31	23.27	22.86	22.95	23.33	23.46	23.42	23.01
Al_2O_3	7.18	7.11	7.20	7.35	7.39	6.23	6.15	6.20	6.24	6.40	7.25	7.17	7.22	7.26	7.42	6.94	6.86	6.91	6.95	7.11	6.69	6.61	6.66	6.7	6.86
Fe_2O_3	3.16	3.15	3.09	3.25	3.40	2.82	2.81	2.78	2.90	2.99	3.03	3.02	2.99	3.11	3.20	3.05	3.04	3.01	3.13	3.22	3.00	3.09	3.06	3.18	3.27
CaO	62.35	62.28	62.10	62.55	62.39	61.91	61.95	61.83	61.80	61.98	61	61.04	60.90	60.89	61.07	64.20	64.24	64.1	64.09	64.27	60.10	60.14	60	59.99	60.17
MgO	2.64	2.75	2.49	2.55	2.80	2.55	2.60	2.38	2.46	2.65	2.91	2.96	2.74	2.82	2.98	3.26	3.31	3.09	3.17	3.33	2.74	2.79	2.57	2.65	2.81
SO_3	0.33	0.32	0.36	0.38	0.31	0.46	0.43	0.48	0.52	0.45	0.64	0.61	0.66	0.70	0.63	0.22	0.19	0.24	0.28	0.21	0.47	0.44	0.49	0.53	0.46
Na_2O	0.24	0.28	0.22	0.29	0.25	0.24	0.28	0.22	0.29	0.25	0.24	0.28	0.22	0.29	0.25	0.24	0.28	0.22	0.29	0.25	0.25	0.29	0.23	0.30	0.26
K_2O	1.31	1.34	1.36	1.31	1.38	1.42	1.45	1.48	1.41	1.49	1.36	1.39	1.42	1.35	1.43	1.18	1.21	1.24	1.17	1.25	1.43	1.46	1.49	1.42	1.5
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO_2	0.38	0.33	0.35	0.32	0.38	0.34	0.29	0.31	0.28	0.34	0.39	0.34	0.36	0.33	0.39	0.30	0.25	0.27	0.24	0.3	0.38	0.33	0.35	0.32	0.38
Mn_2O_3	0.09	0.08	0.07	0.08	0.09	0.09	0.08	0.07	0.08	0.09	0.08	0.07	0.06	0.07	0.08	0.08	0.07	0.06	0.07	0.08	0.09	0.08	0.07	0.08	0.09
Free CaO	2.87	2.85	2.84	2.87	2.88	2.12	2.10	2.09	2.12	2.13	1.84	1.82	1.81	1.84	1.85	3.88	3.86	3.85	3.88	3.89	2.51	2.49	2.48	2.51	2.52
Lime Saturation Factor (LSF)	0.82	0.81	0.79	0.87	0.85	0.86	0.85	0.83	0.91	0.89	0.80	0.79	0.77	0.85	0.83	0.85	0.84	0.82	0.9	0.88	0.80	0.79	0.77	0.85	0.83
Silica Modulus (SM)	2.23	2.26	2.24	2.28	2.21	2.49	2.52	2.50	2.54	2.47	2.26	2.29	2.27	2.31	2.24	2.27	2.3	2.28	2.32	2.25	2.37	2.4	2.38	2.42	2.35
Alumina Modulus (AM)	2.27	2.28	2.25	2.24	2.26	2.20	2.21	2.18	2.17	2.19	2.37	2.38	2.35	2.34	2.36	2.27	2.28	2.25	2.24	2.26	2.24	2.25	2.22	2.21	2.23
Liter Weight.	1300	1310	1305	1314	1308	1320	1330	1325	1334	1328	1334	1344	1339	1348	1348	1317	1327	1322	1331	1331	1314	1324	1319	1328	1328

Table.11-8. Parameter percentage present in clinker during the five trials each of five days

11.3.3. Cement property analysis

The cement property analysis was carried to gauge the parameters like blaine, setting time, soundness and compressive strength. The day-1 parameter value was considered as a benchmarked value for each of the five trials with which the cement parameters were compared, during and after co-processing. The blaine parameter of the cement were near the pre co-processing value; it changed marginally during the trial period, from day 2 – 5 for all the five trials. The cement properties like soundness and compressive strength decreased marginally from their pre co-processing value. Although the parameter deviated by some margin, the changes are within the tolerance limit of the product specified by the Bureau of Indian standards (IS 269:2015) and is normally associated with the process deviation. The values, as obtained for trial-1 are presented (table.11-9).

Parameters		**Day 1**	**Day 2**	**Day 3**	**Day 4**	**Day 5**
Blaine (m^2 / kg)		328	329	327	328	329
Setting Time (Minutes)	Initial setting time	140	138	135	136	139
	Final setting time	185	190	188	195	184
Soundness	Le – Chat (mm)	1.0	1.0	0.5	1.0	0.5
	Autoclave (%)	0.06	0.04	0.06	0.08	0.07
Compressive Strength (MPa)	3 days	21.6	20.4	22.7	21.1	23.5
	7 days	35.3	35.2	36	35.5	36
	28 days	47.4	48.4	49	47.8	48.2

Table.11-9. Cement analysis parameter during the trial-1

11.3.4. Leach test of clinker

The leaching test of the clinker was carried out based on the USEPA 1311 protocol using three samples for each of the five trials. A comparison of the leaching behaviour of the cement before, during and after the trial-1 indicates that amount of leached heavy metals and other non heavy metals is within the acceptable level and there were not any noticeable deviation from the normal product i.e. when ATS was not co-processed (table.11-10). The analysis of the other four trials reveals similar trends.

Parameter	**Unit**	**Day-1**	**Day-2**	**Day-3**	**Day-4**	**Day-5**
Antimony	(mg/kg)	<5	<5	<5	<5	<5
Arsenic	(mg/kg)	<1	<1	<1	<1	<1
Cadmium	(mg/kg)	<1	<1	<1	<1	<1
Chromium	(mg/kg)	<1	<1	<1	<1	<1
Cobalt	(mg/kg)	<1	<1	<1	<1	<1
Copper	(mg/kg)	<1	<1	<1	<1	<1
Lead	(mg/kg)	<1	<1	<1	<1	<1
Manganese	(mg/kg)	<1	<1	<1	<1	<1
Nickel	(mg/kg)	<1	<1	<1	<1	<1
Thallium	(mg/kg)	<1	<1	<1	<1	<1
Vanadium	(mg/kg)	<1	<1	<1	<1	<1
Mercury	(mg/kg)	<1	<1	<1	<1	<1
Zinc	(mg/kg)	<1	<1	<1	<1	<1
Tin	(mg/kg)	<5	<5	<5	<5	<5
Selenium	(mg/kg)	<1	<1	<1	<1	<1
Iron	(%)	<1	<1	<1	<1	<1

Table.11-10. Clinker leach test analysis during the trial-1

11.3.5. Ambient air quality around the cement plant

The analyses of the ambient air quality during the trials were carried out in three locations at different distances from the kiln-2, so as to study four major parameters of the ambient air. The parameters are quantity of NOx, SO_2, RSPM (Respirable suspended particulate matter) and SPM (suspended particulate matter). The norms for NOx, SO_2, RSPM and SPM have been defined by national ambient air quality standards – 2009. The limit for NOx - 80 $\mu g/m^3$, SO_2 – 80 $\mu g/m^3$, RSPM - 60 $\mu g/m^3$ and SPM – 100 $\mu g/m^3$. The first location was approximately 2 km from kiln-2; the sampling of the air for five days of the different trials revealed marginal changes in all the four parameters, during the trial-1 the maximum deviation noted was in the parameter SPM and RSPM. The highest deviation of SPM and RSPM from its initial level was noticed on day-2 and day-5 during the trial-1 (figure.11-7).

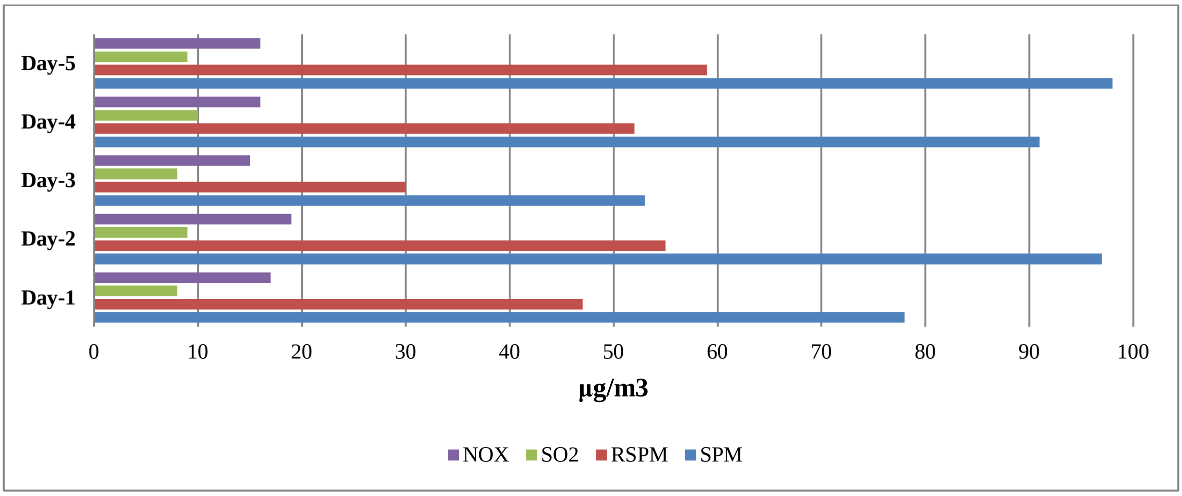

Figure.11-7. Ambient air quality of location 1 during trial-1

Similar analysis of the ambient air was carried out for the second location, this time the location being 1 km away from kiln-2. The sampling of air showed marginal change of all the parameters excluding SPM and RSPM which again showed high deviation from the day-1 during trial-1. The SPM on day-2 and day-4 increased drastically from its initial level of 52$\mu g/m^3$ to 90$\mu g/m^3$ and 88$\mu g/m^3$ respectively (figure.11-8).

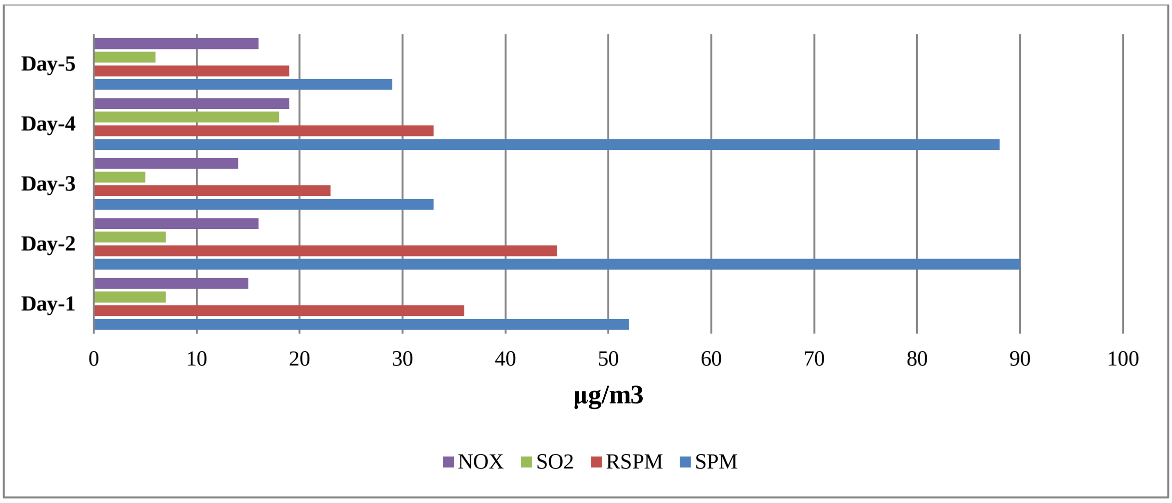

Figure.11-8. Ambient air quality of location 2 during trail-1

The sampling of ambient air for the third location was at 0.7 km from kiln-2. It revealed similar characteristics with minimal deviation from the normal value. The SPM has showed maximum deviation and on day-4 it exceeded the national ambient air quality standards - 2009 by 5 µg/m^3 from its initial value of 93 µg/m^3, but on day-5 it was again under the norms, and as per the standards 2% of the measurement annually is allowed to exceed, although the limit must not exceed consecutively for two days (figure.11-9). This deviation in the three locations is attributed to the production process and metrological consideration rather than the co-processing of ATS, as can be seen by the fall and consecutive increase of the parameter from day-1 to 5 during the trial-1 (figure.11-7 to 11-9). Marginal deviation was reported for other four trials but all were under the national ambient air quality standards-2009.

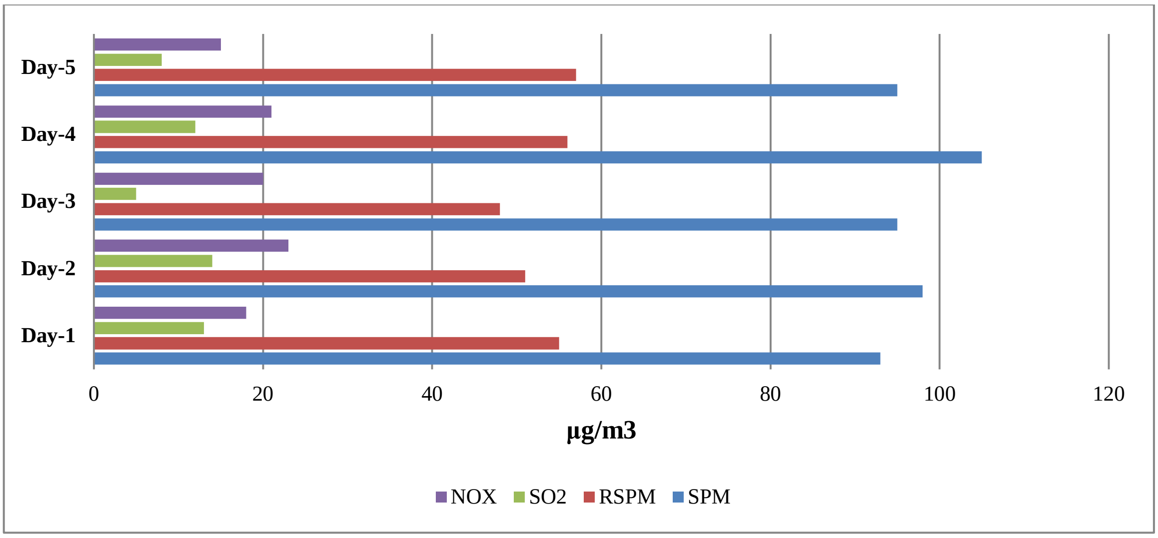

Figure.11-9. Ambient air quality of location 3 during trial-1

The co-processing of ATS in cement plants had no impact on any of the parameters like emission, production process, clinker quality, cement property and leach behaviour when the 0.4 TPH of ATS was co-processed. The study was primarily carried out to gauge the disposal potential of highly hazardous waste ATS in cement kiln rather than to find the economical potential; although cement plant was provided with a disposal fee by the steel plant. The ATS has a considerable amount of calorific value as analysis of the sample revealed a value of 5900 kcal/kg thus acting as an alternative fuel. Although the substitution benefit was not studied as primarily the focus was on to analyse the possibility of disposal of the waste without affecting the environment and production process. The study showed some marginal deviation for certain parameters of emission although they were well below the norms, although the 0.4 tph doesn't affect the process and emission as per the norms and product quality but the feeding rate can be further reduced to 0.3 tph so that this minute deviation which was observed can be further addressed. The steel plant produces around 2000 tonnes of ATS annually and based on the 0.3 tph feeding rate the cement plant that is only kiln – 2 can co-process 2350 tonnes annually, which is more than enough to meet the steel plant ATS disposal needs. Thus the trials indicating sustainability of the disposal methodology of co-processing in cement kiln.

11.4. Conclusion

The co-processing trials of acid tar sludge (ATS) demonstrated that ATS to coal feed ratio of 0.04:1 has insignificant impact on the emission levels of the cement kiln and clinker quality. The trials result showed that the emissions from cement kiln were largely independent of co-processing, though the feeding rate of ATS is a detrimental factor which requires effective controlling, so as not to affect the environment and quality of the product. The effect on the ambient air quality in term of NOx, SO_2, SPM, RSPM were also not affected due to co-processing of ATS and marginal deviation were within the norms. Moreover inherent factors of cement production process and critical controlling of ATS feeding rate reduces the chances of formation of dioxin/furan. Also the availability of cement plants in all developing countries, makes it an effective and economical methodology for disposal of hazardous waste instead of incinerator or other conventional hazardous waste treatment methodology.

Chapter 12

Purified Terephthalic Acid Disposal in Cement Plant and Metal Mass Balance Analysis (Addressing Objective – 4)

12.1. Introduction

Purified Terephthalic Acid (PTA) is used primarily for the production of polyester. The production process generates a number of by-products which are needed to be disposed of safely, due to their hazardous characteristics as defined by numerous legislations in different countries - in India it is defined under the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016. Thermal decomposition is the best possible methodology for disposal of hazardous waste, but most of the developing countries lack hazardous waste incinerators or non-combustion technologies and exporting to other countries for disposal is economically unsustainable (Karstensen et al., 2010). But cement kilns are present in large numbers in major developing countries and India being the second largest producer of cement, provides ample opportunity. The cement kiln is ideally suited for disposal of waste-derived fuel and hazardous waste (HW) (Baidya et al., 2017; Liu et al., 2015; Mokrzycki et al., 2003; Mokrzycki and Uliasz-Bochénczyk, 2003; Parlikar et al., 2016), but heavy metal accumulation and emission are areas of concern when co-processing different waste streams particularly hazardous waste (Cong et al., 2015; Huang et al., 2012). Co-processing in cement kilns is now, despite perceptions, an integral component in the spectrum of viable options for treating industrial hazardous wastes (Karstensen, 2008).

Co-processing of different hazardous wastes has been studied as referenced in numerous articles, though till date a specific study on co-processing of PTA waste mix hasn't been reported in literature. The current work not only shows the disposal potential but also develops a basis for standardisation of Indian co-processing guidelines based on the results of trial. The objective of the study is to gauge the sustainability and potential of PTA waste mix as AFRs in cement kiln through a five day trial as a pilot study. The emission monitoring, clinker and cement quality result of the trial will form the basis for gauging the environmental effectiveness.

12.2. Materials and Method

The cement plant is located in central part of India; the plant getting the PTA waste mix from a chemical industry located in a state at eastern part of India. The wastes are generated as a by product of the chemical process. The chemical plant has to dispose of the hazardous waste in environmentally sustainable way, in accordance with Hazardous Wastes (Management, Handling and Trans-boundary Movement) Rule 2016 of India. So a trial run of five days was carried in the cement plant for the disposal of the generated PTA waste mix. The cement plant has two kilns; both modern cyclone preheated dry process type. The capacity of the cement plants is 4.42 million tonnes/year. The trial feeding was carried out at one of the kiln. The kiln, in which the feeding was carried out, is equipped with a feeding system for PTA solid mix waste. The kilns have a six stage pre heater tower with a diameter of 3.75m and are 54m long. The kiln rotates with a speed of 1.6 rounds per minute. The study specifically discusses the trial result and presents the potential of cement kiln as a sink for PTA waste mix. The effect on environment and clinker quality is also analysed in details and lastly metal mass balance was also carried out to gauge the environmental sustainability in term of hazardous trace element accumulating in clinker.

12.2.1. PTA generation

The manufacturing of PTA comprises of 4 stages. 1) CTA stage in which crude teraphythalic acid is manufactured. 2) PTA stage in which CTA is purified into PTA. 3) CAT stage in which CTA oxidation – catalyst is recovered and regenerated. 4) Utility section with number of support facilities. In the CTA stage paraxylene is oxidized by air in presence of Co/Mn catalyst and acetic acid, which is used as solvent, at a temperature of 200°C and 15 kg/cm^{2}G pressure in a reactor. The off gas is led into a gas turbine from where it is vented off. CTA thus produced is crystallized, filtered, to separate CTA from solvent and catalyst. Thereafter CTA is dried in a drier and send to PTA stage for purification. CTA stage involves acetic acid distillation process where water is removed. Water is formed as a by-product in the teraphythalic acid production. Methyl acetate produced during side reaction is recycled. In the PTA stage the CTA formed is purified by dissolving it in pure water and converting the intermediate products i.e. 4-carboxyl benzaldehyde to para toluic acid, at a pressure of 85 kg/cm^{2}G and in a temperature of 290°C, in presence of Pd catalyst at hydrogen atmosphere. The hydrogen required for purification of CTA is generated by methanol reforming and pressure swing adsorption process. Para-toluic acid thus formed is recycled back into the process for further oxidation to produce PTA. The pure teraphthalic acid is subsequently crystallized, dried and packed in one tonne flexible container bags or in bulk containers depending upon the requirement. In the CAT stage the CTA catalyst is recovered and regenerated.

12.2.2. Storage and feeding arrangement of PTA at cement plant

The solid organic waste which is coming from the chemical industry is stored at a shed having capacity of 3000 tonnes. The stored material is transferred by trucks/forklift/hydra to the covered storage area, near kiln and then lifted by bucket elevator and charged into the calciner vessel at the temperature of 1000°C to 1200°C.

12.2.3. Co-processing trials monitoring

The co-processing of PTA waste mix was carried out in three phases, namely, pre co-processing (Day-1), co-processing (Day 2-4) and post co-processing (Day-5). The clinker quality and leaching behaviour was monitored in every stage of co-processing. The trial of PTA waste mix was carried out with a kiln stabilization period of 24 hours during the day- 1, with conventional fuel. The emission measurement for different elements during each phase of the co-processing was carried out. The sampling range varied from 4 samples per day to 1 sample per day depending on the compound/element as per the guidelines of the central pollution control board (CPCB) India (table.12-1).

Sl. No.	Parameter	Method	Frequency
1	Particulate matter (PM)	USEPA 5	4 samples per day
2	SO_2	USEPA 6	4 samples per day
3	HCl	USEPA 26A	4 samples per day
4	CO	USEPA 10B	4 samples per day
5	NO_X	USEPA 7	4 samples per day
6	Total Organic Carbon	USEPA 30 & 10	1 samples per day
7	HF	USEPA 26A	4 samples per day
8	VOC	USEPA 30&31	2 samples per day
9	PAH (Poly-Aromatic Hydrocarbons)	USEPA 29	2 samples per day
10	Metal (both particulate and vapour phase) Cd, Th, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Zn, Sn, Se	USEPA 29	1 samples per day
11	Dioxin & Furan	USEPA 23A	1 samples per day
12	Cyanide	CTM27	1 samples per day

Table.12-1. Typical analysis method during each phase of co-processing trial

During the five day co-processing trial, samples of raw meal, coal, clinker and PTA waste mix were collected as per the guidelines and one composite sample was made daily, different parameters of the prepared sample were analysed using the mentioned method in table.12-2. The raw meal analysis was done to understand the chemical composition of the feed to the kiln, as each and every component decides the emission and clinker quality (table.12-3). A proximate and chemical analysis of the PTA waste mix was also done to gauge the different constituents going in to the kiln so as to control the feeding rate during the trial. The PTA waste mix was analysed for different polychlorinated biphenyl (PCB), metal, poly chlorophenols (PCP) and organo-chlorins (table.12-4 to 12-8). The PTA waste mix leaching behaviour was analysed through toxicity characteristic leaching procedure (TCLP) to understand possible implication on the final product i.e. clinker (table.12-9).

Sl. No.	Parameter	Method	No. of sample
A	**Hazardous Waste Characterisation**		
1	VOC	USEPA 8260B	2 samples per day
2	Semi Volatile Organic Compounds (SVOCs)	USEPA 8270B	2 samples per day
3	Total Petroleum Hydrocarbons (TPH)	USEPA 9071	2 samples per day
4	GCV	ASTM E711	2 samples per day
5	Proximate Analysis	ASTM Method	2 samples per day
6	Ultimate Analysis	SOP: 26/AN/02	2 samples per day
7	Metals	USEPA 3050B AND USEPA 7000 Series	2 samples per day
8	Poly Chloro Biphenyls (PCBs)	USEPA 8082	2 samples per day
9	Poly Chlorophenols (PHPs)	As per USEPA method with GC/MS	2 samples per day
10	Organo Chlorines	USEPA 8081	2 samples per day
11	TCLP test	ASTM D-5233-92	2 samples per day

Sl. No.	Parameter	Method	No. of sample
B	**Coal Analysis**		
12	Proximate Analysis	IS: 1350 (Part-1)	1 samples per day
13	Ultimate analysis	SOP: 26/AN/02	1 samples per day
14	Calorific Value	IS: 1350 (Part-2)	1 samples per day
15	Metal	ICP – OES/AAS	1 samples per day
C	**Raw Meal and Clinker**		
16	Chemical composition	IS:4032	1 samples per day
17	Trace metals	ICP-OES/AAS	9 samples per day
18	Leachability studies	USEPA 1311	1 samples per day

Table.12-2. Typical analysis of hazardous materials and other components

Sl. No.	Parameters	Units	Result
1	F	mg/ kg	12.6
2	SO_4	%	34.7
3	Al_2O_3	%	43.9
4	SiO_2	%	0.51
5	Fe_2O_3	%	1.61
6	Cd	mg/ kg	9.1
7	Cr	mg/ kg	23.4
8	Cu	mg/ kg	29.6
9	Co	mg/ kg	1.3
10	Mn	mg/ kg	122.1
11	Ni	mg/ kg	18.6
12	Pb	mg/ kg	17.4
13	Zn	mg/ kg	88.2
14	As	mg/ kg	2.1
15	Hg	mg/ kg	1.6
16	Se	mg/ kg	1.8
17	Sb	mg/ kg	4.1
18	V	mg/ kg	40.6

Table.12-3. Raw meal chemical compositions

Sl. No.	Parameters	Units	Result
Proximate Analysis			
1	Moisture Content	%	7.1
2	Ash Content	%	27.4
3	Volatile Matter	%	37.1
4	Fixed Carbon	%	28.4
Ultimate Analysis			
1	Carbon	%	47.1
2	Hydrogen	%	8.36
3	Nitrogen	%	7.34
4	Sulphur	%	0.7
5	Mineral Matter	%	29.2
6	Oxygen	%	7.3
7	Gross Calorific Value	Kcal/mol	3980

Table.12-4. PTA waste mix – proximate & ultimate analysis

Sl. No.	Parameters	Units	Result
1	2-Chlorobiphenyl	µg/ Nm^3	BDL
2	2,3-Dichlorobiphenyl	µg/ Nm^3	BDL
3	2,2’, 3,3’, 4,4’,4’, 6-Heptachlorobiphenyl	µg/ Nm^3	BDL
4	2,2’, 4,4’,5, 6’-Hexachlorobiphenyl	µg/ Nm^3	BDL
5	2,2’, 3’,3’, 4,5’,6, 6’-Octachlorobiphenyl	µg/ Nm^3	BDL
6	2,2’, 3’, 4, 6-Pentachlorobiphenyl	µg/ Nm^3	BDL
7	2,2’, 4, 4’-Tetrachlorobiphenyl	µg/ Nm^3	BDL
8	2, 4, 5-Trichlorobiphenyl	µg/ Nm^3	BDL

Table.12-5. PTA waste mix – polychlorinated biphenyl (PCB) composition

Sl. No.	Parameters	Units	Result
1	Cd	mg/ kg	0.41
2	Cr	mg/ kg	0.98
3	Cu	mg/ kg	4.8
4	Co	mg/ kg	4.6
5	Mn	mg/ kg	6.52
6	Ni	mg/ kg	1.1
7	Pb	mg/ kg	0.9
8	Zn	mg/ kg	6.4
9	As	mg/ kg	0.42
10	Hg	mg/ kg	0.13
11	Sb	mg/ kg	0.82
12	V	mg/ kg	<0.1
13	Tl	mg/ kg	0.71
14	Sn	mg/ kg	0.98
15	Fe	mg/ kg	18.9
16	Se	mg/ kg	<0.1

Table.12-6. PTA waste mix – metal composition

Sl. No.	Parameters	Units	Result
1	4-Chloro 3-methylphenol	µg/ kg	BDL
2	2-Chlorophenol	µg/ kg	BDL
3	2,4-Dichlorophenol	µg/ kg	BDL
4	Pentachlorophenol	µg/ kg	BDL
5	2,4,6-Trichlorophenol	µg/ kg	BDL

Table.12-7. PTA waste mix – poly chlorophenols (PCP) composition

Sl. No.	Parameters	Units	Result
1	Aldrin	µg/ kg	BDL
2	Alpha-BHC	µg/ kg	BDL
3	Beta-BHC	µg/ kg	BDL
4	Delta-BHC	µg/ kg	BDL
5	Dieldrin	µg/ kg	BDL
6	Endosulfan I (Alpha)	µg/ kg	BDL
7	Endosulfan II (Beta)	µg/ kg	BDL
8	Endosulfan Sulfate	µg/ kg	BDL
9	Endrin	µg/ kg	BDL
10	Endrin Aldehyde	µg/ kg	BDL
11	Endrin Ketone	µg/ kg	BDL
12	Gamma-BHC	µg/ kg	BDL
13	Heptachlor	µg/ kg	BDL
14	Heptachlor Epoxide Isomer B	µg/ kg	BDL
15	Methoxychlor	µg/ kg	BDL
16	4,4’ DDD	µg/ kg	BDL
17	4,4’ DDE	µg/ kg	BDL
18	4,4’ DDT	µg/ kg	BDL

Table.12-8. PTA waste mix–organo-chlorins

Sl. No.	Parameters	Units	Result
1	Cd	mg/L	0.01
2	Cr	mg/L	0.01
3	Cu	mg/L	0.08
4	Fe	mg/L	0.41
5	Co	mg/L	0.02
6	Mn	mg/L	0.09
7	Ni	mg/L	<0.01
8	Pb	mg/L	0.02
9	Zn	mg/L	0.07
10	As	mg/L	0.01
11	Hg	mg/L	<0.01
12	Se	mg/L	<0.01
13	Sb	mg/L	0.02
14	V	mg/L	<0.01
15	Tl	mg/L	0.01
16	Sn	mg/L	<0.01

Table.12-9. PTA waste mix – TCLP test

12.3. Results and Discussion

During the five day trial period different production and emission parameters were sampled as per the requirements of the individual parameters, ranging from single sample per day to four samples per day. The average coal feeding rate from day 1-5 was 46.2, 45.7, 46.8, 47.38 and 46.5 tph respectively. The average PTA waste mix (scrap PTA, PTA contaminated liners, process sludge, oily rags and ETP sludge) feed rate during the co-processing stages was 22 tonnes/day although exact feed rate was measured during co-processing (day 2-4) of the trial with 0.73 tph on day - 2, 0.61 and 0.53 tph on day 3 and 4 respectively. The percentage substitution of coal with PTA waste mix stands at 1.59%, 1.31% and 1.12% respectively from day 2-4. The PTA waste mix co-processing led to the thermal replacement of 98% based on GCV of the waste and coal. Thus approximately 67 tonnes of coal was saved per day during the co-processing stage based on the GCV of waste when compared with coal. Due to co-processing no significant CO_2 reduction was observed although approx USD 35 per tonne of economical gain was obtained based on the coal cost and waste cost through substitution.

12.3.1. Results of emission monitoring during co-processing trial

The particulate matter (PM) was sampled using protocol USEPA 5, with 4 samples each day. The CPCB norm for particulate matters (PM) is 30 mg/Nm^3 for cement plant co-processing hazardous waste but the average emissions as measured during the trial were 22, 18.95, 17.18, 17.75 and 18.83 mg/Nm^3 respectively from day 1-5. The concentration of PM varied from 20.6 to 23.2 during pre co-processing; 15.6 to 20.6 during co-processing and on post co-processing stage the value observed was in between 17.1 – 21.1 mg/Nm^3 (table.12-10 to 12-14). The analysis revealed that the PM in flue gas decreased by 3.17 mg/Nm^3 from day-1 to 5.

The total organic compounds (TOC) were sampled using USEPA Method No. 30 & 10. The norm for cement plant co-processing hazardous waste is 10 mg/Nm^3, and the concentration of TOC was 9.8 mg/Nm^3 on pre co-processing day and during co-processing days it was in between 8.3 – 9.2 mg/Nm^3. The concentration of TOC was 9.6 mg/Nm^3 on post co-processing day, a decrease of 0.2 mg/Nm^3 from the pre co-processing value (table.12-10 to

12-14). The fluctuation of both PM and TOC is attributed to the production process deviations and effect of PTA waste mix was marginal (figure.12-1).

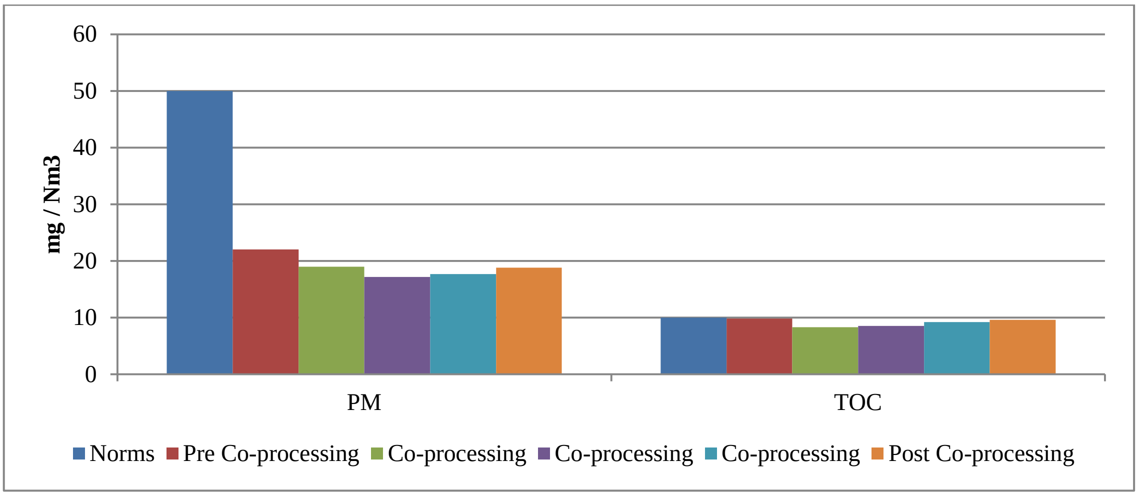

Figure.12-1. Emission of PM, TOC during the five day trial

Hydrogen chloride (HCl) and hydrogen fluorides (HF) were sampled using USEPA Method No.26A; hydrogen chloride emission varied from 9.2 to 9.8 mg/Nm^3 on day - 1, 7.3 to 9.3 mg/Nm^3 during co-processing stage and on day-5 it was found to be in between 8.1 to 9.3 mg/Nm^3. Hydrogen Fluoride emission varied from 1.9 to 2.5 mg/Nm^3 on day – 1, 1.4 to 2.2 mg/Nm^3 during co-processing stage and the measured value was in between 1.8 to 2.2 mg/Nm^3 on day- 5. The emission of poly aromatic hydrocarbons (PAH) during pre co-processing stage as measured was varying between 1.11 to 1.32 mg/Nm^3, during co-processing stages it was between 0.8 to 0.92 mg/Nm^3 and on post co-processing stage the emission was between 0.98 to 0.99 mg/Nm^3. The fluctuation in HCl, HF and PAH values are due to the normal production fluctuation rather than PTA waste mix co-processing affect. All the emissions during the five day trial were within the guidelines of cement plant co-processing hazardous waste given by ministry of environment, forest and climate change, government of India (figure.12-2).

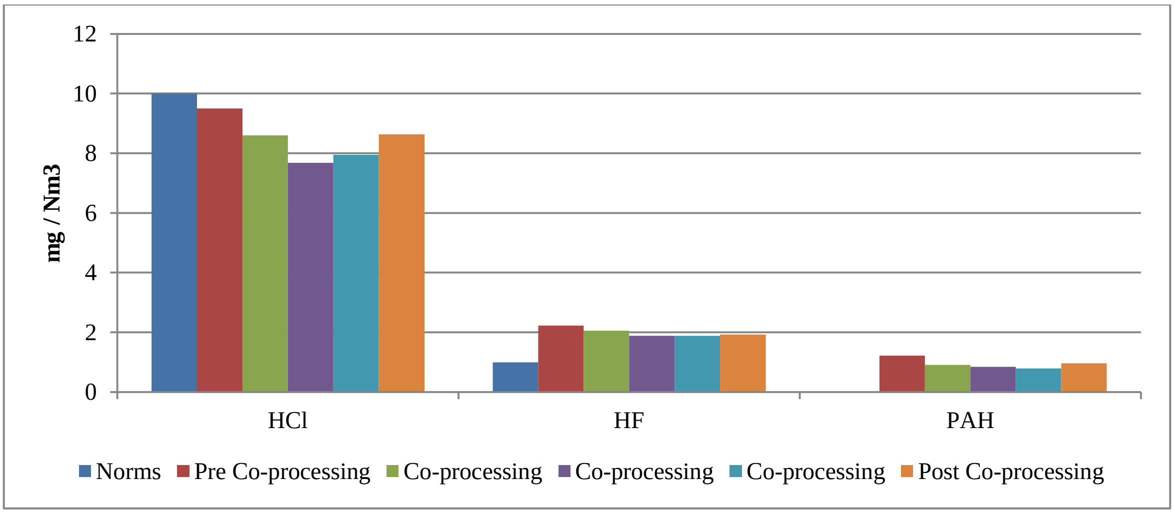

Figure.12-2. Emission of HCl, HF and PAH during the five day trial

The gases like oxides of nitrogen, carbon monoxide and sulphur dioxides were sampled using procedure – NO_X (USEPA Method No. 7), CO (USEPA Method No. 10B) and SO_2 (USEPA Method No. 6). In general CO content in stack emission reveals the state of combustion in the kiln, as its concentration is dependent on the oxidation of carbon content of the feed, CO is considered to be the product of incomplete combustion. There is no defined CO emission standards under co-processing guidelines, thus for the purpose of analysis the pre co-processing stage is used as a benchmarked value for comparison of emission during the trial. CO emission varied between 58 – 72 mg/Nm^3 during pre co-processing stage, 55 – 68 mg/Nm^3 during co-processing stage and 58 - 69 mg/Nm^3 on the post co-processing day. The norms for SO_2 and NOx for cement plant co-processing hazardous waste is 100 mg/Nm^3 and 800 mg/Nm^3 respectively and maximum observed emission were < 3.2 mg/Nm^3 and 789.75 mg/Nm^3 respectively for SO_2 and NOx. The emission of heavy metal was sampled using USEPA Method No. 29 and detail measurement was given in table.12-10 to 12-14. There wasn't any noticeable deviation for any of the metals, all the emission were under the norms.

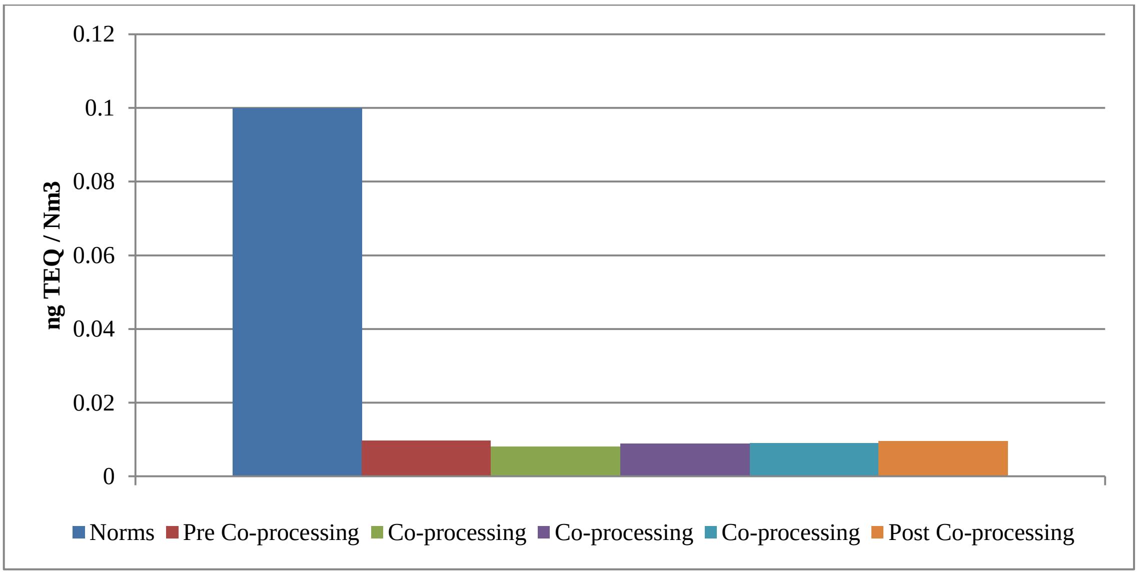

Figure.12-3. Total dioxin/furan emission during five day trial

The concentration of total dioxin/furan on day-1 were found to be 0.0098 ngTEQ/Nm^3, 0.0081-0.0091 ngTEQ/Nm^3 during day 2 - 4 and on day-5 it was 0.0096 ngTEQ/Nm^3, all the emissions were below the norms for dioxin / furan of 0.1 ngTEQ/Nm^3 (figure.12-3). The USEPA Method No. 23A protocol has been used to measure the dioxin/furan emission. No major variation in the emissions were noticed during the three phase of the trial (table.12-10 to 12-14).

Pre Co-processing Stage (Day – 1)									
Sl. No.	**Parameters**	**Unit**	**S1**	**S2**	**S3**	**S4**	**Average**	**Norms for Common Hazardous Waste Incinerator**	**Norms for Cement Plant Co-processing HW**
1	Flue gas Temperature	°C	135	148	145	150	144.5	NA	NA
2	Velocity	m/sec	14.15	14.85	13.4	12.65	13.8	NA	NA
3	Volumetric flow rate	Nm^3/sec	300.5	305.9	277.9	259.2	285.9	NA	NA
4	Particulate Matters	mg/ Nm^3	21.3	22.8	20.6	23.2	22	50	30

Pre Co-processing Stage (Day – 1)

Sl. No.	Parameters	Unit	S1	S2	S3	S4	Average	Norms for Common Hazardous Waste Incinerator	Norms for Cement Plant Co-processing HW
5	SO$_2$	mg/ Nm^3	<3.2	<3.2	<3.2	<3.2	<3.2	200	100
6	NOx	mg/ Nm^3	798	778	789	792	789.5	400	800
7	HC	mg/ Nm^3	ND	-	ND	-	ND	NA	NA
8	CO	mg/ Nm^3	72	58	69	67	66.5	100	NA
9	O$_2$	%	11.01	10.59	11.7	10.27	10.9	NA	NA
10	CO$_2$	%	9.82	9.21	9.3	9.82	9.54	NA	NA
11	HCl	mg/ Nm^3	9.6	9.2	9.4	9.8	9.5	50	10
12	HF	mg/ Nm^3	2.2	2.5	1.9	2.3	2.23	4	1
13	TOC	mg/ Nm^3	-	9.8	-	-	9.8	20	10
14	PAH	µg/ Nm^3	1.32	-	1.11	-	1.22	NA	NA
15	VOC	µg/ Nm^3	ND	-	-	ND	BDL	NA	NA
16	Cyanide	µg/ Nm^3	-	<0.02	-	-	<0.02	NA	NA
17	Mercury	µg/ Nm^3	-	2.8	-	-	2.8	0.05	0.05
18	Cadmium + Thorium	mg/ Nm^3	-	0.016	-	-	0.016	0.05	0.05
19	Total Metals	mg/ Nm^3	-	0.246	-	-	0.246	0.5	0.5
20	Total Dioxin and Furans	ngTEQ/ Nm^3	0.0098	-	-	-	0.0098	0.1	0.1

Table.12-10. Emission monitoring during pre co-processing stage (day – 1)

During Co-processing Stage (Day – 2)

Sl. No.	Parameters	Unit	S1	S2	S3	S4	Average
1	Flue gas Temperature	°C	150	157	159	157	155.75
2	Velocity	m/sec	11.51	13.44	11.76	11.664	12.094
3	Volumetric flow rate	Nm^3/sec	235.8	271.01	236.14	234.67	244.41
4	Particulate Matters	mg/ Nm^3	19.2	17.4	20.6	18.6	18.95
5	SO$_2$	mg/ Nm^3	<3.2	<3.2	<3.2	<3.2	<3.2
6	NOx	mg/ Nm^3	790	746	788	792	779
7	HC	mg/ Nm^3	ND	-	ND	-	ND
8	CO	mg/ Nm^3	68	64	56	63	62.75
9	O$_2$	%	9.89	11.2	8.6	9.11	9.7
10	CO$_2$	%	9.74	8.6	10.87	10.39	9.9
11	HCl	mg/ Nm^3	9.2	8.6	8.1	8.5	8.6
12	HF	mg/ Nm^3	2.1	1.8	2.2	2.1	2.05
13	TOC	mg/ Nm^3	-	8.3	-	-	8.3
14	PAH	µg/ Nm^3	0.92	-	0.89	-	0.91
15	VOC	µg/ Nm^3	ND	-	-	ND	ND
16	Cyanide	µg/ Nm^3	-	<0.02	-	-	<0.02
17	Mercury	µg/ Nm^3	-	1.9	-	-	1.9
18	Cadmium + Thorium	mg/ Nm^3	-	0.011	-	-	0.011
19	Total Metals	mg/ Nm^3	-	0.218	-	-	0.218
20	Total Dioxin and Furans	ng/ Nm^3	0.0081	-	-	-	0.0081

Table.12-11.Emission monitoring during co-processing stage (day – 2)

During Co-processing Stage (Day – 3)

Sl. No.	Parameters	Unit	S1	S2	S3	S4	Average
1	Flue gas Temperature	°C	154	157	156	155	155.5
2	Velocity	m/sec	11.39	11.67	11.03	11.64	11.433
3	Volumetric flow rate	Nm^3/sec	231.19	234.53	223.8	234.67	231.05
4	Particulate Matters	mg/ Nm^3	18.9	15.6	17.3	16.9	17.18
5	SO$_2$	mg/ Nm^3	<3.2	<3.2	<3.2	<3.2	<3.2
6	NOx	mg/ Nm^3	798	762	787	796	785.75
7	HC	mg/ Nm^3	ND	-	ND	-	ND

During Co-processing Stage (Day – 3)							
Sl. No.	**Parameters**	**Unit**	**S1**	**S2**	**S3**	**S4**	**Average**
8	CO	mg/ Nm^3	56	55	59	58	57
9	O_2	%	8.56	9.08	9.03	9.21	8.97
10	CO_2	%	8.75	9.13	8.07	8.22	8.54
11	HCl	mg/ Nm^3	7.3	7.9	7.4	8.1	7.68
12	HF	mg/ Nm^3	1.9	2.2	1.7	1.7	1.88
13	TOC	mg/ Nm^3	-	8.5	-	-	8.5
14	PAH	µg/ Nm^3	0.88	-	0.82	-	0.85
15	VOC	µg/ Nm^3	ND	-	-	ND	ND
16	Cyanide	µg/ Nm^3	-	<0.02	-	-	<0.02
17	Mercury	µg/ Nm^3	-	2.1	-	-	2.1
18	Cadmium + Thorium	mg/ Nm^3	-	0.013	-	-	0.013
19	Total Metals	mg/ Nm^3	-	0.229	-	-	0.229
20	Total Dioxin and Furans	ng/ Nm^3	0.0089	-	-	-	0.0089

Table.12-12. Emission monitoring during co-processing stage (day – 3)

During Co-processing Stage (Day – 4)							
Sl. No.	**Parameters**	**Unit**	**S1**	**S2**	**S3**	**S4**	**Average**
1	Flue gas Temperature	°C	152	156	150	152	152.5
2	Velocity	m/sec	11.46	11.31	11.57	11.46	11.45
3	Volumetric flow rate	Nm^3/sec	233.3	228.47	237.17	233.9	233.21
4	Particulate Matters	mg/ Nm^3	18.8	17.1	17.9	17.2	17.75
5	SO_2	mg/ Nm^3	<3.2	<3.2	<3.2	<3.2	<3.2
6	NOx	mg/ Nm^3	778	762	779	798	779.25
7	HC	mg/ Nm^3	ND	-	ND	-	ND
8	CO	mg/ Nm^3	59	56	61	58	58.5
9	O_2	%	8.95	9.7	10.2	9.7	9.64
10	CO_2	%	8.7	9.9	8.5	8.6	8.93
11	HCl	mg/ Nm^3	8.1	7.6	7.8	8.3	7.95
12	HF	mg/ Nm^3	1.6	1.9	2.2	1.8	1.88
13	TOC	mg/ Nm^3	-	9.2	-	-	9.2
14	PAH	µg/ Nm^3	0.77	-	0.82	-	0.79
15	VOC	µg/ Nm^3	ND	-	-	ND	ND
16	Cyanide	µg/ Nm^3	-	<0.02	-	-	<0.02
17	Mercury	µg/ Nm^3	-	1.5	-	-	1.5
18	Cadmium + Thorium	mg/ Nm^3	-	0.014	-	-	0.014
19	Total Metals	mg/ Nm^3	-	0.231	-	-	0.231
20	Total Dioxin and Furans	ng/ Nm^3	0.0091	-	-	-	0.0091

Table.12-13. Emission monitoring during co-processing stage (day – 4)

Post Co-processing Stage (Day – 5)							
Sl. No.	**Parameters**	**Unit**	**S1**	**S2**	**S3**	**S4**	**Average**
1	Flue gas Temperature	°C	150	155	152	150	151.7
2	Velocity	m/sec	11.64	11.72	11.39	11.76	11.63
3	Volumetric flow rate	Nm^3/sec	234.62	235.67	231.19	236.14	234.41
4	Particulate Matters	mg/ Nm^3	18.2	21.1	17.4	18.6	18.83
5	SO_2	mg/ Nm^3	<3.2	<3.2	<3.2	<3.2	<3.2
6	NOx	mg/ Nm3	798	776	797	788	789.75
7	HC	mg/ Nm3	ND	-	ND	-	ND
8	CO	mg/ Nm^3	59	62	71	58	62.5
9	O_2	%	9.17	9.22	9.08	9.89	9.34
10	CO_2	%	9.12	9.16	9.32	9.69	9.32
11	HCl	mg/ Nm^3	9.3	8.6	8.1	8.5	8.63

12	HF	mg/ Nm^3	1.6	2.1	2.2	1.8	1.93
13	TOC	mg/ Nm^3	-	9.6	-	-	9.6
14	PAH	µg/ Nm^3	0.98	-	0.99	-	0.96
15	VOC	µg/ Nm^3	ND	-	-	ND	ND
16	Cyanide	µg/ Nm^3	-	<0.02	-	-	<0.02
17	Mercury	µg/ Nm^3	-	1.9	-	-	1.9
18	Cadmium + Thorium	mg/ Nm^3	-	0.015	-	-	0.015
19	Total Metals	mg/ Nm^3	-	0.238	-	-	0.238
20	Total Dioxin and Furans	ng/ Nm^3	0.0096	-	-	-	0.0096

Table.12-14. Emission monitoring during post co-processing Stage (day – 5)

12.3.2. Clinker quality monitoring during trail

The clinker quality is a defining property for the final products; it was monitored extensively during the trial period. The quality of the clinker mainly depends on the elements going in to the clinker and their internal combined molecular properties. Different elemental quantities are kept fixed with in a fixed predefined tolerance level as per the industry standards. The chemical composition of clinker was analysed using standards IS:4032 and it revealed negligible deviation from day 1-5 (table.12-15).

Sl. No.	**Chemical Constituents [%]**	**Pre- Co-processing**	**During Co-processing**			**Post Co-processing**
		Day-1	**Day-2**	**Day-3**	**Day-4**	**Day-5**
1	LOI	0.32	0.31	0.30	0.31	0.30
2	SiO_2	20.99	21.01	21.0	21.01	21.03
3	Al_2O_3	5.18	5.21	5.19	5.21	5.58
4	Fe_2O_3	3.55	3.58	3.60	3.59	3.61
5	CaO	63.98	63.93	63.98	63.97	64.03
6	MgO	2.02	2.03	2.01	2.04	2.04
7	SO_3	0.74	0.73	0.71	0.69	0.71
8	CaO (Free Lime)	1.58	1.6	1.58	1.62	1.61
9	Na_2O	0.27	0.28	0.27	0.29	0.29
10	K_2O	1.41	1.41	1.39	1.39	1.38
11	Cl	0.02	0.01	0.01	0.02	0.02

Table.12-15. Clinker chemical composition analysis

The clinker metal content, TOC content and cyanide content are within the range during the trial, this were analysed using ICP-OES/AAS. None of the elements have shown abnormal deviation, the marginal deviation as revealed during the trial was due to production process fluctuation (table.12-16).

Sl. No.	**Parameters**	**Units**	**Pre Co-processing**	**During Co-processing**			**Post Co-processing**
			Day-1	**Day-2**	**Day-3**	**Day-4**	**Day-5**
1	Cd	mg/ kg	16.1	16.7	16.5	16.7	16.8
2	Cr	mg/ kg	44.8	44.1	44.9	45.2	44.2
3	Cu	mg/ kg	60.1	61.8	62.1	60.8	60.1
4	Iron	mg/ kg	23142	23462	23884	23488	23810
5	Co	mg/ kg	2.5	2.7	2.6	2.7	2.6
6	Ni	mg/ kg	35.8	35.8	36.8	36.8	35.4
7	Pb	mg/ kg	33.4	33.4	34.1	34.8	34.1
8	As	mg/ kg	3.8	3.8	3.9	3.8	3.7
9	Hg	mg/ kg	2.8	2.9	3	2.9	2.8

Sl. No.	Parameters	Units	Pre Co-processing	During Co-processing			Post Co-processing
			Day-1	Day-2	Day-3	Day-4	Day-5
10	Selenium	mg/ kg	3.1	3.2	3.3	3.3	3.2
11	Sb	mg/ kg	7.4	7.6	7.5	7.9	7.9
12	V	mg/ kg	73.4	75.8	76.2	77	76
13	Zinc	mg/ kg	159.4	162.8	160.8	162.1	160.1
14	Manganese	mg/ kg	202.2	198.1	203.4	203.8	202.1
15	Thorium	mg/ kg	3.7	3.5	3.2	3.5	3.6
16	TOC	%	0.02	0.01	0.01	0.02	0.03
17	Cyanide	mg/ kg	<0.2	<0.2	<0.2	<0.2	<0.2

Table.12-16. Clinker metal, TOC and cyanide composition analysis

12.3.3. Leach test of clinker

The leaching test of the clinker during the trial period was carried out based on the USEPA 1311 protocol using one sample each day. The comparison of the leaching behaviour of the cement obtained from day-1 to day -5 indicates the amount of leached heavy metals and other non heavy metals; the results indicates negligible deviations and all the values are within the acceptable levels of the industry standards as practised (table.12-17).

Sl. No.	Parameters	Units	Pre- Co-processing	During Co-processing			Post Co-processing
			Day-1	Day-2	Day-3	Day-4	Day-5
1	Cd	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
2	Th	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
3	Hg	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
4	Sb	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
5	As	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
6	Cr	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
7	Co	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
8	Cu	mg/L	0.01	0.01	0.02	0.02	0.01
9	Mn	mg/L	0.02	0.03	0.02	0.03	0.02
10	V	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
11	Zn	mg/L	0.06	0.04	0.05	0.04	0.04
12	Sn	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
13	Se	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
14	Cyanide	mg/L	<0.02	<0.02	<0.02	<0.02	<0.02

Table.12-17. Clinker toxicity characteristic leaching procedure (TCLP) analysis

12.3.4. Cement property analysis

The cement property was analysed to gauge blaine, setting time, soundness and compressive strength, as this are the parameters which decide the cement properties. The day-1 values were considered as the benchmarked criteria for gauging any deviation in the properties. All the cement property fluctuated marginally from their pre co-processing value but the changes are within the industry tolerance limit as practised and are in accordance with the bureau of Indian standards (IS 269:2015) and are mainly normal fluctuation as per the production process deviation (table.12-18).

Sl. No.	Physical Parameters	Pre- Co-processing	During Co-processing			Post Co-processing
		Day-1	Day-2	Day-3	Day-4	Day-5
1	Blain (m^2/kg)	421.9	403.0	421.1	416.4	411.2
2	Initial Setting Time (minutes)	210	205	200	200	180
3	Final Setting Time (minutes)	260	255	245	250	225
	Soundness					
4	Le –Chat (mm)	0.5	0.5	0.5	0.5	0.5
5	Autoclave (%)	0.02	0.03	0.02	0.03	0.03
	Compressive Strength					
6	3-Days (MPa)	33.2	33.1	34.7	34.0	32.4
7	7-Days (MPa)	43.0	40.0	43.5	42.7	40.8
8	28-Days (MPa)	55.8	55.3	52.0	56.9	55.1

Table.12-18. Physical test of cement (hourly sample homogenized on daily basis)

12.3.5. Ambient air quality around the cement plant during the trial

The ambient air quality was gauged at three different locations from kiln, for analysing the effect of co-processing, four major parameters were analysed. The parameters measured are NOx, SO_2, RSPM (Respirable suspended particulate matter) and SPM (suspended particulate matter) and there norms are defined by national ambient air quality standards – 2009. The limit for NOx - 80µg/m^3, SO_2 – 80 µg/m^3, RSPM – 60 µg/m^3 and SPM – 100 µg/m^3.The first location was approximately 1.75 km from kiln; the sampling of the ambient air during the five day trial revealed normal fluctuations (figure.12-4).

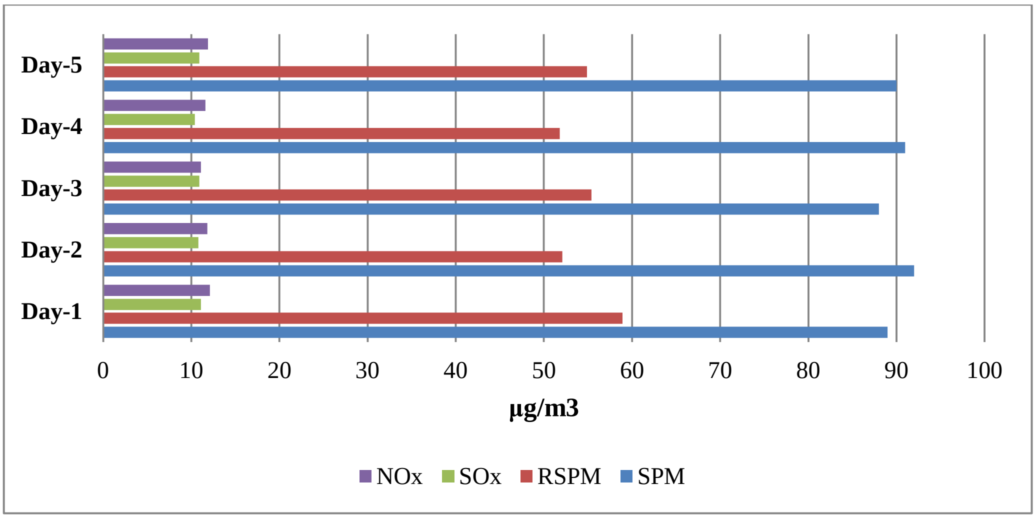

Figure.12-4. Ambient air quality of location 1 during trial period

Similar analysis was carried out at the second location which was around 1 km away from kiln. The sampling showed marginal change for all the parameters, with SPM and RSPM revealed maximum deviation from location-1. The deviation is primarily attributed to location being near to mines and kiln (figure.12-5).

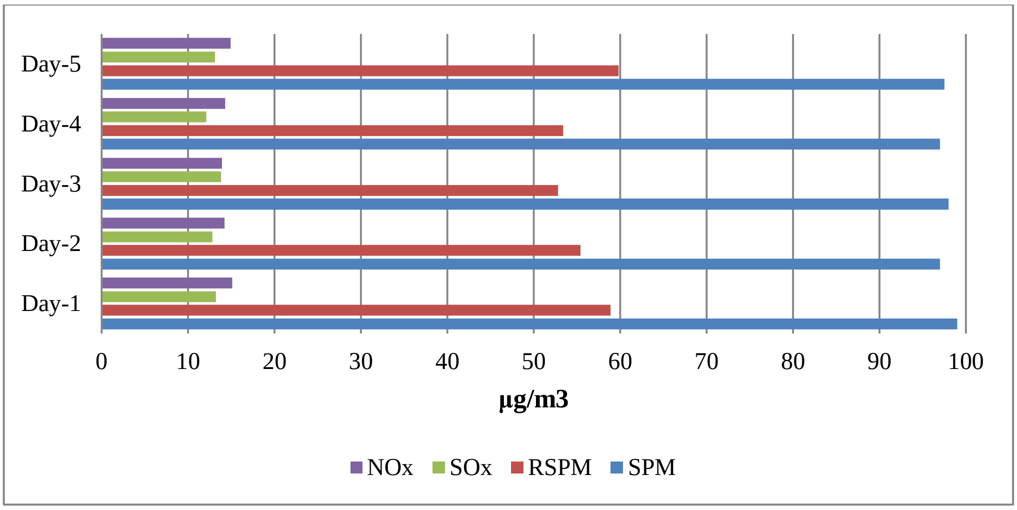

Figure.12-5. Ambient air quality of location 2 during trial period

The third location was at 0.7 km from kiln-2. It revealed similar fluctuation across the days. The SPM has showed maximum deviation on day-3 (figure.12-6). This marginal deviation of parameters in different locations at different distance is attributed to the production process, specific operation at that location and minutely on metrological consideration rather than the co-processing of PTA waste mix. The meteorological data of the five day was monitored in details and it also revealed marginal deviation in ambient temperature, humidity level, rainfall and wind speed. The wind speed during the trials was 1.6 - 19 km/hr and maximum ambient temperature reached was 24.5°C which are normal metrological condition around the area (table.12-19).

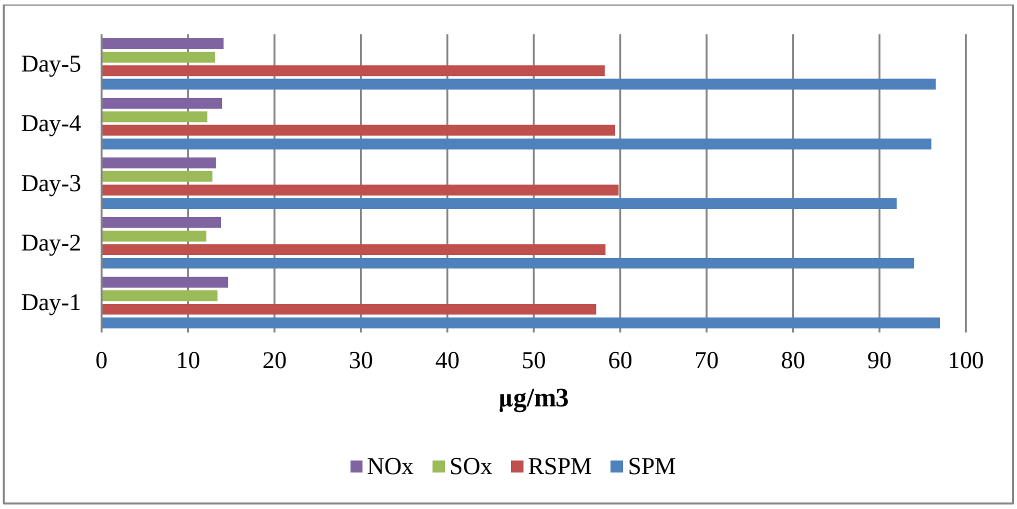

Figure.12-6. Ambient air quality of location 3 during trial period

Days	Ambient Temperature		Relative Humidity	Rainfall
	Maximum	Minimum	Average %	mm
Pre Co- processing (Day – 1)	23	9.0	54	Nil
During Co- processing (Day – 2)	25	11	56	Nil
During Co- processing (Day – 3)	25	11	53	Nil
During Co- processing (Day – 4)	24.5	9.5	52	Nil
Post Co- processing (Day – 5)	21.5	8.0	72	Nil

Table.12-19. Meteorological data during five day trial period

12.4. Metal Mass Balance

Due to the high toxicity, carcinogenic and mutagenic properties of different metal in the PTA waste mix the environmental and health risk of the trace elements, an analysis of trace element flow was carried out. The trace elements can be classified in to groups I, II and III based on their thermodynamic nature within the pre process. The group I was classified as non volatile elements (remains in clinker): Co, Cr, Fe and Ni; group II was classified in to volatile and condensable elements (mostly condensed and remain in the pre-heater and kiln forming a recirculation system with the flue gases): As, Cd, Cu, Pb, Se, V and Zn; group III was classified in to volatile and non-condensable elements (mostly present in gaseous form): Hg. All the materials are volatized in the burning zone and condensed downstream, generally become fume particles smaller than 0.1 µm in size. These particles exhibit Brownian motion and rapidly colloid with other particles, combining to form particles > 0.1 to 1.0 µm in size. Volatile metals in the burning zone tend to accumulate on surface of the small particles of feed materials in cooler area. As the feed material, which has trapped volatile components, moves into hotter region, the volatile components once again evaporate and re-circulate within the pyrosystem. In addition to element content in each mass stream, the flow rates of all the streams are necessary for metal mass balance calculation. The estimation of their magnitudes during each sampling period (i.e. each test) was made from plant operating records.

12.4.1. Metal mass balance calculation

The flow rate of each trace element was calculated based on the analysis of the trace element in ingoing and outgoing stream, and on the flow rate of each stream based on the below mentioned equations (Tolvanen, 2004).

$Q_{ij} = C_{ij}\, q_j$ equation-1

Q_{ij} = the flow rate of the element ‘i’ in the ingoing or out coming material stream ‘j’ of the plant in mg/h

C_{ij} = the content of the element ‘i’ analysed in the representative sample of the material stream ‘j’ of the plant (mg/kg in dry basis for solid samples, $\mu g/Nm^3$ in NTP for dry flue gas samples, mg/m^3 for water samples)

Q_j = the flow rate of the material stream j of the plant (kg/h in dry basis for solid streams, Nm^3/h in NTP for dry flue gases, m^3/h for water streams)

The sum of all the ingoing and out flow rates of each trace elements gives the total ingoing ($Q_{i,in}$) and out coming ($Q_{i,out}$) streams of each elements respectively as shown in equation 2&3.

$Q_{i,in} = \sum(Q_{ij})$. When j= 1….n equation-2

$Q_{i,out} = \sum(Q_{ij})$. When j= n+1…….n+m equation-3

Where n= number of the ingoing streams of the plant m= number of the out coming streams of the plant

The steady-state mass balance of each element is then given by equation – 4.

$Q_{i,in} - Q_{i,out} + r_i = 0$ equation-4

Where r_i = recovery factor

The recovery factor in the calculation has been taken as zero in order to reveal information about the success of the experimental tests and the ability of the experimental methods. This is studied based on the closure of each elements mass balance.

The closure of each element mass balance, (Out/In)i, means the ratio between out coming and ingoing streams of the element as shown in equation-5.

$(Out/In)_i = Q_{i,out}/Q_{i,in}$ equation-5

When the ratio (Out/In)i, is close to 1.0, the mass balance has been determined successfully. When the ratio is below 1.0, the out coming stream is too low compared to the ingoing stream. This happens when all the ingoing streams of the element have not been detected effectively in the out coming streams or the real ingoing stream of element is lower than the determined one. But when the ratio is more than 1.0, the out coming stream is too high to be compared to the ingoing stream. This happens when the real out coming flow of the element is lower than the determined one, or the ingoing streams of the element have been detected too low. The criterion for the applicability of the results was the range of closure must be within 0.7 – 1.3. The mass balance was then calculated for all the elements using data of the element contents (C_{ij}) and the flow rate of the material streams of the plant (q_j) using the above discussed method. The high closure of a steady – state mass balance for trace elements means that the measured ingoing flows are equal to the measured out coming flows for each trace element. The objective of this analysis is to check that the total out-coming stream for each element deviates less than 30% from the total ingoing stream. When the experimental results deviate more than 30%, the streams are needed to be adjusted with recovery factors. In the test, the steady state mass balances for trace elements were determined. Coal as the main and PTA waste mix as alternate fuel during the trial period. The closure of the mass balance in the current calculations was determined without using any recovery factors. The mass balance for metals was found to be in agreement with criteria for applicability of the range of the closure (table 12-20 to 12-24).

Pre Co-processing	**Kiln Feed TPH**		**Coal**		**PTA Waste Mix**		**Clinker**		**Flue Gas Emission**		**Mass Balance**
Day-1	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. µg/nm3**	**Conc. g/hr**	
Cd	9.1	5370.82	2.9	133.98	0	0	16.1	5313.00	9.20	2.87	0.97
Cr	23.4	13810.68	15.8	729.96	0	0	44.8	14784.00	8.00	2.50	1.02
Cu	29.6	17469.92	48.1	2222.22	0	0	60.1	19833.00	16.90	5.28	1.01
Iron	13124	7745784.8	2864	132316.8	0	0	23142	7636860.00	97.20	30.37	0.97
Co	1.3	767.26	2.1	97.02	0	0	2.5	825.00	8.80	2.75	0.96
Ni	18.6	10977.72	18.8	868.56	0	0	35.8	11814.00	12.90	4.03	1.00
Pb	17.4	10269.48	19.6	905.52	0	0	33.4	11022.00	8.80	2.75	0.99
As	2.1	1239.42	0.1	4.62	0	0	3.8	1254.00	6.60	2.06	1.01
Hg	1.6	944.32	0.01	0.462	0	0	2.8	924.00	4.10	1.28	0.98

Pre Co-processing	Kiln Feed TPH		Coal		PTA Waste Mix		Clinker		Flue Gas Emission		Mass Balance
Day-1	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. µg/nm3**	**Conc. g/hr**	
Selenium	1.8	1062.36	0.11	5.082	0	0	3.1	1023.00	9.20	2.87	0.96
Sb	4.1	2419.82	2.4	110.88	0	0	7.4	2442.00	12.60	3.94	0.97
V	40.6	23962.12	24.4	1127.28	0	0	73.4	24222.00	14.10	4.41	0.97
Zinc	88.2	52055.64	34.1	1575.42	0	0	159.4	52602.00	37.80	11.81	0.98

Table.12-20. Metal mass balance during pre co-processing phase (day-1)

During Co-processing	Kiln Feed TPH		Coal		PTA Waste Mix		Clinker		Flue Gas Emission		Mass Balance
Day-2	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. µg/nm3**	**Conc. g/hr**	
Cd	9.1	5427.24	2.9	132.53	0.41	0.2993	16.7	5564.44	8.10	2.63	1.00
Cr	23.4	13955.76	15.8	722.06	0.98	0.7154	44.1	14694.12	7.10	2.30	1.00
Cu	29.6	17653.44	48.1	2198.17	4.8	3.504	61.8	20591.76	15.10	4.90	1.04
Iron	13124	7827153.6	2864	130884.8	18.9	13.797	23462	7817538.40	84.20	27.30	0.98
Co	1.3	775.32	2.1	95.97	4.6	3.358	2.7	899.64	7.20	2.33	1.03
Ni	18.6	11093.04	18.8	859.16	1.1	0.803	35.8	11928.56	10.10	3.27	1.00
Pb	17.4	10377.36	19.6	895.72	0.9	0.657	33.4	11128.88	7.20	2.33	0.99
As	2.1	1252.44	0.1	4.57	0.42	0.3066	3.8	1266.16	5.10	1.65	1.01
Hg	1.6	954.24	0.01	0.457	0.13	0.0949	2.9	966.28	3.10	1.01	1.01
Selenium	1.8	1073.52	0.11	5.027	0	0	3.2	1066.24	9.20	2.98	0.99
Sb	4.1	2445.24	2.4	109.68	0.82	0.5986	7.6	2532.32	10.80	3.50	0.99
V	40.6	24213.84	24.4	1115.08	0	0	75.8	25256.56	12.10	3.92	1.00
Zinc	88.2	52602.48	34.1	1558.37	6.4	4.672	162.8	54244.96	39.00	12.65	1.00

Table.12-21. Metal mass balance during co-processing phase (day-2)

During Co-processing	Kiln Feed TPH		Coal		PTA Waste Mix		Clinker		Flue Gas Emission		Mass Balance
Day-3	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. µg/nm3**	**Conc. g/hr**	
Cd	9.1	5445.44	2.9	134.792	0.41	0.2501	16.5	5441.70	7.60	2.35	0.98
Cr	23.4	14002.56	15.8	734.384	0.98	0.5978	44.9	14808.02	9.00	2.78	1.00
Cu	29.6	17712.64	48.1	2235.688	4.8	2.928	62.1	20480.58	16.20	5.00	1.03
Iron	13124	7853401.6	2864	133118.72	18.9	11.529	23884	7876943.20	90.50	27.95	0.99
Co	1.3	777.92	2.1	97.608	4.6	2.806	2.6	857.48	6.80	2.10	0.98
Ni	18.6	11130.24	18.8	873.824	1.1	0.671	36.8	12136.64	11.00	3.40	1.01
Pb	17.4	10412.16	19.6	911.008	0.9	0.549	34.1	11246.18	7.00	2.16	0.99
As	2.1	1256.64	0.1	4.648	0.42	0.2562	3.9	1286.22	6.00	1.85	1.02
Hg	1.6	957.44	0.01	0.4648	0.13	0.0793	3	989.40	4.10	1.27	1.03
Selenium	1.8	1077.12	0.11	5.1128	0	0	3.3	1088.34	9.20	2.84	1.01
Sb	4.1	2453.44	2.4	111.552	0.82	0.5002	7.5	2473.50	11.40	3.52	0.97
V	40.6	24295.04	24.4	1134.112	0	0	76.2	25130.76	13.10	4.05	0.99
Zinc	88.2	52778.88	34.1	1584.968	6.4	3.904	160.8	53031.84	37.10	11.46	0.98

Table.12-22. Metal mass balance during co-processing phase (day-3)

During Co-processing	Kiln Feed TPH		Coal		PTA Waste Mix		Clinker		Flue Gas Emission		Mass Balance
Day-4	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. µg/nm3**	**Conc. g/hr**	
Cd	9.1	5427.24	2.9	137.692	0.41	0.2173	16.7	5475.93	7.10	2.35	0.98
Cr	23.4	13955.76	15.8	750.184	0.98	0.5194	45.2	14821.08	8.10	2.68	1.01
Cu	29.6	17653.44	48.1	2283.788	4.8	2.544	60.8	19936.32	15.10	5.00	1.00
Iron	13124	7827153.6	2864	135982.72	18.9	10.017	23488	7701715.20	95.60	31.67	0.97
Co	1.3	775.32	2.1	99.708	4.6	2.438	2.7	885.33	7.20	2.39	1.01
Ni	18.6	11093.04	18.8	892.624	1.1	0.583	36.8	12066.72	10.50	3.48	1.01

During Co-processing	Kiln Feed TPH		Coal		PTA Waste Mix		Clinker		Flue Gas Emission		Mass Balance
Day-4	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. µg/nm3**	**Conc. g/hr**	
Pb	17.4	10377.36	19.6	930.608	0.9	0.477	34.8	11410.92	8.10	2.68	1.01
As	2.1	1252.44	0.1	4.748	0.42	0.2226	3.8	1246.02	5.60	1.86	0.99
Hg	1.6	954.24	0.01	0.4748	0.13	0.0689	2.9	950.91	3.90	1.29	1.00
Selenium	1.8	1073.52	0.11	5.2228	0	0	3.3	1082.07	8.80	2.92	1.01
Sb	4.1	2445.24	2.4	113.952	0.82	0.4346	7.9	2590.41	10.80	3.58	1.01
V	40.6	24213.84	24.4	1158.512	0	0	77	25248.30	12.10	4.01	1.00
Zinc	88.2	52602.48	34.1	1619.068	6.4	3.392	162.1	53152.59	38.10	12.62	0.98

Table.12-23. Metal mass balance during co-processing phase (day-4)

Post Co-processing	Kiln Feed TPH		Coal		PTA Waste Mix		Clinker		Flue Gas Emission		Mass Balance
Day-5	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. mg/kg**	**Conc. g/hr**	**Conc. µg/nm3**	**Conc. g/hr**	
Cd	9.1	5419.96	2.9	134.85	0	0	16.8	5545.68	7.60	2.37	1.00
Cr	23.4	13937.04	15.8	734.7	0	0	44.2	14590.42	8.90	2.78	0.99
Cu	29.6	17629.76	48.1	2236.65	0	0	60.1	19839.01	18.00	5.62	1.00
Iron	13124	7816654.4	2864	133176	0	0	23810	7859681.00	97.20	30.37	0.99
Co	1.3	774.28	2.1	97.65	0	0	2.6	858.26	6.80	2.12	0.99
Ni	18.6	11078.16	18.8	874.2	0	0	35.4	11685.54	9.90	3.09	0.98
Pb	17.4	10363.44	19.6	911.4	0	0	34.1	11256.41	7.10	2.22	1.00
As	2.1	1250.76	0.1	4.65	0	0	3.7	1221.37	6.00	1.87	0.97
Hg	1.6	952.96	0.01	0.465	0	0	2.8	924.28	5.80	1.81	0.97
Selenium	1.8	1072.08	0.11	5.115	0	0	3.2	1056.32	9.00	2.81	0.98
Sb	4.1	2441.96	2.4	111.6	0	0	7.9	2607.79	11.00	3.44	1.02
V	40.6	24181.36	24.4	1134.6	0	0	76	25087.60	11.80	3.69	0.99
Zinc	88.2	52531.92	34.1	1585.65	0	0	160.1	52849.01	38.90	12.15	0.98

Table.12-24. Metal mass balance during post co-processing phase (day-5)

The co-processing of PTA waste mix in cement plants had no impact on any of the parameters including emission, clinker, cement property and leach behaviour when PTA waste co-processed at 22 tonnes/day. The study revealed the disposal and resource recovery potential of the co-processing in cement kiln. The studies also provide the basis for standards for PTA waste mix in India. The PTA waste mix has a considerable amount of calorific value of around 3980 kcal/mol thus acting as an alternative fuel. The economical benefit obtainable from co-processing can run to thousands of USD as approximately 67 tonnes of coal was saved per day. The trial revealed negligible deviations of different parameters of emission, clinker quality and cement property. The metal mass balance analysis also revealed negligible accumulations of trace metals. Thus the trial shows the sustainability of co-processing hazardous waste in cement kiln.

12.4. Conclusion

The co-processing trials of Purified Terephthalic Acid (PTA) waste mix demonstrated that the 0.63 TPH feeding rate has insignificant impact on cement kiln emission levels. The analysis of the clinker quality, leach behaviour and cement property analysis revealed zero implication on the final products. The analysis of different emission parameters shows negligible effect due to co-processing of PTA waste mix although the feed rate is a detrimental factor and needs to be controlled effectively so as not to effect the environment and final quality of the product. The ambient air quality analysed based on NOx, SO_2, SPM, RSPM reveals no major deviation, and minute fluctuations in the values, as noticed was contributed to production process fluctuation and weather conditions. The inherent characteristics of cement kiln and critical controlling of PTA waste mix reduces the chances of dioxin/furan formation. Further cement plants availability in major developing nations, makes the hazardous waste disposal/utilization an effective and economical methodology and can be seen as a better option than traditional thermal disposal techniques.

Chapter 13

Conclusion

The study analysed sustainability of energy and resource recovery technology/process for Indian scenario based on multiple field study and experimental trials. The WTE plants are plagued with numerous constraints, the primary challenging issues as revealed are, quality of MSW, waste segregations, low calorific value of the wastes and seasonal variation. The sustainability of the WTE plant can be improved if the economical aspects like tipping fee, incentives in unit price of the electricity generated are implemented. An effective policy implementation, as per the legislation and the implementation of rules will improve sustainability of the plant to the greater extent. A number of energy and resource recovery technologies/processes from waste are at different stages of commercialization in India and selection of the most sustainable technology /process framework is required to be identified. The ambit of the study was limited to the thermo-chemical process. A selection framework for the same was developed for analysing energy and resource recovery technology, considering different constructs under four pillars of sustainability. The qualitative constructs were analysed by AHP. The selection framework revealed co-processing as the most sustainable methodology for Indian scenario followed by gasification, incineration and pyrolysis. The co-processing process has some disadvantage in term of logistics and firing rate but has more advantages like firing of multiple waste streams, negative impact on emission, zero by-products, low operating and capital cost. The framework can be applied to decision making of other developing countries, having similar waste management system.

The sustainability of co-processing in cement kiln as a method of resource & energy recovery in cement plant was studied. The study showed that the cement plants were able to reduce their carbon footprint by co-processing different industrial waste stream and agro waste. The cement plants are highly capable of co-processing fragments of MSW that lead to savings of enormous amount of traditional raw materials and fuels.The low carbon cement manufacturing potential was also gauged based on case studies at cement plants in India based on a statistical data obtained from the cement plant. Numerous parameters like TSR%, AFRs utilized, traditional fuel (TF) and traditional raw material (TR) replaced by AFRs and substitution benefit obtained in term of monetary gain were analysed. Experimental trial was carried out on different waste streams, so that the optimization of the feeding rate can be done and standards can be framed for Indian case. The co-processing technology not only reduces the consumption of conventional resources but also helps the industries to dispose of their waste sustainably. The co-processing technique is a highly suitable business model in the Indian context and for other developing countries, based on the evaluation of the co-processing technique to environmental, economic, operational and social facets.

The BF flue dust co-processing was carried out at the cement plant in India. The trial was carried out for one month. The study tried segregation of BF flue dust into iron rich and energy rich materials using magnetic separator which was not effective and also the percentage substitution of BF Flue dust is very small ranging in between 0.12 – 0.18% of raw materials. The techno-economical potential was gauged and the flue dust can be utilised effectively at the range of about USD 35 - 39/t. Co-processing of BF flue dust reduces the carbon footprint of both steel plant and cement plant as 870t of conventional resource was saved without any effect on stack emissions and clinker quality. The process is highly adaptable for other cement plants as high profit is obtainable, both in term of CV and iron substitution. The findings of the study revealed that the BF flue dust, waste from steel plant, can be gainfully co-processed in the cement plant as AFRs and there exists techno-economic potential for the same. Marble slurry, a major waste of marble processing industry, was used as AFRs in cement plant for four years, spread over 2012-2015. The sustainability of co-processing marble slurry in the cement kiln was examined based on the data. The monitoring of stack emission during the observation period showed no adverse effect; moreover high economic gain was obtained due to substitution of traditional raw materials. No impact on the product quality was found based on the clinker quality and leach test. The cement property also showed no effect of co-processing. Marble slurry which is considered process waste, can lead to substantive economic gains.

Another trial with acid tar sludge (ATS), hazardous waste and a by-product of steel production process was carried out for five days each of five trials. During the co-processing trial ATS to coal feed ratio of 0.04:1 was maintained. The co-processing has insignificant impact on the emission and clinker quality, although the feeding rate is a detrimental factor, requires effective controlling, so as not to affect the environment and quality of the product. Further, inherent characteristics of cement plant critical controlling of ATS feeding reduces the chances of formation of dioxin/furan.

Another trial with a different hazardous waste was carried out. The purified terephthalic acid (PTA) is used for production of polyester, during processing by product hazardous organic waste is produced. The co-processing trial of five days was carried out to gauge the potential of treating the purified terephthalic acid (PTA) waste mix. The trial showed that 0.63 TPH feeding rate had insignificant impact on kiln parameters like clinker quality, leach behaviour, cement property and emissions. Due to high toxicity, carcinogenic and mutagenic property of the PTA waste mix a metal mass balance of the process was carried out to assess the environmental and health risk of the trace elements during the co-processing experimental trial. The effect on the ambient air quality in term of NOx, SO_2, SPM, RSPM was also not affected in all the experimental trials with different hazardous wastes. Additionally, cement plant availability in major developing nations, makes the hazardous waste disposal/utilization an effective and economical methodology and can be seen as a better option than traditional thermal disposal techniques. The environmental sustainability of the co-processing was analysed in term of average stack emission, the emission result showed negative deviation. The economical analysis revealed enormous monetary gain with no effect on the quality of the clinker. Thus waste utilization as AFRs can solve the two way problem of waste disposal and resource recovery addressing the waste management system of the country. India being the second largest cement producer, using of AFRs to its full potential can impact positively to global carbon mitigation efforts. The study also revealed different aspects on which the future scope of the work should be carried out. The study shows the effectiveness of industrial waste co-processing in cement kiln as a way of resource recovery from waste leading to resource circulation. The current work may further be expanded with different waste stream including hazardous waste.

Following are the summary of the conclusion:

1. **Primary issues and challenges of a WTE plants**: The primary issues and challenges of a WTE plants in India was revealed. Economical aspects are needed to be addressed for sustainable supply chain framework for WTE plants. (Refer Chapter – 4).

2. **Co-processing as the most sustainable process**: Selection framework was developed for analysing sustainable energy and resource recovery thermo-chemical process with the aid of AHP. The selection framework revealed co-processing as the most sustainable process for different waste stream in India (Refer Chapter – 5).

3. **Carbon footprint reduction via co-processing utilizing AFRs:** Cement plants were able to reduce their carbon footprint by co-processing different waste stream including industrial waste, fragments of MSW, with high economical gain and enormous savings both in term of traditional raw materials and fuels (Refer Chapter – 6, 7 & 8).

4. **Techno-economic feasibility**: Blast Furnace flue dust, waste from steel plant can be gainfully co-processed in the cement plant as AFRs and there exists a techno-economic potential in the range of about USD 35 - 39/t (Refer Chapter – 9).

5. **Case study demonstrating economic gains:** Marble slurry a marble processing industry waste co-processing was analysed based on trail over a span 2012-2015 revealing sustainability of the process with substantive economic gains (Refer Chapter – 10).

6. **Insignificant adverse impact on environment of co-processing ATS**: Acid tar sludge (ATS) a hazardous waste a by-product of steel production process was co-processed via five experimental trials of five days each. The experimental trials showed insignificant impact of co-processing ATS at the current feed ration of coal to ATS of 0.04:1 (Refer Chapter – 11).

7. **Insignificant adverse impact on environment of co-processing PTA:** Purified terephthalic acid (PTA) waste mix co-processing trial of five days at feeding rate of 0.63 tph had insignificant impact on the cement kiln process, emission and final products. The metal mass balance of the process also showed no impact due to co-processing (Refer Chapter – 12).

8. **Future scope of research:** The scope for further research exists using different waste streams including hazardous waste. The impact of co-processing on product quality and emission level may be gauged so as to develop the process as an ultimate sink for different hazardous waste. Different business cases may be developed for making the process more profitable fulfilling four sustainability pillars and encouraging more cement manufactures for co-processing of different waste stream. The future study may also consider the increase of substitution rate in kiln firing to a comparable range as in different European countries. The implementation of co-processing in standalone clinker grinding unit may also be studied that may require a major technological and process intervention.

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