Co-processing of non-recyclable hazardous plastic waste in cement kiln

Confederation of Indian Industry

SUSTAINABLE RECYCLING INDUSTRIES

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss Confederation

WORLD RESOURCES FORUM

EMPA
Materials Science & Technology

Toxics Link
for a toxics-free world

November 2016

Table of Contents

A. **Abbreviation**

1. **Introduction** 1
2. **Plastic waste generation in India** 2
3. **Waste management through Co-processing** 3
4. **BFR and its properties** 4
5. **Advantages of co-processing in Cement kiln** 7
6. **Guidelines for Co-processing Non – recyclable plastics in Cement kiln** 8
7. **Suitability/acceptance of waste material for co-processing** 9
8. **Trial Run and Monitoring of waste Co-processing in Cement kiln** 11
9. **Parameters to be documented during trial period** 23
10. **Quantity estimates for plastic waste Co-processing in Cement kilns** 25
11. **Way Forward** 31
12. **Annexure** 33

Total number of pages: 37

Abbreviations

MoEFCC	**-**	**Ministry of Environment, Forest and Climate Change**
CPCB	**-**	**Central Pollution Control Board**
SPCB	**-**	**State Pollution Control Board**
AFR	**-**	**Alternate Fuel and Raw Material**
BAU	**-**	**Business as Usual**
MSW	**-**	**Municipal Solid Waste**
HWM	**-**	**Hazardous Waste Management Rules**
LCA	**-**	**Life Cycle Approach**

1.0 Introduction

Sustainable recycling industries (SRI) is working on the initiative of converting waste in to resources. This program is built on the success of e-waste recycling systems with various developing countries for more than 10 years. The programme is funded by the Swiss State Secretariat of Economic Affairs (SECO) and is jointly implemented by the Institute for Materials Science & Technology (Empa), the World Resources Forum (WRF) and ecoinvent.

The main objective of Sustainable Recycling Industries (SRI) project in India is to design and pilot test of a system to remove hazardous plastic waste from the recycling chain. The project is implemented by the CII-Sohrabji Godrej Green Business Centre, Hyderabad. The major deliverables of the project includes

1. Developing a mechanism by applying scientific research and technological partnerships to remove hazardous plastic from the recycling chain & capacity building for recyclers of formal & informal sector

2. Developing Technical standards & guidelines for the handling, transport and destruction of critical plastics

3. Pilot for destroying the hazardous plastics through environmentally sound technologies

Currently this critical plastic enters the recycling chain and cross-contaminates a high fraction of the recycled plastic out of which toys and other sensitive products are manufactured. Additives like BFRs and heavy metals, extensively used in electronic and electrical equipment & exposure can lead to adverse health impacts.

This document is an attempt to explain the process of cement kiln co-processing for non -recyclable hazardous plastic waste and guidelines for successful co-processing of waste stream. The content is more of various process involved & parameters to be monitored in waste co-processing from acceptance to destruction and we hope this document will be useful to cement plant personnel, Co-processing units and other stake holders involved in co-processing.

We also request you to share your feedback/suggestions/comments to improve the document. Your feedback will encourage us at CII- Sohrabji Godrej Green Business Centre to take more initiatives in the future.

2.0 Plastic waste Generation in India

The word “plastic” derived from Greek meaning, “capable of being shaped or molded” and Plastics are responsible for countless facets of the modern life, due to their relatively low cost, ease of manufacture, versatility, and imperviousness to water, plastics are used in an enormous and expanding range of products, from paper clips to spaceships.

Generally “plastic” includes materials composed of various elements such as carbon, hydrogen, oxygen, nitrogen, chlorine, and sulfur. Plastics are typically organic polymers of high molecular mass (each molecule can have thousands of atoms bound together) and also called polymers, are produced by the conversion of natural products or by the synthesis from primary chemicals generally coming from petrochemicals.

WEEE (Waste Electrical and Electronic Equipment) plastics are the greatest concern for the recycling and disposal. This material should be safely managed due to hazardous components like brominated retardants. Due to better capabilities than normal plastics and economic factors, these waste are highly recycled but the hazardous substance has to be separated from it and disposed of in a scientific way.

As per the study conducted b

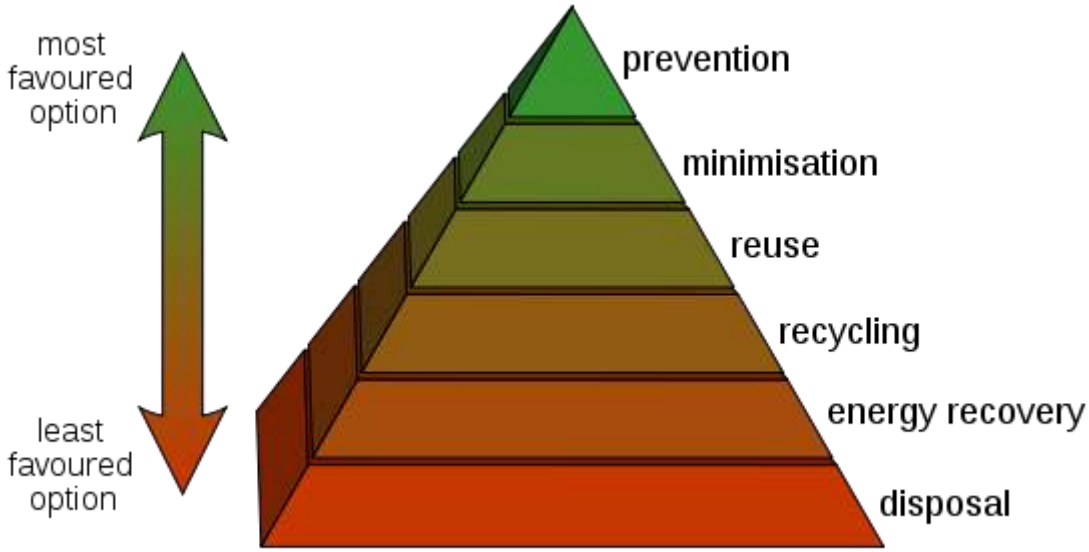
y Central Pollution Control Board (CPCB) in 60 major cities of India, it has been observed that around 4059 T/day of plastic waste is generated from these cities. The fraction of plastic waste in total Municipal Solid Waste (MSW) varies from 3.10% (Chandigarh) to 12.47% (Surat). Average plastic waste generation is around 6.92% of MSW.

With extrapolation of per capita plastic waste generation data from 60 major cities, it is estimated that approximately 9.46 million tons per annum of plastic waste is generated in India, which is around 25,940 T/day. As per the results of the study, out of total plastic waste, around 94% waste comprises of thermoplastic content, which is recyclable such as PET, LDPE, HDPE, PVC etc. and remaining 6% belongs to the family of thermoset and other categories of plastics such as SMC, FRP, multi-layered, thermocol etc., which is non-recyclable.

As per an estimation, every year approximately 0.56 million tons of non-recyclable plastic waste is dumped in India and most of plastic recycling was carried out by the informal sector and the level of recycling are higher than the developed countries. In addition, some thermoplastics contain hazardous additives, such as brominated flame retardants (BFRs), which have been banned but still occur in old waste. As per the SRI-projects estimation, roughly 110’000 tons of BFR-plastic waste are generated every year in India, which need to be collected and disposed before they used to manufacture new products.

3.0 Waste management through Co-processing

As per waste hierarchy, which is the cornerstone of most waste management strategies, prevention and minimization of waste generation is the most preferred option for waste management. Use of recyclable material and other alternate substitute which could be easily fit into the environmental chain is the best option for any waste management in the country.



As per the Basal Convention, variety of wastes including hazardous wastes, can be disposed in an environmentally safe and sound manner through the technology of co-processing in cement kiln.

Co-processing refers to the use of waste materials as alternative fuels or raw material (AFR) to recover energy or resource, which will reduce the use of conventional fuels or raw materials. Co-processing stands above the other disposal methods for waste management like land filling and incineration.

Co-processing is a more environmentally friendly and sustainable method of waste disposal as compared to land filling and incineration because of reduced emissions and no residue after the treatment.

4.0 BFR and its properties

Flame Retardants (FR) is a mixture of synthetic material used as additives for manufacturing several products due to their flame retarding properties which slow down ignition and spread of flames. There are more than 175 different types of flame retardants, which are generally divided into classes that include brominated, chlorinated, phosphorus-containing, nitrogen-containing, and inorganic flame retardants. Bromine, phosphorus, nitrogen and chlorine are commonly used in flame retardants.

These flame retardants have improved public safety by reducing the flammability of everyday items including computers, furnishings and mattresses. BFR is the largest group of retardants used nearly 19.7% of total global retardant consumption. Furthermore, BFR can also be used together with enhancers to increase the effects of these flame retarding properties.

There are different types of BFR based on properties and applications. The main types and its usage are listed below

1. Polybrominated diphenyl ethers (PBDEs) – plastics, textiles, electronic castings, circuitry
2. Hexabromocyclododecane (HBCDD) – thermal insulation in the building industry
3. Tetrabromobisphenol A (TBBPA) and other phenols – printed circuit boards, thermoplastics (mainly in TVs)
4. Polybrominated biphenyls (PBBs) – consumer appliances, textiles, plastic foams
5. Other brominated flame retardants.

Some brominated flame retardants were identified as persistent, bioaccumulative, and toxic to both humans and the environment and were suspected of causing neurobehavioral effects and endocrine disruption (mainly PBDEs PBBs and HBCDD) BFR-treated products, whether in use or waste, ‘leach’ BFRs into the environment and contaminate the air, soil and water.

These contaminants may then enter the food chain where they mainly occur in food of animal origin, such as fish, meat, milk and derived products. Depending on the type of BFR, these substances can be carcinogens, irritants, ecotoxic or even toxic to reproduction.

As a result, these substances have been banned and regulated in various national and international legislations. RoHS as developed in the EU and introduced in India through the e-waste rules (2012) limits the use of all PBDEs and PBBs in new electronic products. The Stockholm convention bans the production application and to most extent the recycling of PBDEs (penta and octa) and HBCDD

and mandate the proper decontamination of waste through full destruction of these chemical compounds.

Bromine properties

Bromine (Br)	**Name was derived from the Ancient Greek βρῶμος "stench", referencing its sharp and disagreeable smell.** Chemical element, noxious liquid and a member of the halogen elements
Odour	pungent odour
Colour	reddish brown
Discovered in year	1826
Discovered by	**Mr** Antoine-Jérôme Balard in France and **Mr**Carl Löwig in Germany
Group	17
Period	4
Block	P
Atomic Weight	79.904
Atomic number	35
Electron configuration	[Ar] 3d104s24p5
Melting point	−7.2°C, 19°F, 266 K
Boiling point	58.8°C, 137.8°F, 332 K
Density (g cm−3)	3.1028
Relative atomic mass	79.904
Key isotopes	79Br
CAS number	7726-95-6
Electron affinity (kJ mol−1)	324.537

Heat of fusion	10.571 kJ/mol
Heat of vaporisation	29.96 kJ/mol

Today, flame retardants are used predominantly in four major areas:

Electronics and Electrical Devices : Television and other electronic device casings, Computers and laptops, including monitors, keyboards and portable digital devices, Telephones and cell phones, Refrigerators, Washers and dryers, Vacuum cleaners, Electronic circuit boards, Electrical and optical wires and cables, Small household appliances, Battery chargers

Building and Construction Materials: Electrical wires and cables, including those behind walls, Insulation materials (e.g., polystyrene and polyurethane insulation foams), Paints and coatings which are applied to a variety of building materials, including steel structures, metal sheets, wood, plaster and concrete Structural and decorative wood products, Roofing components, Composite panels, Decorative fixtures

Furnishings: Natural and synthetic filling materials and textile fibers, Foam upholstery, Carpets, Curtains and fabric blinds

Transportation (Airplanes, Trains, Automobiles): Overhead compartments, Seat covers and fillings Seats, headrests and armrests, Roof liners, Textile carpets, Curtains, Sidewall and ceiling panels, Internal structures, including dashboards and instrument panels, Insulation panels, Electrical and electronic cable coverings, Electrical and electronic equipment, Battery cases and trays, Car bumpers, Stereo components, GPS and other computer systems

BFR as well as the enhancers are especially present in plastics found in electrical and electronic equipment and are therefore found in waste electrical and electronic equipment (WEEE). The main brominated flame retardants found in WEEE plastics are polybrominated diphenyl ethers (PBDE), tribromophenoxyethane (TBPE), polybromobiphenyl (PBB or HexaBB), pentabromo phenyl ethane (EBP), tetrabromobisphenol A (TBBPA) and hexabromocyclododecanes (HBCDD)..

It is therefore important and necessary to dispose the waste contains in an environmentally sound manner and cement kiln co-processing can be explored for the effective management of this hazardous waste.

5.0 Advantages of co-processing in cement kiln

1. Due to the high temperature in cement kiln 1250-1450°C, all types of wastes can be effectively disposed.
2. Residence time of 4-5 sec in cement kilns
3. oxygen rich atmosphere, which aids complete combustions of the waste material and better efficiency then incinerators
4. The thermal stability due to temperature and long residence time, makes complete destruction of the waste material
5. Waste materials in the kiln are in contact with a large flow of alkaline (basic) materials that neutralize potential acid off-gases from combustion. destruction of the waste material
6. No ash left over after co-processing, minerals are trapped in the matrix of the clinker
7. Cement kiln co-processing technology is accepted by Basel convention for disposal of hazardous wastes
8. The cement kiln co-processing technology is accepted by Montreal protocol for disposal of POPs
9. Reduces the overall Greenhouse gas emissions and Conservation of fossil fuel resources.
10. Integrated solutions to waste management.
11. Immobilisation of toxic and heavy metals.

6.0 Guidelines for Co-processing Non – recyclable plastics in Cement kiln:

Co-processing of non-recyclable plastic waste has to be carried out in phased manner. This includes various processes which can support in effective disposal of waste without adverse effect on the environment and stake holders.

The various steps are involved in Co-processing of waste in cement kiln are as follows.

1. Suitability/acceptance of material for co-processing
2. Trial run and monitoring of Waste Co-processing
    a. Process monitoring for co-processing
    b. Quality assurance of the final product
    c. Emission monitoring for co-processing
    d. Parameters to be monitored and documented during trial priod
3. Quantity estimates for BFR plastic co-processing
4. Environmental guidelines in India for waste co-processing

7.0 Suitability/acceptance of waste material for co-processing

Selection of waste streams for co-processing should be done based on scientific analysis of the waste streams. This will have an impact on the emissions from cement kiln and final product produced.

1. A waste should be co-processed in cement kiln with respect to waste management hierarchy.
2. Waste should either have an energy content to use as a fuel or material value to use as a raw material or better and safe technology for destruction of particular waste, which will facilitate towards creating better environment
3. The Clinker or cement quality produced from Co-processing waste should meet the product quality requirement and strength
4. Quality of the waste is key parameter in deciding the suitability of material for co-processing. Physical and chemical properties of the waste has to be tested including heavy metals, mineral composition and other parameters, since it has impacts on environment, product quality and operational stability of cement kiln.
5. The acceptance criteria should be reviewed on a regular basis in accordance with local regulation & updated.

Suitability of material for Co-processing based on quality parameters

If hazardous waste used for material recovery

Parameter	Limit
Volatile organic Hydrocarbon	< 5000 ppm
Total organic Carbon (TOC)	< 1000 ppm
$CaO + SiO_2 + A1_20_3 + Fe_20_3 + SO_3$ (In Ash)	> 80 %
Chloride	< 1.5 %
Sulphur	< 1.5 %
PCB/PCT (ppm)	< 5.0
Heavy Metals (ppm) Hg Cd+Tl+Hg	 < 10 < 100

As+Co+Ni+Se+Te+Sb+Cr+Sn+Pb+V	< 10,000

If hazardous waste used as energy recovery

Parameter	Limit
Ash **-Liquid** **-Solid**	 **< 5%** **< 20%**
Chloride	**< 1.5 %**
Sulphur	**< 1.5 %**
PCB/PCT (ppm)	**< 50**
Heavy Metals (ppm) **Hg** **Cd+Tl+Hg** **As+Co+Ni+Se+Te+Sb+Cr+Sn+Pb+V**	 **< 10** **< 100** **< 25,00**
pH	**4 to 12**
Viscosity (cSt) for Liquid	**< 100**
Flash point (Deg Centigrade) (for Liquid)	**> 60**

8.0 Trial Run and Monitoring of waste Co-processing in Cement kiln:

Trial run is very important in establishing the capability of cement kiln to destroy the waste in an environmentally sound manner without any adverse impacts on the product and environment. Trail runs will bring more confidence on destruction technology and facilitate other units also to take such initiative. Trial run can be planned with necessary arrangements like

1. Co-processing company should have a proper technologies, systems, process and persons for ensuring nil effects on product, environment, health and safety
2. Suitable technologies or methods for processing of waste has to identified (separation, homogenization and size reduction) in order to ensure smooth operation of cement kiln.
3. Emission monitoring equipments should be in place and exhaust gases should be discharged in control manner.
4. State of art testing laboratories and technologies for assuring product quality and strength and supporting process team in smooth operation of the plant
5. The storage of alternative fuels and raw materials should take into account health and safety, firefighting, local conditions and comply with all applicable local regulations
6. Co-processing facility should have a team of trained & skilled people who are competent enough to manage the waste disposal in an environmentally sound manner
7. Co-processing facility should also ensure all monitoring parameters in process and quality are listed down and dedicated teams are working on each of these areas.

Process monitoring can be further classified in to operating condition, process parameters and product quality monitoring. All of them are important aspects to be ensured during waste co-processing in cement kiln.

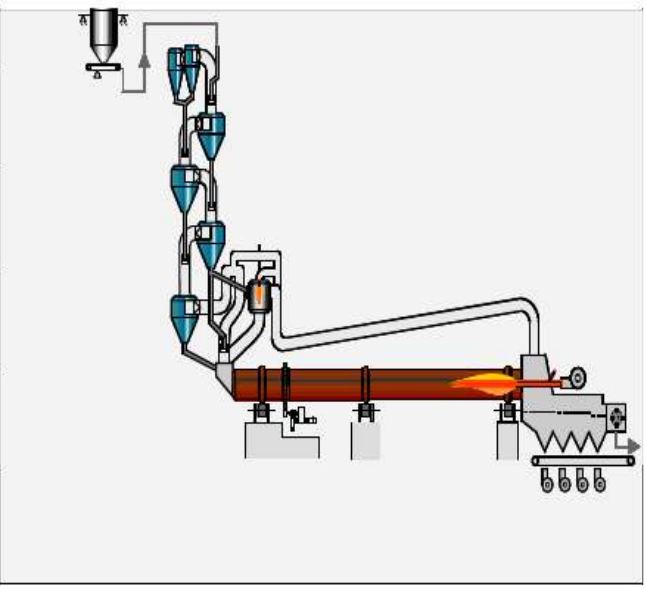
Operating condition of the kiln should be stable before the co-processing of waste. The temperature of the gas resulting from co-processing of waste should be raised to the temperature of at least 1100 °C in unfavorable conditions as per Central Pollution Control Board (CPCB) of India guidelines. The plant should have an automated system for controlling the feed rate of waste involved in co-processing. Whenever the temperature is not maintained in the range of 1100°C, waste should not be co-processed. The plant should be operated by the trained person for the activity and all emission norms should be comply while co-processing.

Cement processing involves different temperature levels at different areas. Preferred feed point is kiln main burner and can also be selected as per the waste processed and its physical, chemical and

toxicological characteristics. Hazardous wastes are generally recommended to burn at the main burner to ensure complete and safe destruction of the waste. Specific installation or technological advancements should be properly used in the plant to control the feed rate and stable operation of the plant without affecting environment.

Temperature and residence time during cement production

Characteristics	Value
Temperature at main burner	>1450°C: material >1800°C: flame temperature.
Residence time at main burner	>12-15 sec > 1200°C >5-6 sec > 1800°C
Temperature at precalciner	> 850°C: material >1000°C: flame temperature
Residence time at precalciner	> 2 - 6 sec > 800°C
Residence time at precalciner	> 2 - 6 sec > 800°C



8.1 Recommended Process monitoring parameters to be monitored during trial run for Co-processing Non-recyclable plastic waste

Process parameters is a tool or indicator which can help us in understanding the effective operation of the manufactuing process. With advancements in technologies most of this parameters can be monitored on contionus basis.

Process parameters can also be interlocked with latest intelligent control systems, ex.,when temperature of gas on the bottom stage increases, fuel can be reduced correspondingly. In this way process parameters help us to operate the plant at optimised condition with reduced energy consumtion.

Listed are important process parameters to be monitored during co-processing for better operation of the plant. Preferred frequency of monitoring each parameter is listed for quick reference and significance of monitoring each of this parameters is also highlighted. This will help in understanding the purpose of monitoring each parameters.

S.no	Parameter	Unit	Preferred Frequency	Purpose / Significance of measurement
1	waste consumption	TPH	Hourly	To monitor and ensure waste consumption, accuracy of feeding system
2	Kiln feed	TPH	Hourly	To control waste feeding within acceptable limits
3	Conventional fuel consumption	TPH	Hourly	To maintain stability of the kiln system, co processing condition, quantity savings achieved
4	Burning Zone temperature	°C	Continuous	To ensure complete destruction of waste and stability of the kiln system
5	Kiln Inlet temperature	°C	Continuous	To prevent back end burning, control circulation of volatile components in feed and waste

6	Bottom stage gas temperature	°C	Continuous	To understand and ensure delayed burning of wastes fed in calciner
7	Pre heater exit temperature	°C	Continuous	To understand the impact of increase / decrease in the process thermal energy consumption
8	Pre calciner top temperature	°C	Continuous	To ensure complete combustion of waste fed in calciner
9	Shell radiation temperature in burning zone	°C	Continuous	Indication of kiln burning zone condition, refractory condition
10	Tertiary air temperature	°C	Continuous	Indication of burning zone condition
11	Clinker temperature in cooler exit	°C	4 hours once	To ensure process stability
12	Kiln inlet Co	Ppm	Continuous	To avoid partial combustion of waste fed in kiln
13	Kiln inlet oxygen	%	Continuous	To ensure complete combustion of waste
14	Kiln inlet NOx level	ppm	Continuous	Indication of burning zone condition, excess air
15	PH outlet oxygen	%	Continuous	To ensure complete combustion of waste fed in calciner
16	PH outlet CO	Ppm	Continuous	To avoid partial combustion of waste fed in calciner
17	PH outlet pressure	mmWC	Continuous	To understand and control the effect of waste in System characteristics (for eg., Build ups in preheater)

18	PH fan inlet pressure	mmWC	Continuous	To understand and control the effect of waste in System characteristics (for eg., Build ups in preheater)
19	Kiln Speed	Rpm	Continuous	Know the effect of waste feed in kiln system
20	Kiln Torque	Amp	Continuous	Indication of kiln stability
21	Pressure drop across cyclone	mmWC	Continuous	Indication of preheater system stability
22	Temperature indicator in cyclones	mmWC	Continuous	Change positive / negative due to waste addition
23	Kiln start/ stops duration	Nos	Based on operation	Observe and record the behavior of kiln system due to waste addition
24	Heat balance for calculating sp. Thermal energy	Kcal/kg of clinker	Once during trial	To understand and estimate the economic impact of waste addition
25	Sp. Electrical energy of overall system and major equipments	kWh/Mt	Day average	To understand and estimate the economic impact of waste addition
26	PH fan speed	RPM	Continuous	Indication of preheater system stability

8.2 Recommended Quality monitoring parameters for Co-processing of Non-recyclable plastic waste

Quality assurance is an vital for any product or manufacturing process to sustain. The quality of the final product in this case cement, produced from Alternate fuel should meet the physical and chemical standards of cement produced with conventional fuel.

Quality parameters will also help us in deciding the quanitiy of AFR utilisation and its possible effects on the environment and product. The raw material quality has to be fine tuned based on the Alternate fuel parameters to match the desired product quality.

Qulaity of the clinker will also have impact on the grinding power and productibvity of the equipment. Quality plays a huge role in usability of cement for different purposes and special applications. Quality assurance systems must be developed to control the composition of all inputs to the manufacturing process and optimising of outputs from the process.

S.no	Parameter	Unit	Frequency	Purpose / Significance of measurement
1	Clinker analysis	%	Once in two hours	XRF / XRD , to understand fixing of heavy metals and other components in clinker, circulation behaviour
2	Loss on Ignition, klin feed	%	hourly	Understand varation in kiln feed quality
3	Liter weight, clinker	g/l	hourly	Indicator of kiln stability
4	Free lime in clinker	%	hourly	Indication of burning zone condition
5	Calcination	%	hourly	Indication of calciner stability
6	Clinker Leachability study		Once in trial	To know the fixing of heavy metals
7	Kiln Feed Analysis	%	hourly	To understand kiln feed chemistry

8	Total Organic Carbon (TOC)		hourly	To know the contribution from kiln feed
9	Calorific value of AF	Kcal/kg	hourly	Control and maintain kiln stability and waste feed rate
10	Ultimate analysis of AF		Once in every trial	Understand constituents of wastes
11	Proximate analysis AF		Once in a shift	Control and maintain kiln stability and waste feed rate
12	Characteristics study of waste for Chlorine, Fluorine, Mercury, Metals, Copper, Nickel and other toxic substance Total Petroleum Hydrocarbon Organo - chlorine compounds, VOCs and Semi-VOCs, Poly Chloro Biphenyls (PCBs) and Poly Chloro Phenols (PCPs)		Once in a shift	Control and maintain kiln stability and waste feed rate
13	Halogens(F+I), TOC Bromine has to be measured individually		hourly	Control and maintain kiln stability and waste feed rate
14	Physical testing of cement – Compressive strength 3 days 7 days 28 days	Mpa	Once in a shift	Record variation in clinker / cement quality
15	Blaines, cement	m^2/kg	hourly	

16	Setting time Initial setting Final setting	min	Once in a shift	Record variation in clinker / cement quality
17	Soundness ➢ Le – Chat ➢ Autoclave	mm %	Once in a shifty	
18	Kiln feed raw meal residue	mic	Hourly	Needed to maintain kiln stability
19	Conventional fuel Fineness/residue	mic	hourly	Needed to ensure complete combution
20	Material size/fineness of AF		hourly	Needed to ensure complete combution

8.3 Emission Monitoring for Co-processing waste in Cement kiln:

Emissions from cement industry is of paramount importance since it is affecting the environments and stake holders associated with cement industry. Cement production process is the decarbonisation of limestone, which results in the emission of large quantities of carbon dioxide and Indian Cement Industry one of the most efficient in the world produces 137 $MtCO_2$ in 2010, approximately 7% of the India's total man made emissions.

Emissions from cement industry is of various range of gases. Emission standards and guidelines (http://www.cpcb.nic.in/Guidelines_Non_Recyclable.pdf) were notified by Ministry of Environment Forest and Climate Change (MoEFCC) and CPCB respectively. Cement plants co-processing waste should set up a continuous emission monitoring system and monitor the important parameters like NO_X, PM, SO_2 and stack monitoring of heavy metals, dioxins, furans and other additional parameters required, based on quality of waste co-processed.

Emission monitoring for waste co-processing should be carried out in holistic manner. Analysis should be carried out in 3 phases of the co-processing trial. Emission before co-processing, during co-processing and after co-processing.

Time period	Emission monitoring
1 day	Before waste co-processing, plant running with normal conventional fuel
During co-processing period	Emission monitoring at fixed rate of waste material fed to kiln
1 day	After waste Co-processing, plant running with normal conventional fuel

S.No	Parameters	Concentration not to exceed, in mg/Nm^3	Frequency
1	Particulate Matter (PM) or dust	30	4 samples / day
2	SO_2	100,700 and 100 based on pyrite Sulphur in limestone is less than 0.25%, 0.25-0.5% and more than 0.5% respectively.	4 samples / day

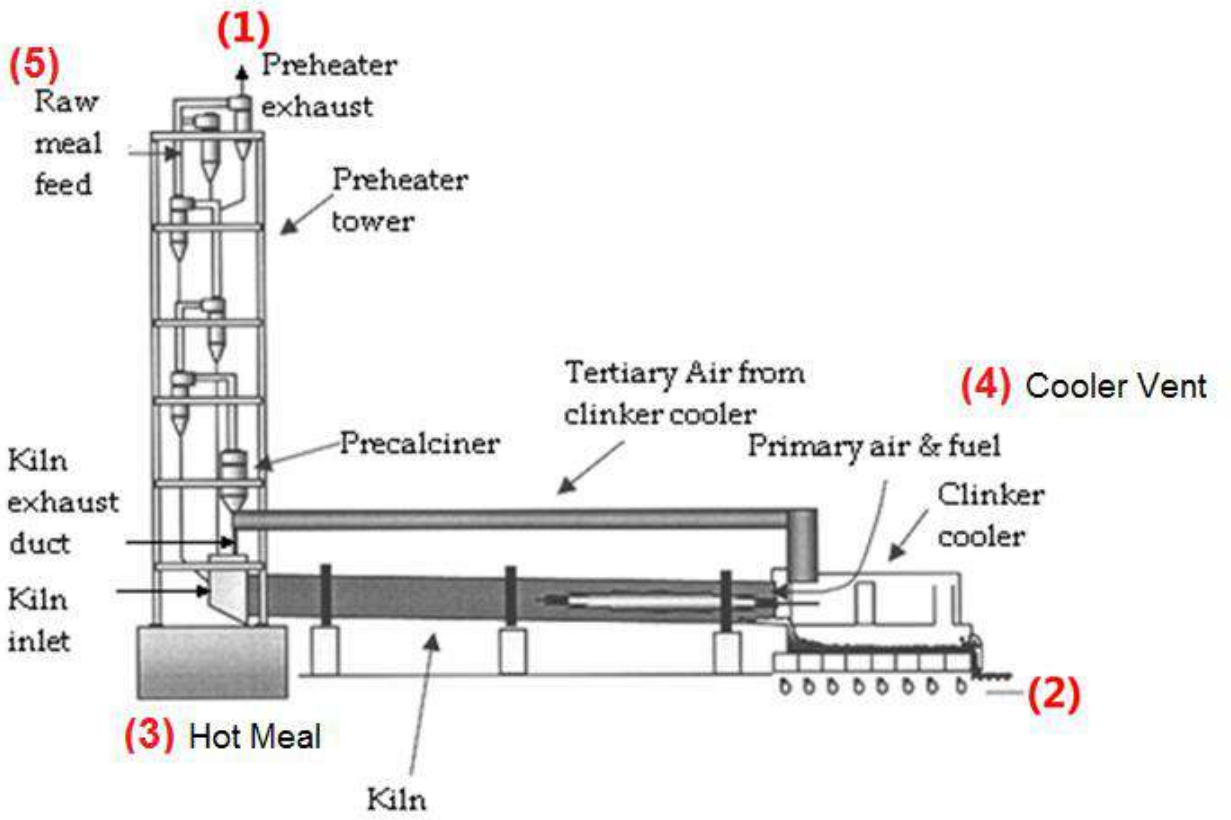
3	NOx	600, 800, 1000 based on ILC and SLC technology	4 samples / day
4	HCl	10 mg/Nm^3	2 samples / day
5	Sb+As+Pb+Co+Cr+Cu+ Mn+Ni+V and their compounds	0.5 mg/Nm^3	1 sample / day
6	Total Organic carbon	10 mg/Nm^3	1 sample /day
7	HF	1 mg/Nm^3	4 samples / day
8	Hg and its components	0.05 mg/Nm^3	2 Samples/day
9	Dioxins and Furans	0.1 ngTEQ/Nm^3	1 sample / day
10	Opacity		Continuous
11	Particulate matter	0.125 kg/ton ofcliner	
12	PAH and VOC		2 samples/day
13	Cyanide		1 sample/day

Ambient air quality has to be measure at 3 locations (1 in upwind and 2 in down wind direction) & carried out during the whole trial period. National air quality standards attached as annexure 1.

Hydrocarbons: 10 ppm over an hourly rolling average dry basis and reported as propane.

Opacity: While operating properly at rated capacity, the system shall have a visible emission rate of less than or equal to 10% except for condensed water vapor, from the discharge stack to atmosphere (one hour rolling average).

In addition to this specific to burning of BFR plastics in the brick kiln following emissions has to be monitored:



Sampling to be performed:

- **(1)** Air Emission
- **(2)** Clinker
- **(3)** Hot Meal – recycled back to Kiln inlet
- **(4)** Clinker Cooler Dust Emission from Stack
- **(5)** Raw Meal

Substances Monitoring in Exhaust emissions (1,4)

Substance/Group	Reason	Sampling	Measurement Method	Details
PBDEs	Main contaminant	Stockholm Convention sampling method	chromatographic techniques coupled with a mass spectrometer / Electron Capture Detector (ECD)	

PXDD/Fs	Potential hazardous product formed	Stockholm Convention sampling method	chromatographic techniques coupled with a mass spectrometer	
HBr / Br_2	Emissions could be	International Standard IEC 62321 Ed.1	gas chromatography	
Brominated Volatile organic compounds (Br-VOCs, Methanobromide)	Br-VOCs are potent ozone depleting substances			
Sb (Antimony)	Br-plastics contain significant amounts of Antimony	Stockholm Convention sampling method	Mass Spectroscopy	

Substances Monitoring in Clinker & Hot meal (2,3)

Substance/Group	**Reason**	**Sampling**	**Measurement Method**	**Details**
PBDEs	Main contaminant	Stockholm Convention sampling method	chromatographic techniques coupled with a mass spectrometer / Electron Capture Detector (ECD)	
PXDD/Fs	Potential hazardous product formed	Stockholm Convention sampling method	chromatographic techniques coupled with a mass spectrometer	

Total Br (3)	Mass Balance of Br	International Standard IEC 62321 Ed.1	chromatographic techniques coupled with a mass spectrometer	
Sb (Antimony)	Antimony may be beneficial or may need careful management to have consistent cement quality	Stockholm Convention sampling method	Mass Spectroscopy	

Substances Monitoring in Raw Feed/Meal (5)

Substance/Group	Reason	Sampling	Measurement Method	Details
Total Br (3)	Mass Balance of Br	International Standard IEC 62321 Ed.1	chromatographic techniques coupled with a mass spectrometer	

9.0 Parameters to be documented during trial period

1. Physical and chemical of Hazardous waste utilized for co-processing
2. Output of all equipments in Kiln section during co-processing
3. Detailed write up on process, system, facilities and technologies in the co-processing unit
4. Screen shots of all equipments in the co-processing unit during the trial
5. Thermal energy and electrical energy consumption
6. Physical and chemical testing results of clinker manufactured
7. Physical and chemical testing of cement produce from clinker manufactured with waste material
8. Physical and chemical analysis of raw material

9. Records on process parameters monitored during the trial
10. Records of Stack emissions monitoring
11. Records of Ambient air quality monitoring
12. Write up on storage, handling and feeding of waste in the process
13. Write up and records on safety, environment and product quality
14. Kiln stoppages with time duration, frequency and reasons
15. Problems faced during the trial of waste co-processing
16. Photographs of the trial run
17. Daily log sheets from Control room, quality assurance and environment department
18. Documents and records on Safety procedures followed during different phases of co-processing
19. Quantity of waste consumed, cement produced and reduction in conventional fuel

10 Quantity estimates for plastic waste Co-processing in Cement kilns

Detailed analysis and review has been carried out to develop this estimations on waste quantity required for cement kiln co-processing. The estimates were arrived based on 2 different set of conditions.

1. Based on kiln output
2. Based on Bromine level in plastic waste

Few important elements has to be explained and understood before estimating the quantity of waste for co-processing. In cement manufacturing process (Annexure 2) Pyro processing section or in particular cement kiln is the area where co-processing of waste takes place. Understanding the behavior of compounds inside the kiln and preheater system is of vital importance for co-processing waste in cement kiln.

Circulation Phenomenon is Kiln system

Sulphur, potassium, sodium and chlorine are elements that circulate in the cement kiln system. The intensity of the cycles vary between different systems and there are also considerable

variations within one single kiln system, depending on the operating conditions. High concentrations of this elements will cause build up formation in kiln inlet and preheaters, which will cause restrictions or blockages and interrupt the operation of the plant.

Based on volatility circulating elements evaporate at high temperature zones and condense in low temperature zones and incoming raw meal with the support moving gases. This elements return to high temperature zone along with raw meal and reevaporates, this cycle repeats and finally reach equilibrium.

If the concentrations are too high because of high input or volatility of the element installation of kiln bypass system which is like an external cycle for circulation of elements.

	K		Na		Ca	
Compound	Melting point	Boiling point	Melting point	Boiling point	Melting point	Boiling point
Chlorides	768	1411	801	1440	772	1600
Bromides	730	1380	755	1390	760	1810

Circulation factor

The circulation factor Ck of a given component is the ratio of the flow rate of this component into the kiln in precalcined meal and the total inflow of the component into the kiln (which is the sum of the inflows and fuel)

Residual factor

The residual factor Rk of a given component k is the ratio of the flow rate of this component in the clinker to the total inflow of the component into the kiln

Valve factor

The cyclone valve factor V of a given component k can be defined as the ratio of the gas/dust flow of this component out of cyclone stages and out of the kiln

Assumption made

Few assumptions were made in the estimates and the same is listed below

S.no	Parameter	Unit	Value
1	Concentration of Br in the plastic	%	5
2	Maximum limit for Br in the kiln feed	%	0.015
3	Trial hours needed with plastic	hrs	72
4	Margin for handling loss, disturbance, sampling etc	%	20

The table below shows the allowable limit of volatile components for kiln systems without bypass on LOI free basis

Parameters	Normal Limit
Technology	ILC,SLC & SLC-I
Chlorine as CL	0.023%
Sulphur as S-Total	1.5%
Technology	Sp & ILC – E
Chlorine as CL	0.029%
Sulphur as S-Total	1.5%

Parameter	Value
From Raw meal	0
From Fuel	0.0138
From Raw meal & Fuel	**0.0138**
Hot meal Br	3.000
Hot meal LOI	2
Hot meal Br Loss free basis	3.061
Clinker Br	0.050
Evaporation factor	0.984
Circulation factor	221.088
Residual Component	3.61
Valve	-0.012

Plastic waste estimates for Co-processing at different Kiln outputs (TPD)

S no	Parameter	Unit											
1	Concentration of Br in the plastic	%	5	5	5	5	5	5	5	5	5	5	5
2	Maximum limit for Br in the kiln feed	%	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
3	Trial hours needed with plastic	hrs	72	72	72	72	72	72	72	72	72	72	72
4	Margin for handling loss, disturbance, sampling etc	%	20	20	20	20	20	20	20	20	20	20	20
5	**Kiln output**	**TPD**	**1000**	**2000**	**3000**	**3300**	**4000**	**5000**	**6000**	**7000**	**8000**	**9000**	**10000**
6	Kiln feed raw meal Loss On Ignition	%	35	35	35	35	35	35	35	35	35	35	35
7	Total coal (Fuel) to clinker factor	ratio	0.138	0.138	0.138	0.138	0.138	0.138	0.138	0.138	0.138	0.138	0.138
8	Weighted average ash content in total Fuel	%	10	10	10	10	10	10	10	10	10	10	10
9	Raw meal to clinker factor	ratio	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52
10	Raw meal to clinker factor default		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
11	Kiln By pass gas quantity	Nm^3/ kg clinker	0	0	0	0	0	0	0	0	0	0	0
12	Specific heat consumption of the Kiln	kcal / kg clinker	760	760	760	760	760	760	760	760	760	760	760

13	Net calorific value of total fuel (Wt Average)	kcal / kg	5500	5500	5500	5500	5500	5500	5500	5500	5500	5500	5500
14	Top cyclone efficiency	%	90	90	90	90	90	90	90	90	90	90	90
15	NCV of Plastic feed	kcal / kg	8000	8000	8000	8000	8000	8000	8000	8000	8000	8000	8000
16	Br input from fuel on LOI free basis		0.023	0.023	0.023	0.023	0.023	0.023	0.023	0.023	0.023	0.023	0.023
17	Kiln feed quantity - Raw meal	TPH	63	126	190	209	253	316	379	443	506	569	632
18	Amount of Bromine allowed in kiln feed	TPH	0.0095	0.0190	0.0284	0.0313	0.0379	0.0474	0.0569	0.0664	0.0759	0.0853	0.0948
19	**Plastic feed rate**	**TPH**	**0.19**	**0.38**	**0.57**	**0.63**	**0.76**	**0.95**	**1.14**	**1.33**	**1.52**	**1.71**	**1.90**
20	**Plastic feed rate**	**MT needed per trial**	**16**	**33**	**49**	**54**	**66**	**82**	**98**	**115**	**131**	**147**	**164**
21	Total Fuel feed rate	TPH	5.8	11.5	17.3	19.0	23.0	28.8	34.5	40.3	46.1	51.8	57.6
22	Plastic feed rate as % of Fuel	%	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
23	Plastic feed rate as % TSR	%	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8

Plastic waste estimates for Co-processing at different Br concentrations

S no	Parameter	Unit										
1	**Concentration of Br in the plastic**	**%**	**0.5**	**1**	**1.5**	**2**	**2.5**	**3**	**3.5**	**4**	**4.5**	**5**
2	Maximum limit for Br in the kiln feed	%	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
3	Trial hours needed with plastic	hrs	72	72	72	72	72	72	72	72	72	72
4	Margin for handling loss, disturbance, sampling etc	%	20	20	20	20	20	20	20	20	20	20
5	Kiln output	TPD	3300	3300	3300	3300	3300	3300	3300	3300	3300	3300
6	Kiln feed raw meal Loss On Ignition	%	35	35	35	35	35	35	35	35	35	35
7	Total coal (Fuel) to clinker factor	ratio	0.138	0.138	0.138	0.138	0.138	0.138	0.138	0.138	0.138	0.138
8	Weighted average ash content in total Fuel	%	10	10	10	10	10	10	10	10	10	10
9	Raw meal to clinker factor	ratio	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52
10	Raw meal to clinker factor default		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
11	Kiln By pass gas quantity	Nm^3/ kg clinker	0	0	0	0	0	0	0	0	0	0
12	Specific heat consumption of the Kiln	kcal / kg clinker	760	760	760	760	760	760	760	760	760	760
13	Net calorific value of total fuel (Wt Average)	kcal / kg	5500	5500	5500	5500	5500	5500	5500	5500	5500	5500
14	Top cyclone efficiency	%	90	90	90	90	90	90	90	90	90	90
15	NCV of Plastic feed	kcal / kg	8000	8000	8000	8000	8000	8000	8000	8000	8000	8000

16	Br input from fuel on LOI free basis		0.023	0.023	0.023	0.023	0.023	0.023	0.023	0.023	0.023	0.023
17	Kiln feed quantity - Raw meal	TPH	209	209	209	209	209	209	209	209	209	209
18	Amount of Bromine allowed in kiln feed	TPH	0.0313	0.0313	0.0313	0.0313	0.0313	0.0313	0.0313	0.0313	0.0313	0.0313
19	**Plastic feed rate**	**TPH**	**6.26**	**3.13**	**2.09**	**1.56**	**1.25**	**1.04**	**0.89**	**0.78**	**0.70**	**0.63**
20	**Plastic feed rate**	**MT needed per trial**	**541**	**270**	**180**	**135**	**108**	**90**	**77**	**68**	**60**	**54**
21	Total Fuel feed rate	TPH	19.0	19.0	19.0	19.0	19.0	19.0	19.0	19.0	19.0	19.0
22	Plastic feed rate as % of Fuel	%	32.9	16.5	11.0	8.2	6.6	5.5	4.7	4.1	3.7	3.3
23	Plastic feed rate as % TSR	%	47.9	24.0	16.0	12.0	9.6	8.0	6.8	6.0	5.3	4.8

11.0 Way forward

Waste plastic co-processing in cement kiln will be of tremendous shift change in waste management scenario in the country. The Indian cement industry one of the leaders in energy efficiency in the world is also moving towards Alternate fuel utilization. This co-processing waste will solve the dual problems of effective waste management as well as reduction in overall carbon emissions.

This document will provide a first-hand information to cement plants on waste co-processing and parameters to be monitored in the areas of process, quality and environment for effective disposal of waste without affecting the product. We will also update the document further on the basis of co-processing trial and welcome all your suggestion/ feedback/comments on the same to enhance the document.

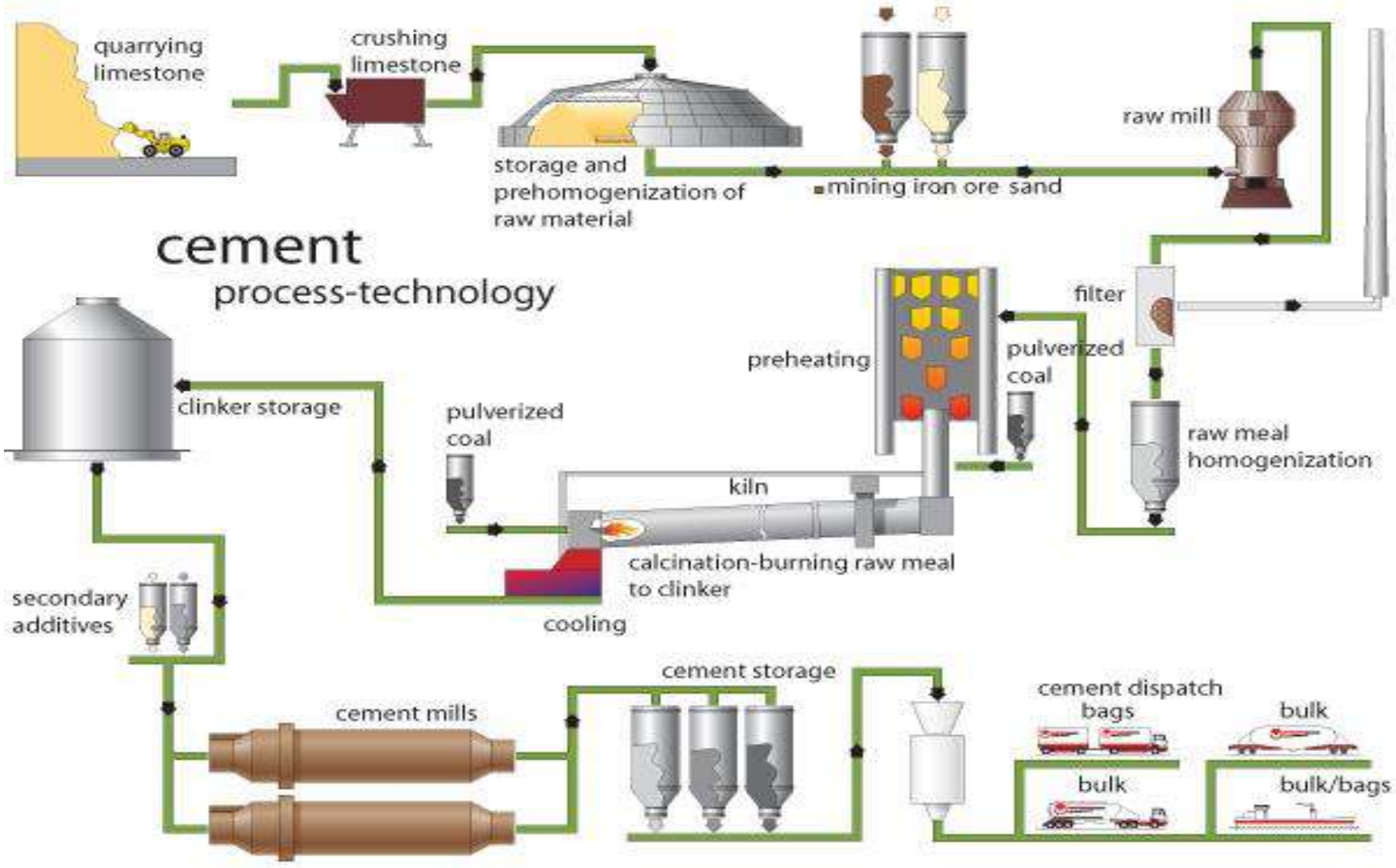
Annexures

Annexure 1 - National Ambient Air quality Standards

Pollutant	Time Weighted Average	Concentration in Ambient Air	
		Industrial, Residential, Rural and Other Areas	Ecologically Sensitive Area (notified by Central Government)
Sulphur Dioxide (SO_2), µg/m^3	Annual* 24 hours**	50 80	20 80
Nitrogen Dioxide (NO_2), µg/m^3	Annual* 24 hours**	40 80	30 80
Particulate Matter (size less than 10 µm) or PM_{10} µg/m^3	Annual* 24 hours**	60 100	60 100
Particulate Matter (size less than 2.5 µm) or $PM_{2.5}$µg/m^3	Annual* 24 hours**	40 60	40 60
Ozone (O_3) µg/m^3	8 hours* 1 hour**	100 180	100 180
Lead (Pb) µg/m^3	Annual* 24 hours**	0.50 1.0	0.50 1.0
Carbon Monoxide (CO) mg/m^3	8 hours* 1 hour**	02 04	02 04
Ammonia (NH_3) µg/m^3	Annual* 24 hours**	100 400	100 400
Benzene (C_6H_6) µg/m^3	Annual*	5	5
Benzo(a)Pyrene (BaP)-particulate phase only, ng/m^3	Annual*	1	1
Arsenic(As), ng/m^3	Annual*	6	60
Nickel (Ni), ng/m^3	Annual*	20	20

* Annual arithmetic mean of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at uniform intervals.
** 24 hourly or 8 hourly or 1 hourly monitored values, as applicable, shall be complied with 98% of the time, they may exceed the limits but not on two consecutive days of monitoring.
Source: National Ambient Air Quality Standards, Central Pollution Control Board Notification in the Gazette of India, Extraordinary, New Delhi, 18th November, 2009

Annexure 2 – Cement Manufacturing process



References

1. http://www.wbcsdcement.org/ - Guidelines for Emissions Monitoring and Reporting in the Cement Industry
2. Basel Convention technical guidelines ion the environmentally sound Co-processing of hazardous waste in cement kiln
3. Stockholm Convention
4. New Hazardous waste Management Rules 2016
5. Plastic waste management rules 2016 (http://pib.nic.in/newsite/PrintRelease.aspx?relid=138144)
6. Solid waste management Rules 2016 http://envfor.nic.in/sites/default/files/Waste%20Management%20Rules,%202016.pdf
7. Guidelines on Co-processing in Cement Industry
8. CSI Guidelines for Co-Processing Fuels and Raw Materials in Cement Manufacturing
9. Guidelines for disposal of thermoset plastic waste Environment (Protection) Third amendment rules 2016
10. Draft Guidelines for disposal of Non –recyclable plastic waste
11. https://www.nachi.org/brominated-fire-retardant-dangers.htm, https://www.efsa.europa.eu/en/topics/topic/bfr
12. https://en.wikipedia.org/wiki/Brominated_flame_retardant, http://www.ebfrip.org/
13. https://www.ncbi.nlm.nih.gov/pubmed/25933174
14. http://www.cementplantsmanufacturers.com/images/cement-plant-process-large.jpg
15. Holderbank notes

Environmental guidelines in India for waste co-processing

Ministry of Environment, Forest and climate change, Government of India has released various rules and notification on cement kiln co-processing.

1. Hazardous waste Management Rules 2016
2. Plastic waste management rules 2016
3. Guidelines on Co-processing in Cement Industry
4. Environment (Protection) Third amendment rules 2016
5. Draft Guidelines for disposal of Non –recyclable plastic waste