

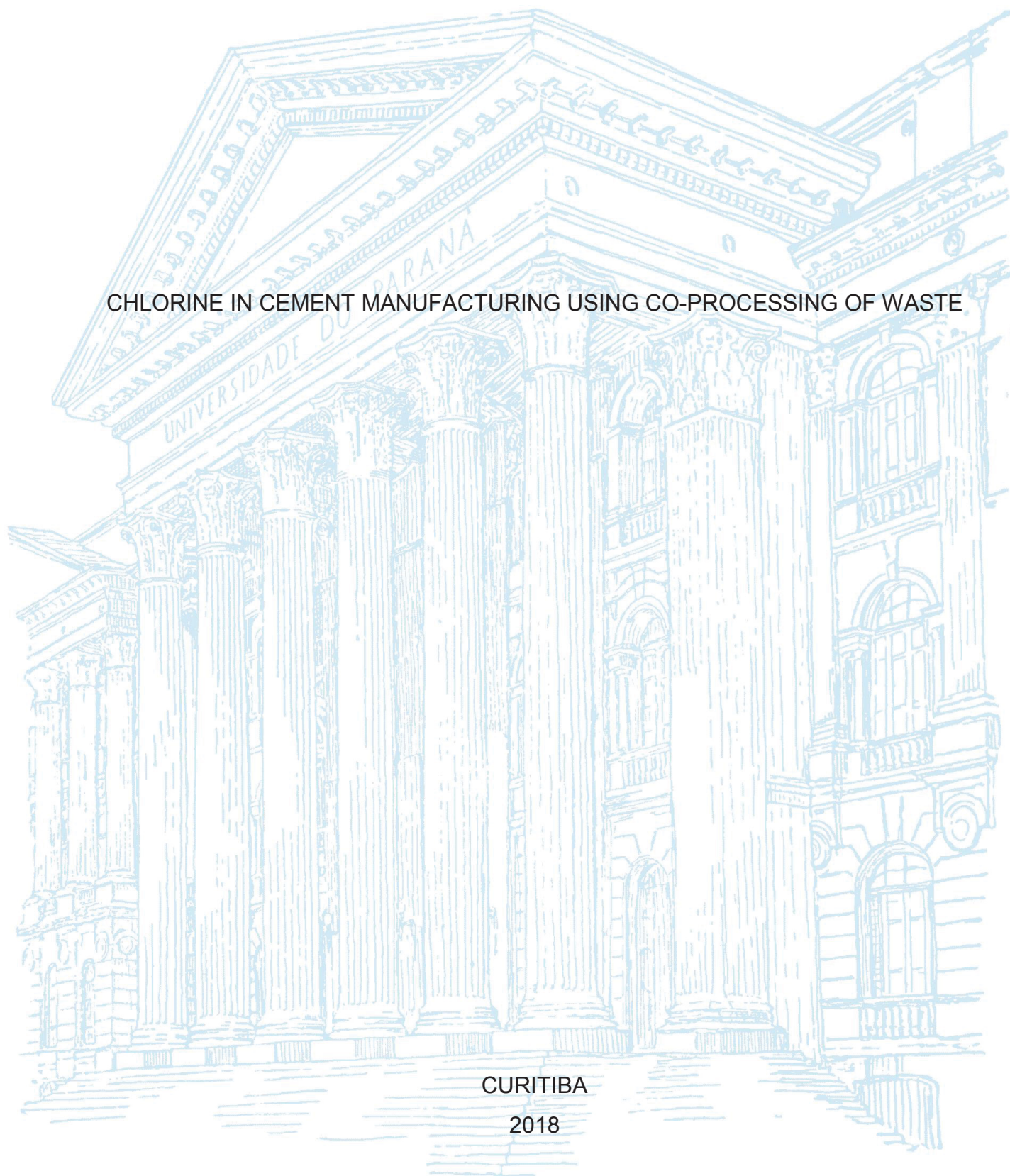
UNIVERSIDADE FEDERAL DO PARANÁ

MAROUANE MERIZAK

CHLORINE IN CEMENT MANUFACTURING USING CO-PROCESSING OF WASTE

CURITIBA

2018



MAROUANE MERIZAK

CHLORINE IN CEMENT MANUFACTURING USING CO-PROCESSING OF WASTE

Dissertação apresentada ao Mestrado em Meio Ambiente Urbano e Industrial na Universidade Federal do Paraná em parceria com a Universidade de Stuttgart e Sistema Nacional de Aprendizagem Industrial no Paraná, como requisito parcial para a obtenção do título de Mestre em Meio Ambiente Urbano e Industrial.

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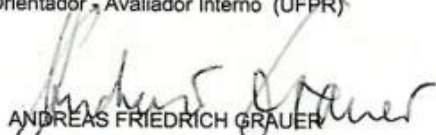
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RESUMO

O cloro é um componente volátil adicional contido nas diferentes entradas do processo de queima do clínquer, nomeadamente a farinha crua, o combustível e o Combustível Derivado de Resíduos (CDR). Com o crescente uso de coprocessamento em fornos de cimento no Brasil, o controle das entradas e saídas de cloro tornou-se vital no processo de fabricação de cimento. O cloro é responsável principalmente por problemas operacionais durante a etapa de clínquerização. Ciclos internos de alto enriquecimento de cloro na ausência de um by-pass podem levar a frequentes paradas do forno de cimento causando grandes danos à fábrica de cimento. A concentração máxima permitida de cloro no produto final e nas emissões também são fatores limitantes que as fábricas de cimento são obrigadas a cumprir. Esta tese tem por objetivo realizar uma análise crítica da atual legislação brasileira relacionada ao cloro no coprocessamento em fornos de cimento, tanto em nível federal quanto estadual. A discussão abrange tanto os padrões de emissão quanto a limitação do teor de cloro que entra no CDR. Este último é importante porque é um fator com a capacidade de restringir a taxa de substituição do CDR levando ao maior consumo de combustíveis fósseis. A análise é acompanhada de uma comparação das normas brasileiras com outros padrões europeus e americanos. Ao final, utilizando os dados disponíveis em um forno de uma indústria de cimento no Paraná, foi realizado e analisado um balanço de massa de cloro com o cálculo da eficiência de remoção.

Palavras-chave: Cloro. CDR. Forno de cimento. Clínquer. Coprocessamento.

ABSTRACT

Chlorine is a minor additional volatile compound contained in the different inputs of the clinker burning process, namely the raw meal, the fuel and the Solid Derived Fuel (SRF). With the increasing use of co-processing in cement kilns in Brazil, controlling chlorine inputs and outputs became vital in the process of cement manufacturing. Chlorine is responsible mainly for cement kiln technical problems during the clinkerization step. High enrichment internal cycles in the absence of a by-pass installation might lead to frequent stops of the cement kiln causing great damage to the cement plant. In addition, the maximum allowed concentration of chlorine in the final clinker product and emission standards are limiting factors with which cement plants are obliged to comply. This thesis aims to carry out a critical analysis of the current Brazilian legislation related to chlorine in co-processing in cement kilns both on the federal and state level. The discussion covers both emission standards and the limitation of chlorine content entering in the SRF. This latter is important because it is a factor with the ability to restrict the SRF thermal substitution rate leading to the use of more fossil fuels. The analysis is accompanied with a comparison of Brazilian standards with other European and American standards. At the end, using the available data on a kiln from a cement industry in Paraná, a mass balance of chlorine with the calculation of the removal efficiency was elaborated and analyzed.

Keywords: Chlorine. SRF. Cement kiln. Clinker. Co-processing.

ZUSAMMENFASSUNG

Chlor ist eine geringfügige zusätzliche flüchtige Komponente, die in den verschiedenen Einträgen des Klinkerbrennprozesses enthalten ist, nämlich das Rohmehl, die Brennstoffe und die Ersatzbrennstoffe. Mit der zunehmenden Verwendung der Ersatzbrennstoffen in Zementdrehöfen in Brasilien wurde die Kontrolle der eingetragenen Chlormengen bei der Zementherstellung unerlässlich. Im System Drehofen/Wärmetauscher ist Chlor hauptsächlich für technische Probleme verantwortlich. Hohe Kreisläufe in Abwesenheit einer Bypass-Installation können zu häufigen Stopps und Reinigungsstillständen des Zementofens führen, was große Schäden an der Zementanlage verursacht. Darüber hinaus sind die maximal erlaubte Konzentration von Chlor im Endprodukt und die Emissionsgrenzwerte limitierende Faktoren, denen die Zementwerke nachkommen müssen. Diese Arbeit zielt darauf ab, eine kritische Analyse der aktuellen brasilianischen Gesetzgebung in Bezug auf Chlor bei der Verwertung von Ersatzbrennstoffen in Zementöfen sowohl auf Bundes- als auch auf Landesebene durchzuführen. Die Diskussion behandelt sowohl Emissionsstandards als auch die Begrenzung des Chlorgehalts in der Ersatzbrennstoffen. Letzteres ist wichtig, weil es ein Faktor ist, der die Ersatzbrennstoffesubstitutionsrate einschränken kann, was zur Verwendung von mehr fossilen Brennstoffen führt. Die Analyse wird von einem Vergleich der brasilianischen Standards mit anderen europäischen und amerikanischen Standards begleitet. Am Ende wurde unter Verwendung der verfügbaren Daten eines Ofens aus einer Zementindustrie in Paraná eine Massenbilanz von Chlor mit der Berechnung der Reduktionseffizienz erarbeitet und analysiert.

Schlüsselwörter: Chlor. Ersatzbrennstoffe. Zementdrehofen. Klinker.

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LIST OF ABBREVIATIONS

17th BImSchV:	Siebzehnte Verordnung zur Durchführung des BundesImmissions-schutzgesetzes (Seventeenth Ordinance for the Implementation of the Federal Pollution Control Act in Germany)
ABCP:	Associação Brasileira de Cimento Portland (The Brazilian Association of Portland Cement)
ABNT:	Associação Brasileira de Normas Técnicas (The Brazilian Association of Technical Standards)
BAT:	Best Available Techniques
CEN:	Comité Européen de Normalisation (European Committee of Standardization)
CONAMA:	Conselho Nacional do Meio Ambiente (National Environmental Council)
CONSEMA:	Conselho Estadual do Meio Ambiente de Rio Grande do Sul (Environmental State Council of Rio Grande do Sul)
COPAM:	Conselho Estadual de Política Ambiental de Minas Gerais (State Council of Environmental Policy in Minas Gerais)
EPA:	Environmental Protection Agency
EIPPCB:	European Integrated Pollution Prevention and Control Bureau
IAP:	Instituto Ambiental do Paraná (Environmental Institute of Paraná)
MSW:	Municipal Solid Waste
NESHAP:	National Emission Standards for Hazardous Air Pollutants from the Portland Cement Manufacturing
PCDD/F:	Polychlorinated Dibenzo-para-dioxins / Dibenzofurans
PNRS:	Política Nacional de Resíduos Sólidos (National Policy of Solid Residues)
SEMA:	Secretaria do Estado de Meio Ambiente e Recursos Hídricos (Secretary of Environment and Water Resources in Paraná)
SISNAMA:	Sistema Nacional do Meio Ambiente (National Environmental System)
SRF:	Solid Recovered Fuel
TEF:	Toxicity Equivalent Factor

TEQ: Toxicity Equivalency

TS: Technical Specification

WHO: World Health Organization

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1 INTRODUCTION

The correct destination of residues represents a big challenge for sustainable development in modern societies. Demographic growth and constant development of industries require definitive solutions to ensure proper waste disposal. In Brazil, waste management public services are struggling to accompany the rapid urbanization and population growth. Thousands of tons of residues are still improperly sent to uncontrolled open-air landfills, despite the prohibition expressed in the Art. 47 of the Federal Law N° 12.305/2010 (BRASIL, 2010a).

Since decades, co-processing of waste in cement kilns has shown a great sustainability as an energy and material recovery process. In 2015, there have been already 57 cement plants with rotary kilns to produce clinker in Brazil. Already 38 of these plants had environmental licenses to co-process waste and the quantity of co-processed residues attained 1.07 million tons. Between 2000 and 2015, destruction of residues in cement rotary kilns increased with almost 500 % (ABCP, 2016).

During cement manufacturing process, raw materials and fuels have to meet characteristics and show chemical elements and components that are necessary for the clinker burning process, as these may affect the production process and clinker quality. Volatile compounds such as chlorine and sulphur are minor additional constituents contained in the different inputs of the clinker burning process. Their behavior during combustion can cause a decrease in kiln production and eventual fatal impacts on the kiln-preheater system (SCHÖFFMANN, 2015).

In addition to possible kiln operational problems, combustion of chlorine also generates harmful emissions that must be controlled and monitored. To control these hazardous compounds such as dioxins and hydrogen chloride, environmental authorities established emission standards and in some cases chlorine content limitations on co-processed waste.

The aim of this research is to determine the influence of chlorine during cement manufacturing process concerning both technical and environmental aspects. The second objective is to analyze the Brazilian co-processing legislation concerning HCl and PCDD/F emissions standards and chlorine content limitations compared to other countries in the world. At the end, a chlorine mass balance inside a cement kiln located in Paraná was elaborated and analyzed.

1.1 GENERAL OBJECTIVE

To study chlorine in the process of cement fabrication using co-processing of waste.

1.2 SPECIFIC OBJECTIVES

- To determine the influence of chlorine in the process of cement production.
- To analyze emission standards related to chlorine in co-processing.
- To analyze permitted chlorine content in solid recovered fuel for co-processing.
- To elaborate a mass balance of chlorine inside a cement kiln in Paraná.

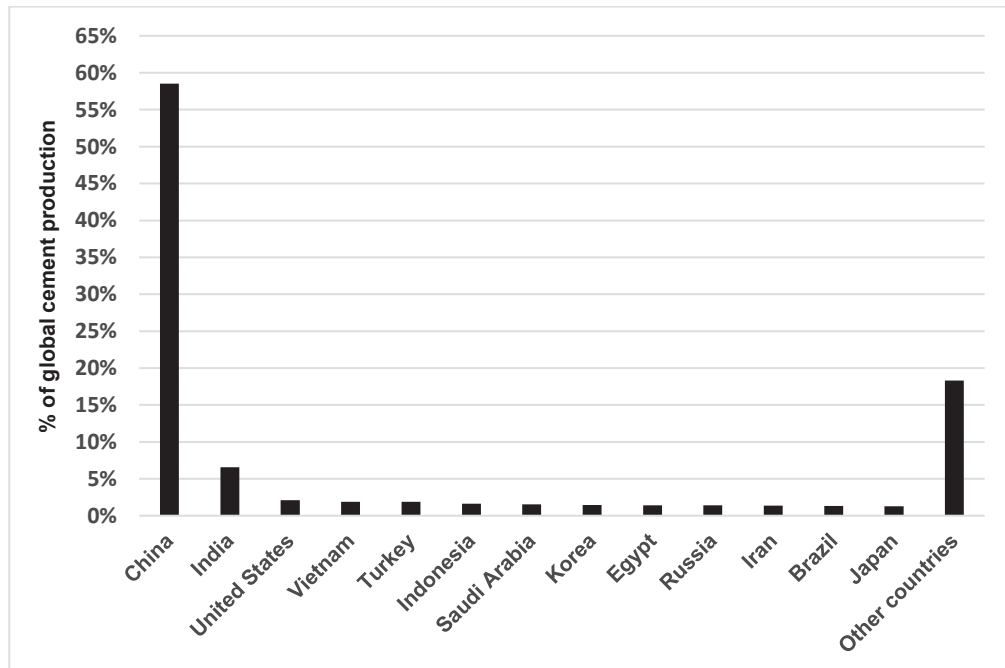
2 LITERATURE REVIEW

2.1 CO-PROCESSING IN CEMENT INDUSTRY

2.1.1 Introduction

The world total Portland cement production is over four billion tons annually. China with an output of 2.4 Gigatons or 58.5 % of the total global production is the world's leading producer, followed by India with 6.6 % and the U.S with 2.1 % of the world's production, as depicted in Figure 1 (USGS, 2018).

FIGURE 1: WORLD CEMENT PRODUCTION SHARES IN 2017. TOTAL 4.1 BILLION TONS



SOURCE: Adapted from USGS (2018)

Knowing that the total cement production amounts to 4.1 Gigatons, figure 1 shows that Brazil comes in the 12th position with a yearly cement production of 54 Megatons or 1.3 % of the global production.

Typically, about 3 to 5 MJ of thermal energy are used to dry, decompose, and sinter the carbonate minerals to produce one kg of clinker that is then ground to cement powder, and mixed with other components. This is equivalent to 60-130 kg coal/ton of cement clinker. Besides, the consumption of fuel is estimated to 30-40 % of the total

cement manufacturing costs (MUT, 2015). Therefore, enhancing the energy efficiency of such an energy-intensive industry does not only contribute to improving its economic competitiveness in the global market but also reduces demand on natural resources and improves the environment quality.

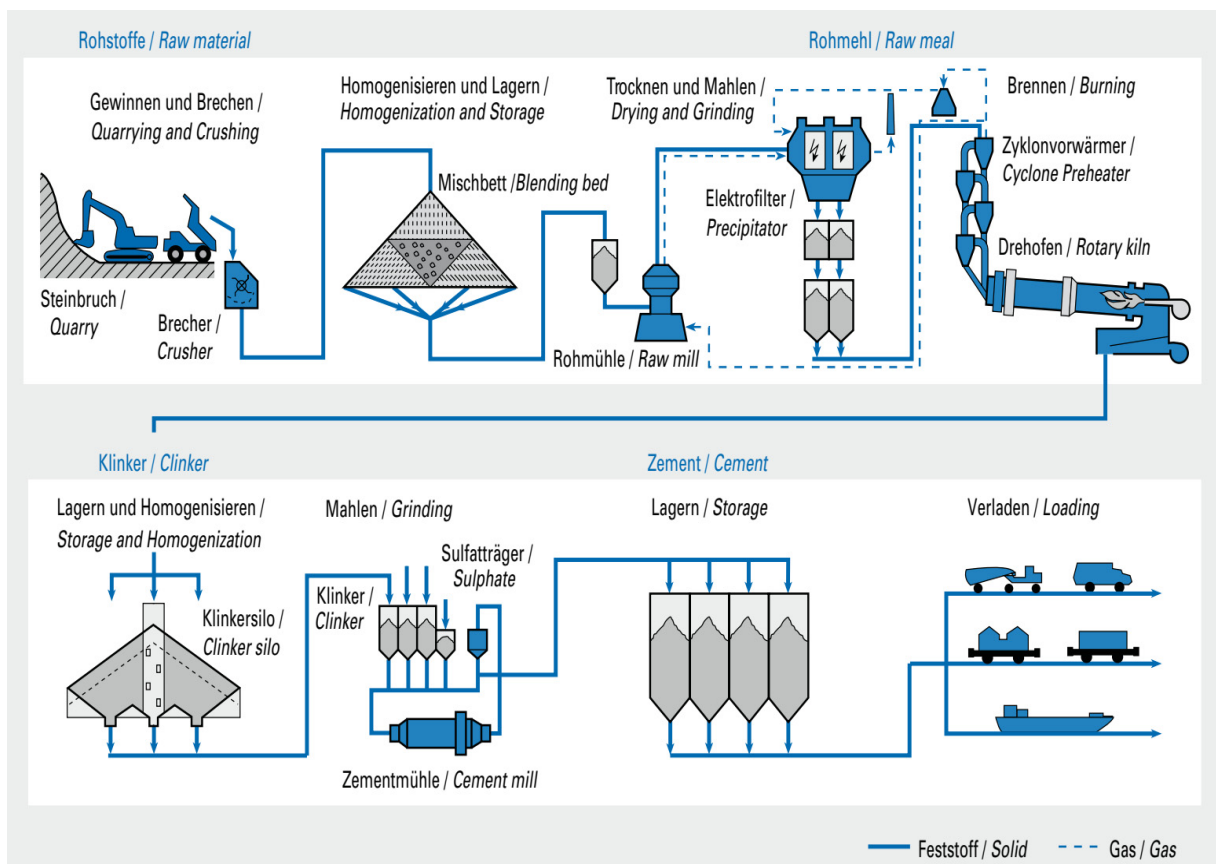
Co-processing is a proven sustainable and cost-effective method that helps achieve these objectives. It is basically the use of waste as raw material, or as a resource of energy, or both to replace natural mineral resources (material recycling) and fossil fuels such as coal, petroleum and gas (energy recovery) in industrial processes, mainly in energy intensive industries. The cement industry recovers a high amount of waste, which replaces fossil fuels up to a level of more than 80 % in some plants in Europe. This enables the cement industry to contribute further to the reduction of greenhouse gas emissions and to the use of fewer natural resources (EIPPCB, 2013).

In Brazil, Co-processing is a regulated activity by the National Environmental Council (CONAMA) and is incorporated in the National Policy of Solid Residues (PNRS). The 9th article of PNRS defines the waste management hierarchy in the following order: avoidance, reduction, reuse, recycling, treatment and final disposal. Sanitary landfills are supposed to be the last destination for waste after all treatment and recovery possibilities have been exhausted (BRASIL, 2010a).

2.1.2 Preheater-kiln system

Portland cement production can be divided into four basic steps: mining of raw materials (mainly limestone and clay), preparation of raw meal, clinkerization and processing of clinker into the final cement product (Figure 2). The essential primary raw materials, such as limestone, shale or clay, chalk and marl are extracted from quarries. Usually, the quarry is close to the plant. After crushing, the raw materials are transported to the cement plant for storage and further preparation. The raw meal should be as chemically homogenous as possible (VDZ, 2016).

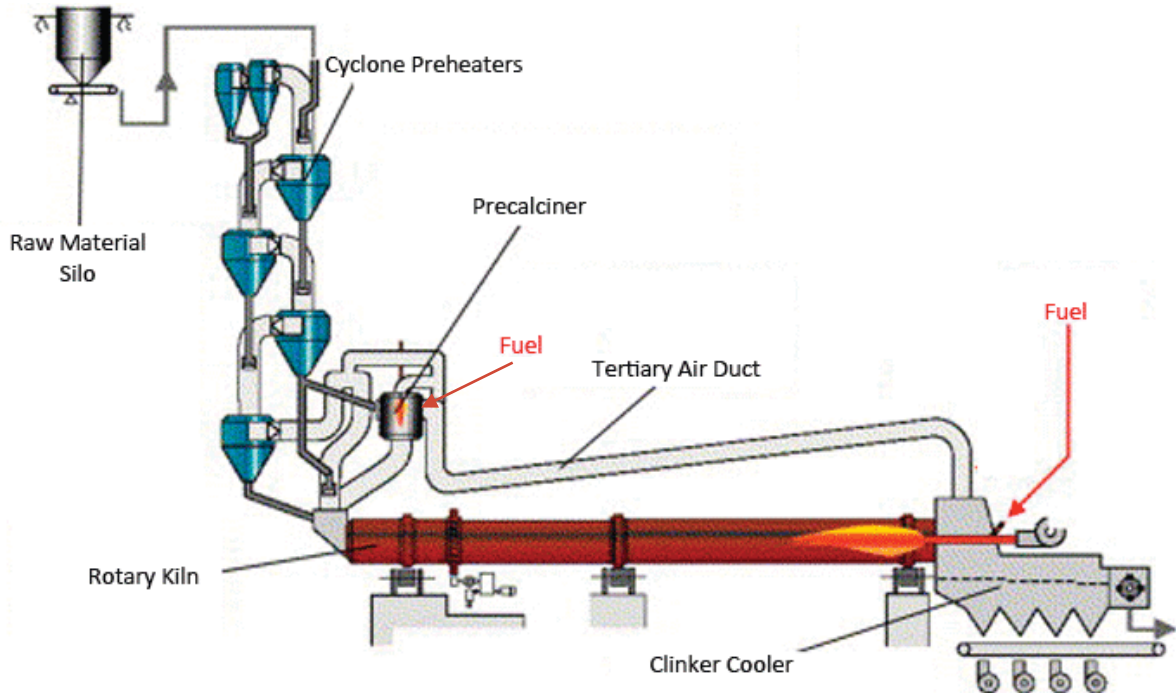
FIGURE 2: GENERAL OVERVIEW OF CEMENT MANUFACTURING PROCESS



SOURCE: VDZ (2016)

The clinkerization step, which is a pyroprocessing of the raw meal, takes place in a preheater-kiln system (Figure 3). It consists of four sequential subprocesses: preheating, calcination, sintering (formation of clinker minerals in the rotary kiln) and cooling. Clinkerization is the most important part of the process in terms of emissions potential and of product quality and cost (EIPPCB, 2013).

FIGURE 3: PREHEATER-KILN SYSTEM WITH PRECALCINATION



SOURCE: Adapted from GIANNOPOULOS et al. (2007)

The basic chemistry of the cement manufacturing process starts with calcination. It is the decomposition of calcium carbonate (CaCO_3) at about $900\text{ }^\circ\text{C}$ to calcium oxide (CaO , lime) and liberation of gaseous carbon dioxide (CO_2). The following step is the clinkering process in which the calcium oxide reacts at a high temperature (typically $1400\text{--}1500\text{ }^\circ\text{C}$) with silica (SiO_2), alumina (Al_2O_3), and ferrous oxide (Fe_2O_3) to form the silicates, aluminates, and ferrites of calcium, which form the clinker. The clinker is then ground together with gypsum and other additives to produce final Portland cement (FLSMIDTH, 2009).

Since the rotary kiln was introduced around 1895, it has become the central part of all modern cement-manufacturing installations. It is the place where necessary chemical reactions for clinker production occur. Rotary kilns are long, cylindrical, slightly inclined furnaces that are lined with refractory material to protect the steel shell and keep heat within the kiln (EPA, 2010). Typical length to diameter ratio of modern rotary kilns is between 10:1 and 38:1. The tube is supported by two to seven (or more) support stations, has an inclination of 2.5 to 4.5 % and a drive rotates the kiln about its axis at 0.5 to 5.0 revolutions per minute (EIPPCB, 2013). The slight inclination of the

kiln and its rotation ensure the transportation and mix of the raw meal to form the clinker.

Dry process kiln systems have been enhanced in productive capacity and thermal efficiency through the addition of cyclone-type preheater installation to the furnace inlet. They are usually between four and six cyclone stages, which are arranged one above the other in series in a tower 50–120 m high. Hot exhaust gases from the rotary kiln pass countercurrently through the downward-moving raw materials in the preheating tower (VDZ, 2016).

Compared to the simple rotary kiln, the heat transfer rate is significantly increased, the degree of heat utilization is greater, and the process time is markedly reduced by the intimate contact of the solid particles with the hot gases. The enhanced heat transfer allows the length of the rotary kiln to be reduced. The hot gases from the preheater tower are often used as a source of heat for drying raw materials in the raw meal (FLSMIDTH, 2009).

The precalcination technique was integrated in the cement industry since 1970. In this procedure, the heat input is divided between two points. Primary fuel combustion occurs in the kiln-burning zone. Secondary burning takes place in a special combustion chamber between the rotary kiln and the preheater. In this chamber up to 65 % of the total fuel can be burned in a typical precalciner kiln. This is because of the significantly longer retention time of the hot meal, the kiln exhaust gases in the bottom area of the cyclone preheater and the use of additional tertiary air. The energy is used to calcine the raw meal, which is almost completely calcined when it enters the kiln. Calcination levels of well above 90 % can be achieved (EIPPCB, 2013).

2.1.3 Solid Recovered Fuel

Since the technical specification of CEN/TS 15357, the European Union uses the common term *Solid Recovered Fuel* (SRF) instead of Refuse Derived Fuel (RDF) in order to establish uniform quality standards for alternative fuel. According to the same norm, SRF is the solid fuel prepared (after processing, homogenizing and upgrading to a quality that can be traded amongst producers and users) from high-calorific fractions of non-hazardous waste materials to be utilized in energy recovery in incineration or co-incineration plants (CEN, 2006a).

The European Committee of Standardization has developed specifications regarding classes, physical and chemical tests, fuel specifications, quality assurance and sampling for SRF. The classification is based on three important parameters, referred to the main SRFs properties: an economical parameter (Net Calorific Value), a technical parameter (chlorine content) and an environmental parameter (mercury content) (CEN, 2006b). The classification is shown on table 1.

TABLE 1: CLASSIFICATION SYSTEM OF SRF ACCORDING TO EUROPEAN NORMS

Classification Property	Statistical Measure	Unit	Classes				
			1	2	3	4	5
Net Calorific Value (NCV)	Arithmetic mean	MJ/kg *ar	≥ 25	≥ 20	≥15	≥10	≥ 3
Chlorine (Cl)	Arithmetic mean	Wt. % *d	≤ 0,2	≤0,6	≤1,0	≤1,5	≤3
Mercury (Hg)	Median	mg/MJ *ar	≤ 0,02	≤ 0,03	≤ 0,08	≤ 0,15	≤ 0,50
	80 th percentile	mg/MJ *ar	≤ 0,04	≤0,06	≤0,16	≤0,30	≤1,00

*ar: as received; *d: dry basis

SOURCE: Adapted from CEN (2006b)

It is important to note that the classes are only a tool to identify and preselect SRF. The norm is non-restrictive and does not forbid the use of any of the above-mentioned classes of waste. The cement plants should consider their design and operating conditions and have a more detailed description of the fuel to decide upon which classes to work with.

According to the norm CEN/TS 15359, a classification example of SRF is the following:

❖ The class code of a SRF having a mean net calorific value of 22 MJ/kg (ar), a mean chlorine content of 0,8 % (d) and a median mercury content of 0,016 mg/MJ (ar) with an 80th percentile value of 0,02 mg/MJ (ar) is designated as:

Class code **NCV 2; Cl 3; Hg 1** (Adapted from norm CEN/TS 15359).

2.1.4 Feeding points for inserting SRF in the kiln

Residues used as raw materials are typically fed to the kiln system in the same way as conventional raw materials, e.g. via the normal raw meal supply. The feed

points used for fuel can also be used for feeding wastes as fuels and/or raw materials into the cement production process. It has to be noted that the way the fuels are fed into the kiln is very important as this can have an effect on the emissions (SMIDTH, 2015). Of these feed points, there is, in general, only one way in which the flue-gases from fuels pass the highest temperature zone of the kiln, namely by feeding them through the main burner. For other feed points, temperature and residence time depend on kiln design and operation (EIPPCB, 2013).

Waste materials, which are fed through the main burner, will be decomposed in the primary burning zone, at high temperatures of up to 2000 °C. SRF fed to a secondary burner, preheater or precalciner will be burned at lower temperatures, which is not always enough to decompose halogenated organic substances. Volatile components in material that is fed at the upper end of the kiln can easily evaporate. These components do not pass the primary burning zone and may not be decomposed or bound in the cement clinker. Therefore, the use of waste containing volatile metals (mercury, cadmium, thallium) or volatile organic compounds can result in an increase of the emissions of mercury, cadmium, thallium or organic emissions (e.g. VOCs) when improperly used. Consideration should be given to these waste materials containing components that can be volatilized at lower temperatures before the calcining zone (e.g. hydrocarbons, solvents, waste oils). They have to be fed into the adequately high temperature zones of the kiln system (ALSOP et al., 2007) (EIPPCB, 2013).

2.2 CHLORINE IN THE CEMENT MANUFACTURING PROCESS

Chlorine is a chemical element belonging to the halogens family. It is found in abundance in the world, but it never occurs on its own due to its extremely reactive nature. Chlorine is neither flammable nor explosive, but it can support combustion (WATT, 2002). In the cement manufacturing process, chlorine is an unwanted trace component found in all the feeds entering the cement kiln.

2.2.1 Chlorine in the raw meal

In addition to the essential oxides (silicon dioxide, calcium oxide, aluminum oxide and iron oxide) necessary to form clinker in the cement kiln, the raw meal, which is made essentially from limestone and clay, contains also other elements that are not

required in the cement manufacturing process. The excess of these elements could create trouble for the burning process especially in the preheater lower stages and after the precalciner, in the kiln inlet area and sometimes in kiln tube itself (MEYSTRE, 2016).

A chemical analysis of raw meal from different cement plants in Europe showed that clay could contain until 1 % of chlorine and limestone and iron ore until 0.6 % (Table 2).

TABLE 2: CHEMICAL ANALYSIS OF RAW MATERIALS AND CEMENT RAW MEALS FROM DIFFERENT EUROPEAN COUNTRIES

Components	Limestone, Lime marl, chalk	Clay	Sand	Fe source	Raw meal (Limestone + Clay + Sand + Fe)
	(Mass %)				
SiO ₂	0,5 – 50	33 – 78	80 – 99	0,5 – 30	12 – 16
Al ₂ O ₃	0,1 – 20	7 – 30	0,5 – 7	0,2 – 4	2 – 5
Fe ₂ O ₃	0,2 – 5,9	4 – 15	0,0 – 4	50 – 93	1,5 – 2,5
Mn ₂ O ₃	0,02 – 0,15	0,09	0,051	0,1 – 4	0,0 – 0,5
CaO	20 – 55	0,2 – 25	0,1 – 3	0,1 – 34	40 – 45
MgO	0,2 – 6	0,3 – 5	0,3 – 0,5	0,5 – 7	0,3 – 5
K ₂ O	0,0 – 3,5	0,4 – 5	0,2 – 3	0,1 – 1	0,1 – 1,5
Na ₂ O	0,0 – 1,5	0,1 – 1,5	0,0 – 1	0,1 – 1	0,1 – 0,5
SO ₃	0,0 – 0,7	0,0 – 4	0,0 – 0,5	0 – 3	0,0 – 1,5
Cl	0,0 – 0,6	0,0 – 1	Traces	0,0 – 0,5	0,0 – 0,3
TiO ₂	0,0 – 0,7	0,2 – 1,8	0,0 – 0,5	0,0 – 3	0,0 – 0,5
P ₂ O ₅	0,0 – 0,8	0,0 – 1	0,0 – 0,1	0,0 – 1	0,0 – 0,8
ZrO ₂		0,02			
CaCO ₃	96				

SOURCE: adapted from EIPPCB (2013)

Table 2 shows example ranges of various components of raw materials and cement raw meals obtained from chemical analyses of different European cement plants. Apart from the main components, these raw materials also contain a number of metals that are not shown in the table. The chemical analysis shows clearly the presence of chlorine in considerable quantities in the kiln input even without co-processing of alternative fuels.

2.2.2 Chlorine in the SRF

The Chlorine content in fossil fuels, such as petcoke and coal, is rather low. However, chlorine contained in SRF fractions, especially PVC, may have a fatal impact

on the cement production process. The acceptable chlorine concentration depends on the individual situation of each plant. However, this concentration is kept as low as possible in order to avoid operational problems in the kiln system (MUT, 2005). When a high amount of chlorine is input, usually a chlorine bypass might be necessary to avoid corrosion, blockings, shutdown, etc. Typical chlorine concentrations in SRF range from 0.5 to 2 %. In some European countries such as Belgium, France and Spain permits were delivered to cement plants with SRF chlorine limit set to 2 % (EIPPCB, 2013).

In Germany, there is no explicit limitation on chlorine content. Each cement plant is treated independently by the authorities. The reason is that each plant has specific design and operation conditions that should be taken into account to determine the safe permitted chlorine inputs (VDZ, 2016).

Chlorine in the SRF has two principal sources: Plastics, mainly Polyvinyl Chloride (PVC), main source of organic chlorine and domestic residues, main source of inorganic chlorine (NaCl, KCl). In Municipal Solid Waste (MSW), PVC is responsible for 38 to 66 % of the chlorine content. As a weight percentage, chlorine from PVC amounts from 0.5 to 0.7 % of the total MSW mass (BERNARD et al., 2000). PVC is one of the most commonly used plastics in the world. In pure PVC polymer, chlorine represents 57 % of the total weight. Depending on the final application, the formulation of PVC can vary widely due to the additives such as stabilizer, plasticizer, flame retardant, pigment, etc...Normally, PVC is an unwanted fraction of the SRF used in co-processing (MEYSTRE, 2016).

2.2.3 Chlorine in the clinker

Chlorine tends to incorporate in the alkaline matrix of clinker or volatilize and stay in the system. In the clinker, it can be found as CaCl_2 , and sometimes as KCl, if it is trapped in the inner core of the clinker nodules (MUT, 2015). High inputs of chlorine increase significantly the incorporation rate in the clinker product and reduces its quality (SALEH, 2015).

Clinker is the most important binder in cement products that form the final concrete structures. Different mechanisms could lead to the deterioration of these structures. Particularly, chloride is considered as the most aggressive and corrosive ion since it contributes to corrosion of steel reinforcement. Therefore, concrete

structures may suffer serious structural damage threatening the stability of civil works (SIPPLE, 2014). Based on this, limitation of the chlorine content in cement products has been introduced. In Europe, EN 197 limits the chlorine content of cement to 0.1 % (CEN, 2000). Cement plants usually use a lower standard due to analysis uncertainties.

2.3 INFLUENCE OF CHLORINE ON THE CEMENT MANUFACTURING PROCESS

2.3.1 Circulation phenomenon

Chlorine, Sulphur and alkalis i.e. sodium and potassium are volatile elements always present in the cement production process. Depending on the degree of volatility, these elements initially bound in the input materials evaporate in the sintering zone of the cement kiln. At temperatures of 1200 – 1300 °C, a high percentage of chlorides is already volatilized. At burning zone temperatures, they are almost entirely volatilized (HOLDERBANK, 2012). Then, they are transported by the hot gases to colder zones at the kiln inlet, where they mainly condense on the raw meal and partly also on the surrounding walls. The condensation of chloride and its compounds occurs mainly between 650 °C and 800 °C. Afterwards they return to the raw meal into the sintering zone where they partly reevaporate depending on the degree of volatility. This repeated process through the kiln leads to the establishment of internal cycles. Theoretically, this recirculation builds up until the output of circulating element discharged with the clinker and the kiln off-gas is equal to their input reaching an equilibrium state (LANZERSTORFER, 2016).

A small part of the volatile elements leaves the kiln system with the exhaust gas dust. This latter is precipitated in the dedusting unit and is normally reintroduced into the kiln system. This is called an external cycle of the circulating elements (SCHÖFFMANN, 2015). The chlorides are so volatile that they hardly leave the kiln via clinker. In exceptional cases, when the burning zone has largely cooled down or when embedded in big material lumps, the chlorides may leave the kiln in major quantities. (HOLDERBANK, 2012).

2.3.2 Operational problems

High internal cycles of volatile compounds especially chlorine have rather severe consequences on the preheater-kiln system. If poorly managed, the results could be frequent kiln stops, higher heat consumption and reduction of the maximum kiln production. (LANZERSTORFER, 2016).

Rings and encrustation deposits are the direct consequence of high input of volatile compounds (Figure 4). They are accumulations of solid matter from the powdery kiln charge. At the beginning, encrustation and build-up formation increase at the kiln inlet area and the lower part of the preheater. Therefore, the pressure loss across the system increases, which restricts the maximum kiln draft and thus the maximum clinker production. In the sintering zone, the presence of rings and build-ups can impede the complete combustion of the fuel (SCHÖFFMANN, 2015). Every now and then, unstable rings and build-ups can break away leading to mechanical damage in the cooler, or to cyclone blockages. Removing encrustations in cyclones generates more expenses to the plant and increases the production cost (FLSMIDTH, 2015). This operation could be done by poking, or the installation of big air blasters ensuring regular automatic removal for plants with persistent preheater blockages. High-pressure water jets may also be used for build-ups removal. In the worst cases, a total shutdown is needed to allow entrance to the damaged area to remove the blockage with compressed air drills. This extreme measure weakens the burning zone refractories and shortens the time until the next shutdown for rebricking (HOLDERBANK, 2012).

FIGURE 4: ENCRUSTATIONS AND BUILD-UP RINGS IN THE CYCLONES



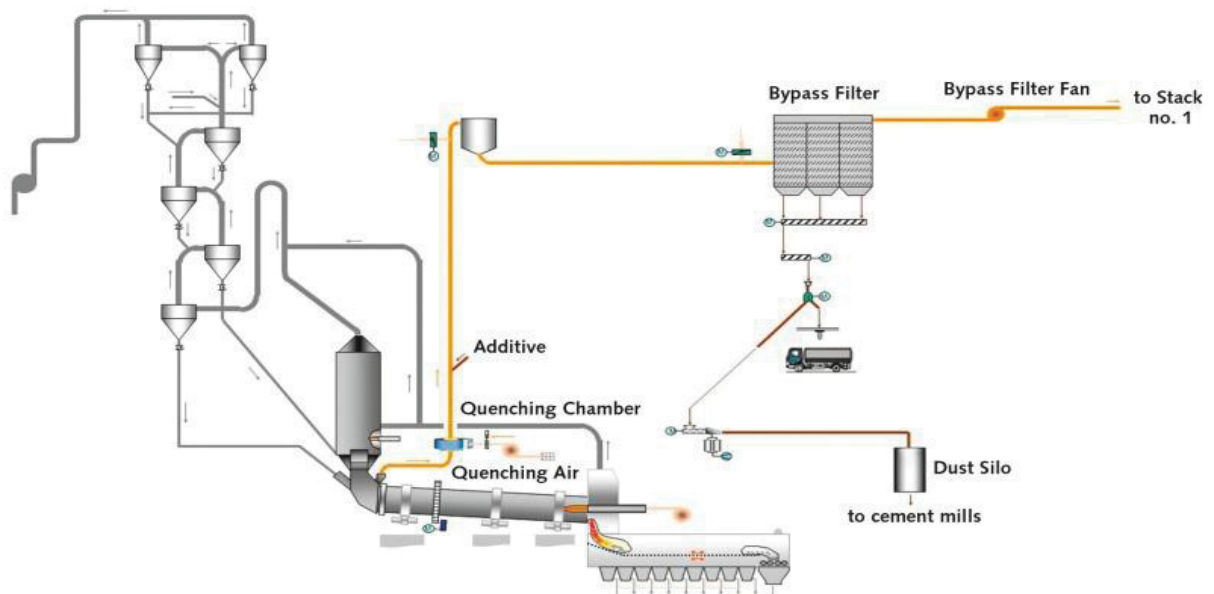
SOURCE: FLSMIDTH (2015)

This being said, all the volatile compounds in the kiln can be hold responsible for encrustations formation. The difference is mainly the position of the build-ups. If they are found up the 2nd lowest cyclone stage or even the third lowest cyclone stage, they are mainly originating from excessive chloride cycles. If build ups are found at the lowest cyclone stage and the kiln inlet, it is probably due to excessive sulphur cycles. The position of the build-ups could be identified using a pressure profile over the preheater (HOLDERBANK, 2012).

2.3.3 Kiln-bypass System

A uniform kiln operation with minimized disturbances is the basis for energy efficient clinker production. Shutdowns resulting from coating formation and clogging should be avoided. There is little chance to decrease chlorine volatility as evaporation occurs at a low temperature range (800 – 1000 °C). Moreover, for preheater-kiln systems dust discarding is normally not very efficient as the accumulation of chlorides in the dust is negligible (EIPPCB, 2013). Chloride bypass is an interesting option used nowadays to control the volatile compounds and ensure a smooth operation of the cement kiln (Figure 5). By deducting a small amount of gas and dust, a higher efficiency of discharge of volatile substances can be achieved. It is important to note that the kiln-bypass does not eliminate the circulation problem of the volatile elements; it only makes the kiln operation smooth and economical (HOLDERBANK, 2012).

FIGURE 5: BYPASS INSTALLATION SCHEME (YELLOW LINE)



SOURCE: A TEC (2014)

According to SCHÖFFMANN (2015), the optimal extraction point for a gas bypass is immediately after the furnace. As long as the gases are over 1000 °C hot, it is ensured that the volatile components, especially chlorine, are still in the gas phase. The withdrawn gas contains the gaseous components, especially chlorine and dust, which must be cooled immediately in a first step. The cooling to approx. 200 - 350 °C takes place in a separate chamber and ensures that the chlorine condenses rapidly on the bypass dust. This process must be quick, as slow cooling leads to the formation of compounds that tend to cake. This tends to happen in the area from the extraction point in the kiln inlet to the cooling chamber and requires regular cleaning (SCHÖFFMANN, 2015).

Modern by-pass systems are usually equipped with two cooling chambers. An air quench chamber that is used to mix ambient air with the extracted kiln gases and a water quench chamber that is used to cool them quickly to lower temperature for dust collection (HOLDERBANK, 2012). The cooling temperature depends on the downstream filter. For cloth filters, it should be less than 200 °C in order to protect the filter fabric and ensure economical fabric life (SCHÖFFMANN, 2015). In the filter, the dust and the separated volatile substances are taken from the bypass gas. A limited quantity of the bypass dust can be recycled back in the clinker, but most of it is usually disposed of as hazardous waste without any reuse or recycling because of its high

load of chlorine and alkaline compounds (RAMZI, 2002). Recently, some new technologies such as ReduDust from A TEC offer solutions to treat by-pass dust. The technology from A TEC uses a leaching and a crystallization method to produce pure KCl and NaCl salt from the By-pass dust. The residual dust can be reincorporated completely to the cement production, without enrichment of the undesired components. Therefore, the lost amount of material removed by the bypass system can be recovered and the costs for disposal can be saved (A TEC, 2014).

The estimation of the amount and characteristics of produced dust is one of the greatest uncertainties in the design of bypass systems. For instance, if the dust particles are too fine and the chlorine content is high (15 % to 18 % were reported in a by-pass dust in Retznei, Austria), it might clump and block the pneumatic transport when pressure is exerted. Therefore, each new design of a bypass plant should plan beforehand the dust transport requirements (SCHÖFFMANN, 2015). Different degrees of volatile compounds reduction are shown in table 3.

TABLE 3: REDUCTION EFFICIENCIES OF A BY-PASS WITH 5 % WITHDRAWAL RATE

Volatile element	Reduction efficiency (%)
Cl	~ 80 %
SO ₃	< 10 %
K ₂ O	< 15 %
Na ₂ O	< 5 %

SOURCE: SCHÖFFMANN (2015)

Table 3 depicts theoretical values referring to a bypass installation with a withdrawal rate of 5 % of the exhaust gas at the kiln inlet. In this case, the bypass discharges approx. 80 % of the total chlorine input. These values may vary from plant to plant depending on the rate of evaporation in the sintering zone (SCHÖFFMANN, 2015).

The by-pass systems installation will eventually generate additional capital investment and higher costs due to higher power and heat consumption in the kiln system. Dust loss must also be considered as an important material loss (HOLDERBANK, 2012).

2.4 KILN EMISSIONS FROM CHLORINE COMBUSTION

The equilibrium products formed by the complete combustion of chlorinated feeds are water, carbon dioxide and hydrochloric acid. Unfortunately, real oxidation processes are not complete and small amounts of products of incomplete combustion are found in stacks (WATT, 2002).

In addition to carbon monoxide and molecular chlorine, common products of incomplete combustion include polycyclic-aromatic hydrocarbons, chlorinated and oxygenated aromatics (e.g. chlorophenols and chlorobenzenes) and more complex molecules such as polychlorinated biphenyls (PCB), dibenzo-dioxins (PCDD), dibenzo-furans (PCDF). Many of those compounds are extremely dangerous to human health and to the environment (MEYSTRE, 2016).

2.4.1 HCl emissions

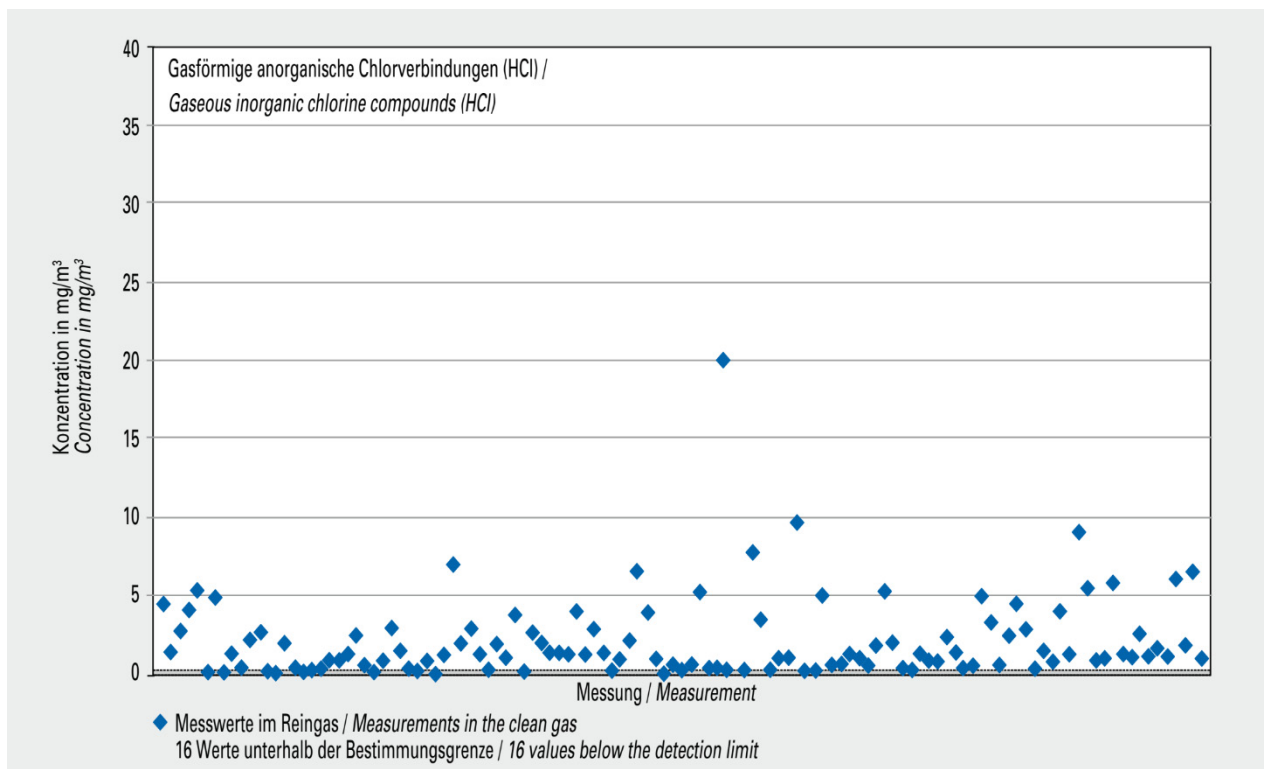
Hydrogen chloride (HCl) is an acidic gas primarily released to air from combustion processes involving inputs containing traces of chlorine. Considering that the most stable oxidation state of chlorine is -1, the major combustion products are chlorides with HCl as the most prominent compound (WATT, 2002). In the United Kingdom in 2015, HCl emissions in the atmosphere amounted to 9.22 Kilotons with almost 44 % from industrial combustion plants (NAEI, 2015). HCl released into the atmosphere as a gas will undergo wet and dry deposition. Besides, it will be readily incorporated into cloud, rain, and fog water. It thus forms a component of acid rain. It also contributes to the processes that cause photochemical smog (WATT, 2002).

Due to the alkaline kiln gas atmosphere, gaseous inorganic chlorides (HCl) are either not emitted at all or only in very small quantities. HCl concentrations detected in the exhaust gas of cement kilns are generally attributable to ultra-fine grain size fractions of alkali chlorides in the clean gas dust. They can pass through measuring gas filters, thus feigning the presence of the gaseous compounds (VDZ, 2016). The use of raw materials and fuels with low chlorine content also reduces the enrichment cycle resulting from the internal circulation of chlorine between the kiln and preheater and thus contributes to further reduction of HCl emissions. Best performance data for

HCl emissions in Europe was reported in a range between 0 and 8 mg/Nm³ as an annual average value (EIPPCB, 2013).

Figure 6 shows 135 HCl concentration values from measurements in the clean gas of 39 rotary kilns. 16 values were below the detection limit of 0.23 mg/Nm³ and only one violation above 10 mg/Nm³ was detected (VDZ, 2016).

FIGURE 6: HCl CONCENTRATIONS MEASURED IN THE CLEAN GAS OF 39 ROTARY KILNS IN 2016 (ANNUAL AVERAGE)

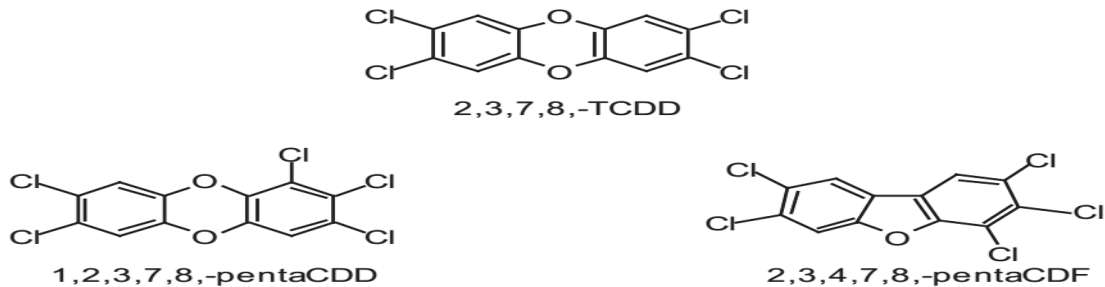


SOURCE: VDZ (2016).

2.4.2 Dioxins and furans

Polychlorinated dibenzo-para-dioxins (**PCDD**) and polychlorinated dibenzofurans (**PCDF**) are planar, aromatic compounds containing two benzene rings. They have at least 4 Cl-atoms. A dioxin molecule is bonded by two oxygen atoms and a furan molecule by a single oxygen atom and a direct bond. Under standard atmospheric conditions, all dioxins are solid and are characterized by limited solubility in water and low vapor pressure (WATT, 2002). The structures of the most toxic forms of dioxin and furan molecules are shown in figure 7.

FIGURE 7: MOST TOXIC ISOMERS OF DIOXINS AND FURANS



SOURCE: KARSTENSEN (2008)

Since the toxicity of the different PCDD/Fs depends on the level of chlorination and location of chlorine atoms on the benzene rings, each congener is attributed a number called Toxicity Equivalence Factor (TEF). Thus, the toxicity of a mixture of dioxins and similar compounds can be expressed in a single number called the **toxicity equivalency** (TEQ). Over the years, several systems of TEQ were adopted (Annex 1). To obtain TEQ the mass of each compound in the mixture is multiplied by its TEF and is then summed with all other products to obtain the total toxicity-weighted mass (EA, 1999).

There is a considerable evidence that production of PCDD/F in large-scale incineration processes is strongly linked to furnace types, their operating conditions, and the type and efficiency of air-pollution control systems. Residence time and temperature distribution in rotary kilns offer particularly favorable conditions for organic compounds to be totally destroyed. Thus, very low concentrations of dioxins and furans can be found in the exhaust gas from cement plants. Investigations have shown that, regardless of chlorine input, PCDD/Fs emissions can be controlled below the emission limit of $0.1 \text{ ng TEQ Nm}^{-3}$ (KARSTENSEN, 2008).

Several recent studies examined the use of different types of alternative fuels, and found that most emissions of PCDD/Fs are lower than the limit value of $0.1 \text{ ng TEQ Nm}^{-3}$ (ZHAN et al., 2016). For example, when sewage sludge and waste tires were used as substitute fuels in cement kilns, the PCDD/F emissions in the exhaust gas varied in a range of $0.0019\text{-}0.0221 \text{ ng TEQ Nm}^{-3}$ (CONESA et al., 2008). In addition, ZEMBA et al. (2011) conducted more than 150 tests using different fuels,

comprising SRF, cokes and hazardous waste and found that the type of waste had only minor impact on dioxins emissions, all reported below 0.1 ng TEQ Nm⁻³ (ZHAN et al., 2016),

2.5 LEGAL FRAMEWORK

Co-processing is an activity that involves the use of residues that could generate toxic pollutants. It is therefore important to have a solid legal framework that regulates the different aspects of this thermal process. This section will be the basis for further discussion and comparison with legislations of other countries.

2.5.1 Waste management in the Brazilian legislation

In Brazil, in addition to the Federal Constitution and the state Constitutions, there is a set of laws, decrees, resolutions, ordinances and norms that show concern for the environment and, more specifically, the issue of waste management.

The Brazilian Federal Constitution of 1988 addressed with more emphasis the environmental issues. It states that the municipality, as an autonomous federal entity, is responsible for urban cleaning services and all solid waste management, from collection to final disposal (BRASIL, 1988).

The National Environmental System (SISNAMA) was created through the Federal Law N° 6 938/1981, which establishes the National Environmental Policy, its purposes and mechanisms of formulation and application, and other measures. Besides establishing the polluter-payer principle, it brought with it an annex containing categories and description of the principal activities to be included in the federal technical register of activities potentially polluting or exploiting environmental resources. It mentioned as well the environmental licensing of such activities from the state agency for construction, installation, expansion and operation and the treatment and destination of solid residues (BRASIL, 1981).

With the approval of the Law Project N° 203, discussed since 1991 at the federal level, the Federal Law N° 12305 was introduced on August 10, 2010. It became known as the "National Policy on Solid Residues (PNRS)", which brought together a set of principles, objectives, instruments, guidelines, goals and actions, to ensure an integrated management of solid residues (BRASIL, 2010a). Regulated by Federal Decree N° 7,404, dated 12/23/2010, it established standards for the implementation of

the PNRS and instituted the concept of shared responsibility, in which the entire society became responsible for an efficient integrated management of solid waste (BRAZIL, 2010b).

Finally, an important legal instrument concerning waste management in Brazil comprises the Resolutions of the National Environmental Council (CONAMA), which is the consultative and deliberative legal body of SISNAMA, linked to the Ministry of the Environment and the Brazilian Association of Technical Standards (ABNT), which is the country's technical standardization organization.

2.5.2 Co-processing in the Brazilian legislation

The Art. 36 of the Federal Decree N° 7.404/2010 includes co-processing in the list of energy recovery processes that could use residues as a fuel, provided that they comply with the norms established by the competent authorities (BRASIL, 2010b).

The general frame that regulates environmental licensing of waste co-processing in cement rotary kilns is the CONAMA Resolution N°264/1999. It is a federal resolution released by the Brazilian Environmental National Council. Besides defining residues that could be co-processed and federal pollutants emission standards, it establishes the specifications for both kiln blank and pilot co-processing test (BRASIL, 1999)

Another federal resolution that is of great importance in the field thermal treatment systems of residues is CONAMA Resolution N°316/2002. It describes procedures and technical criteria necessary for the functioning of any process with minimal temperature above 800°C involving incineration of waste. In addition to establishing operating procedures, emission limits and performance criteria, it also defines control, treatment and final disposal of effluents from these activities in order to minimize the impacts on the environment and public health. It should be mentioned that dioxins and furans emission standards related to co-processing are found in this federal resolution (BRASIL, 2002).

In addition to the federal resolutions, there are many state resolutions that regulate the activity of co-processing in the particulate relevant states. For example, SEMA N° 016/2014 is a state resolution released by Paraná Secretary of Environment and Water Resources. It establishes the measurement methods and the state emission standards in Paraná (PARANÁ, 2014). Other state resolutions include CONSEMA

N°02/2000 in Rio Grande do Sul and SMA n°38/2017 in São Paulo. In Minas Gerais, the normative deliberation COPAM N°154/2010 is the regulation in vigor concerning co-processing in cement kilns (RIO GRANDE DO SUL, 2000) (SÃO PAULO, 2017) (MINAS GERAIS, 2010).

2.5.3 Legal aspects on chlorine

The federal resolution CONAMA N°264/1999 in its section VIII, Art. 28, defines the maximum emission limits in cement rotary kilns using co-processing for various air pollutants (Table 4) (BRASIL, 1999).

TABLE 4: MAXIMUM BRAZILIAN FEDERAL EMISSION LIMITS

Pollutant	Maximum emission limit
HCl	1.8 kg/h or 99 % reduction
HF	5 mg/Nm ³ adjusted to 7 % O ₂ (Dry base)
CO*	100 ppmv adjusted to 7 % O ₂ (Dry base)
Particulate Matter (PM)	70 mg/Nm ³ adjusted to 11 % O ₂ (Dry base)
THC (Expressed in terms of Propane)	20 ppmv adjusted to 7 % O ₂ (Dry base)
Mercury (Hg)	0.05 mg/Nm ³ adjusted to 7 % O ₂ (Dry base)
Lead (Pb)	0.35 mg/Nm ³ adjusted to 7 % O ₂ (Dry base)
Cadmium (Cd)	0.10 mg/Nm ³ adjusted to 7 % O ₂ (Dry base)
Thallium (Tl)	0.10 mg/Nm ³ adjusted to 7 % O ₂ (Dry base)
(As+Be+Co+Ni+Se+Te)	1.4 mg/Nm ³ adjusted to 7 % O ₂ (Dry base)
(As+Be+Co+Cr+Cu+Mn+Ni+Pb+Sb +Se+Sn+Te+Zn)	7 mg/Nm ³ adjusted to 7 % O ₂ (Dry base)

*Hourly average concentrations of CO cannot exceed 100 ppmv

SOURCE: CONAMA (1999)

The federal limitation on HCl emissions is expressed using two conditions. The first alternative is an emission rate of 1.8 kg/h and the second is a reduction efficiency fixed at 99 %. Cement plants have to comply with either one of those conditions. According to Art. 34 of CONAMA N°264/1999, HCl emissions do not need to be monitored continuously (BRASIL, 1999).

In Paraná, the state resolution SEMA N° 016/2014 in its 33rd article (Section II, Subsection IV) uses the federal standards with a slight addition to the second condition. It requires whether a maximum emission rate limit of 1.8 kg HCl/ h or 99 % removal of

HCl for residues with more than 0.5 % chlorine content. In addition, HCl emissions should be monitored on a semestral basis (PARANÁ, 2014).

CONSEMA Resolution N°02/2000 in Rio Grande do Sul keeps the same values of CONAMA. In Minas Gerais, the normative release COPAM N°154/2010 uses the same limitations as Paraná (RIO GRANDE DO SUL, 2000) (MINAS GERAIS, 2010). However, the resolution SMA n° 38/2017 of São Paulo limits chlorine content in SRF to 1.0 % and HCl to 10 mg/Nm³ with 10 % de O₂ (SÃO PAULO, 2017).

3 METHODOLOGY

3.1 INFLUENCE OF CHLORINE IN THE PROCESS OF CEMENT PRODUCTION

Through a bibliographic research and review of previous studies, the influence of chlorine through the cement manufacturing process was elucidated. This influence was particularly divided into two main points: operational problems related to the preheater-kiln system and environmental impacts resulting mainly from hazardous emissions. Finally, eventual procedures applied nowadays to reduce these unwanted impacts were also studied.

3.2 COMPARATIVE ANALYSIS OF EMISSION STANDARDS RELATED TO CHLORINE IN CO-PROCESSING

An inventory of Brazilian emission standards related to chlorine combustion products generated in cement rotary kilns using co-processing of waste was carried out. The emission limits were obtained from the available legal texts whether on the federal or state level. Using the standards in vigor from EU, EPA and Germany, a comparative analysis was proceeded to identify the various converging and diverging points regarding the Brazilian emission limits.

3.3 ANALYSIS OF PERMITTED CHLORINE CONTENT IN SOLID RECOVERED FUEL FOR CO-PROCESSING

To control chlorine impacts during cement manufacturing, environmental authorities put sometimes limits on chlorine content of co-processed waste. Considering cement plants permits and legislation from Brazil, EU and EPA, this limitation criterion was compared and critically analyzed. The aim is to determine the efficiency of this chlorine legal aspect in enhancing co-processing in cement kilns as well as protecting the environment.

3.4 ANALYSIS OF MASS BALANCE OF CHLORINE INSIDE A CEMENT KILN IN PARANÁ

In this section, data related to cement kiln operation and emissions were collected from CIA de Cimento Itambé. The objective was to elaborate a mass balance of chlorine input in the raw meal, fuel and SRF and the output measured as HCl mass flow rate. In Paraná, every cement company is legally obliged by the state environmental institute (IAP) to deliver automonitoring reports on a semestral basis. These reports include detailed atmospheric and wastewater emissions generated by the plant.

CIA de Cimento Itambé is one of the oldest cement companies in Brazil. It started in 1968 as Itambé de Mineração Ltda. Its central activity was mining, mainly limestone, in Campo Largo-PR. In 1970, it already became CIA de Cimento Itambé and purchased the area where it is still now in Balsa Nova. On 18th of December 1976, the company delivered its first cement bag. The factory has 3 cement kilns, with a total production capacity of 2.8 million tons of cement/year (CIA DE ITAMBÉ, 2016).

The cement company has 3 kilns. The data that was possible to obtain were from the kiln N°2 called also (W2). They were collected from the only available semestral automonitoring reports between 2010 and 2013 (1st semester 2010, 2nd semester 2011, 2nd semester 2012, 1st semester 2013). The kiln W2 is run nowadays only when demand is high. The following table shows the characteristics of this kiln (Table 5).

TABLE 5: CHARACTERISTICS OF KILN N°2 (W2) IN CIA DE CIMENTO ITAMBÉ

Characteristic	Kiln n° 2 (W2)
Average daily production of clinker (t/day)	2.200
Start of co-processing	Since 1994
Tour type	With pre-calciner
Kiln configuration	SLC: Separate Line Calciner
Principal filter	Hybrid (electroprecipitator and bag filter)
Thermal consumption	810 kcal/kg of clinker
Bypass	No

SOURCE: Adapted from semestral automonitoring report (2012)

4 RESULTS AND DISCUSSION

4.1 INFLUENCE OF CHLORINE IN THE PROCESS OF CEMENT PRODUCTION

Chlorine was found to be responsible mainly for operational problems inside the preheater-kiln system. High inputs of chlorine lead to the formation of sticky molten salts that glue to the walls of the kiln and crystallize. As a direct consequence, formed rings and build-ups block the cyclone outlets and the pressure loss across the system increases, which restricts the maximum kiln draft. When poorly managed, the results could be frequent kiln stops, higher heat consumption and reduction of the maximum kiln production. Furthermore, removing encrustations in cyclones generates more expenses to the plant and increases the production cost. In the case of total shutdown, the removal of the blockage is done with compressed air drills. This extreme measure weakens the burning zone refractories and shortens the time until the next shutdown for changing the bricks.

It is important to mention that, chlorine is not the only volatile compound responsible for the formation of rings and deposits. Other circulating compounds such as sulphur and alkali elements i.e. sodium and potassium contribute considerably to this undesirable process. The difference is mainly the position of the build-ups that could be identified using a pressure profile over the preheater. If they are found up the 2nd lowest cyclone stage or even the third lowest cyclone stage, they are mainly originating from excessive chloride cycles. If build ups are found at the lowest cyclone stage, the lowest riser dust and the kiln inlet, it is probably due to excessive Sulphur cycles.

An efficient way to reduce the high internal circulation of volatile compounds is using a bypass installation. It allows the extraction of a small amount of gas and dust in order to achieve a better discharge of the circulating elements. High efficiencies can be achieved using a bypass installation. For instance, for a withdrawal rate of 5 %, 80 % of chlorine entering the preheater-kiln system can be discharged (SCHÖFFMANN, 2015).

Nevertheless, designing a bypass system is not an easy task. Uncertainties about the dust characteristics can make the transport requirements tricky. For instance, if the dust particles are too fine and the chlorine content is high, it might clump and block the pneumatic transport when pressure is exerted.

Besides, having a by-pass system does not come without additional costs. They are mainly related to higher power and heat consumption in the kiln system. Dust loss must also be considered as an important material loss. Furthermore, the by-pass dust is highly loaded with chlorine and alkaline elements. Thus, only a limited quantity might be recirculated and the rest must be discarded as hazardous waste. A new technology suggests extracting the enriching elements in the form of salts and reintroducing the rest of it to the cement kiln. However, this method also requires additional costs from the cement plant.

Concerning the environmental aspect, hazardous emissions such as PCDD/F or HCl can be largely ruled out during the process of cement manufacturing. This is due mainly to the highly alkaline atmosphere inside the kiln. Several research studies showed that under good operation conditions, dioxin emissions remained below $0.1 \text{ ng TEQ Nm}^{-3}$. Residence time, high temperature and good turbulence inside rotary kilns offer particularly favorable conditions for such compounds to be destroyed.

The use of raw materials and fuels with reduced chlorine content, typically inferior to 1 %, minimizes the enrichment cycle resulting from the internal circulation between the kiln and preheater and thus contributes to further reduction of HCl and PCDD/F emissions. It is also important to comply with the maximum chlorine content allowed in the cement to assure good quality and avoid concrete structures deterioration.

4.2 COMPARATIVE ANALYSIS OF EMISSION STANDARDS RELATED TO CHLORINE IN CO-PROCESSING

4.2.1 HCl Emission standards

The Brazilian federal resolution CONAMA N°264/1999 sets HCl emissions standards to a mass flow rate 1.8 kg/h or 99 % reduction efficiency (Table 6) (BRASIL, 1999). In addition to being very high, the emission rate of 1.8 kg/h does not take into account the clinker production capacity of each cement plant. Furthermore, the 99 % removal efficiency requires the integration of a by-pass system or very efficient treatment installation of the kiln exhaust gas. It might be much better to adopt one concentration limit as it is the case in Europe or the united stated. The current HCl emission standard for cement plants in Germany is expressed in the 17th ordinance

(17. BImSchV) as 10 mg/Nm³ with 10 % de O₂ for a daily average and 60 mg/Nm³ with 10 % de O₂ for a half-hourly average (GERMANY, 2013). In the United States, the Environmental Protection Agency sets it to a more stringent concentration of 3 ppmv (Dry basis and 7 % O₂).

TABLE 6: INVENTORY OF HCl EMISSION STANDARDS IN DIFFERENT COUNTRIES

Country	Maximum Chlorine content
Brazil (CONAMA N° 264/1999)	1.8 kg/h or 99 % reduction
European Union (DIRECTIVE 2010/75/EU)	10 mg/Nm ³ with 10 % de O ₂ (Daily average)
Germany (17. BImSchV)	- 10 mg/Nm ³ with 10 % de O ₂ (Daily average) - 60 mg/Nm ³ with 10 % de O ₂ (Half-hour average)
United States (NESHAP)	3 ppmvd with 7 % O ₂

SOURCE: adapted from BRASIL (1999), EU (2010), GERMANY (2013), EPA (2017)

Concerning the emission standards on state level, a certain divergence can be noticed. Some states like Rio Grande do Sul, Minas Gerais or Paraná have adopted the same federal limits. In Paraná and Minas Gerais, a new condition was added to the 2nd standard (PARANÁ, 2014) (MINAS GERAIS, 2010) (Table 7).

TABLE 7: INVENTORY OF HCl EMISSION STANDARDS IN DIFFERENT BRAZILIAN STATES

Brazilian state	Maximum Chlorine content
Rio Grande do Sul (CONSEMA N° 02/2000)	1.8 kg HCl/ h or 99 % removal
Paraná (SEMA N° 016/2014)	1.8 kg HCl/ h or 99 % removal of HCl for residues with more than 0,5 % chlorine content
Minas Gerais (COPAM N° 154/2010)	1.8 kg HCl/ h or 99 % removal of HCl for residues with more than 0,5 % chlorine content
São Paulo (SMA N° 38/2017)	10 mg/Nm ³ with 10 % de O ₂ (correction factor)

SOURCE: adapted from RIO GRANDE DO SUL (2000), PARANÁ (2014), MINAS GERAIS (2010), SÃO PAULO (2017)

With the new condition in Paraná, cement plants that co-process waste containing more than 0.5 % chlorine are obliged to achieve a 99 % reduction efficiency of HCl. São Paulo on the other hand, chose to follow the European norm set to 10 mg/Nm³ with 10 % de O₂ correction factor (EU, 2010) (São Paulo, 2017).

4.2.2 Dioxins and furans emission standards

The Brazilian federal standard related to dioxins and furans referred to 11 % O₂ correction factor is 4 times higher than the European and the American standards (Table 8). It should be mentioned that Brazil and the US are using the same TEF whereas Germany is using the WHO-TEF 2005.

TABLE 8: INVENTORY OF DIFFERENT PCDD/F EMISSION STANDARDS

Country	Maximum Chlorine content
Brazil (Standards mentioned in Federal resolution CONAMA N° 316/2002 and not in CONAMA N° 264/99)	0.5 TEQ ng/Nm ³ with 7 % de O ₂ = 0.5/1,4= 0.36 ng/Nm ³ (expressed in TEQ of 2,3,7,8 TCDD) with 11 % de O ₂
European Union (DIRECTIVE 2010/75/EU)	0.1 TEQ ng/Nm ³ with 11 % O ₂ correction factor
Germany (17. BImSchV)	0.1 ng TEQ /Nm ³ with 11 % O ₂ correction factor
United States (NESHAP)	0.1 ng TEQ /Nm ³ with 11 % O ₂ correction factor

*TEF: Annex 1

SOURCE: adapted from BRASIL (2002), EU (2010), GERMANY (2013), EPA (2017)

On state level, the states of São Paulo and Paraná are more restrictive with the standard of 0.1 ng/Nm³ with 11 % O₂ correction factor. Whereas the state of Rio Grande do Sul still follows the old federal limit (Table 9).

TABLE 9: INVENTORY OF PCDD/F EMISSION STANDARDS IN DIFFERENT BRAZILIAN STATES

Brazilian State	Maximum Chlorine content
São Paulo (SMA N° 38/2017)	0.1 ng TEQ/Nm ³ with 11 % O ₂ correction factor
Paraná (SEMA N° 016/2014)	0.14 ng TEQ/Nm ³ with 11 % O ₂ correction factor
Rio Grande do Sul (CONSEMA N° 02/2000)	0.5 ng TEQ/Nm ³ with 7 % de O ₂ = 0.5/1.4= 0.38 ng TEQ/Nm ³ with 11 % de O ₂
Minas Gerais (COPAM N° 154/2010)	Not mentioned

SOURCE: adapted from SÃO PAULO (2017), PARANÁ (2014), RIO GRANDE DO SUL (2000), MINAS GERAIS (2010)

The European Integrated Pollution Prevention and Control Bureau states that most cement kilns can meet the 0.1 ng TEQ /Nm³ Referred to European toxicity

equivalents if primary techniques are applied. These recommended techniques include:

- Including a computer-based automatic control system to optimize the process control;
- Incorporating modern fuel feed systems to the kiln system;
- Avoiding waste fuel feeding during start-ups and shutdowns;
- Selection and use of homogeneous raw materials and fuels with a low content of sulphur, nitrogen, chlorine, metals and volatile organic compounds, if practicable.

However, if elevated concentrations of PCDD/PCDF occur, adsorption on activated carbon can be considered. (EIPPCB, 2013)

4.3 ANALYSIS OF PERMITTED CHLORINE CONTENT IN SOLID RECOVERED FUEL FOR CO-PROCESSING

The European Committee of Standardization considers chlorine content in the SRF as a technical parameter, not as an environmental parameter like mercury content (CEN, 2005). This is mainly because high chlorine content causes operational problems inside the cement kiln like encrustations, clogging in the preheater tower and kiln shell corrosion. Furthermore, the classification set by the technical specification of CEN/TS 15359 is not restrictive. It does not forbid the use of any of the classes of waste. The cement plants should consider their design and operating conditions and have a more detailed description of the fuel to decide upon which classes to work with.

Typical chlorine concentrations in Europe range from 0.5 to 2 % .Certain European countries such as France, Spain and Austria are giving licenses limiting the SRF chlorine input to 2 %. However, operators usually do not exceed 1 % in order to meet the specification for chlorine content in the manufactured cement set to 0.1 %. In Germany, there is no explicit limitation on chlorine content. Each cement plant is treated independently by the authorities. The only restriction on chlorine is observed at the output in the emission concentrations. In Brazil, the Federal Resolution CONAMA N° 264/1999 also does not express any limitation on the chlorine content of the SRF (Table 10).

TABLE 10: INVENTORY OF DIFFERENT PERMITTED CHLORINE CONTENT FOR SRF

Country	Maximum chlorine content
Brazil	No explicit limitation
European Union	No limitation (only classification of SRF quality according to chlorine content)
Germany	No limitation (Each case is treated independently by relevant authorities)
France, Spain, Austria	2 %

SOURCE: adapted from EIPPCB (2013)

Some Brazilian states introduced their own limits (Table 11).

TABLE 11: INVENTORY OF PERMITTED CHLORINE CONTENT FOR SRF IN DIFFERENT BRAZILIAN STATES

Brazilian state	Maximum chlorine content
Paraná (SEMA N° 16/2014)	0.5 % (The interpretation of IAP of 99 % HCl removal efficiency for residues with more than 0.5 % chlorine content)
São Paulo (SMA N° 38/2017)	1 %
Rio Grande do Sul	No limitation
Minas Gerais	No limitation

SOURCE: adapted from SÃO PAULO (2017), RIO GRANDE DO SUL (2000), MINAS GERAIS (2010)

In São Paulo, the Resolution SMA 38/2017 (SÃO PAULO, 2017) sets the chlorine content limit to 1 %. In Paraná, no explicit limit about chlorine content in SRF is mentioned in the Resolution SEMA 16/2014 (PARANÁ, 2014). The only chlorine restriction appears as 99 % removal efficiency for residues with more than 0.5 % chlorine content; however, the state environmental agency (IAP) interprets this condition on HCl emissions as limiting the chlorine content of SRF to 0.5 %. This limit is applied to each fraction composing the SRF even if the percentage of the whole blend does not violate this limit.

This condition expressed by IAP can be frustrating for some cement plants, especially that many kilns are able to co-process waste with more chlorine content without any difficulty. It is not only limiting the thermal substitution rate that might save a lot of fossil fuel, but also wasting a possibility to recover the non-recyclable residues

as a fuel and raw material. In Europe, some individual cement plants recovered SRF, which replaces fossil fuels with a level more than 80 %. In Brazil, the thermal substitution rate reported by ABCP in 2016 was 9.7 %.

Furthermore, this limitation is not required since cement plants have to comply with rigorous HCL and PCDD/F emission standards. Moreover, they are obliged to assure a good quality cement with chlorine content far from 0.1 % due to analysis uncertainties.

4.4 ANALYSIS OF MASS BALANCE OF CHLORINE INSIDE A CEMENT KILN IN PARANÁ

Data concerning chlorine inputs in raw meal, fuel and SRF along with HCl emission rates and chlorine in the clinker were obtained from the last available reports of kiln W2 of CIA Cimento Itambé. Using these values, it was possible to make a chlorine mass balance with the percentage contained in every input (Table 12). The removal efficiency is calculated as the HCl mass emission rate divided by the total chlorine hourly input. In the table 12, it is expressed as retention.

The monitoring of HCl is done normally on a semestral basis and the reported value is expressed as the mean of the measurements of three consequential days. Nevertheless, only one set of values representing one semester of the year was available in the open-access monitoring reports. It is important to mention that the kiln N° 3 of CIA Cimento Itambé is more sophisticated than the kiln N° 2 and is more adapted to co-processing SRF with higher chlorine content. Unfortunately, data from the new kiln N°3 were not yet available.

TABLE 12: CHLORINE MASS BALANCE AND REMOVAL EFFICIENCY IN KILN W2 OF CIA CIMENTO ITAMBÉ

1st Semester 2010																
	INPUT						OUTPUT						RETENTION EFFICIENCY**			
	RAW MEAL			COKE			RESIDUE		SUM OF INPUT MASS	CLINKER		HCl EMISSION*		CHLORINE MASS DIFFERENCE (IN-OUT)		
MASS(t/h)	146,72		9,08	8,65	164,45	94,17										
Cl'	mg/kg 97	kg/h 14,23	mg/kg 64	kg/h 0,01	mg/kg 4118	% 0,01	kg/h 0,58	% 0,41	kg/h 35,62	kg/h 50,43	mg/kg X	kg/h X	kg/h 0,05	kg/h X	% 99,90	
2nd Semester 2011																
	INPUT						OUTPUT						RETENTION EFFICIENCY**			
	RAW MEAL			COKE			RESIDUE		SUM OF INPUT MASS	CLINKER		HCl EMISSION*		CHLORINE MASS DIFFERENCE (IN-OUT)		
MASS(t/h)	145,25		9	7,45	161,7	93,25										
Cl'	mg/kg 118	kg/h 17,14	mg/kg 119	% 0,01	kg/h 1,07	mg/kg 2055	% 0,21	kg/h 15,31	kg/h 33,52	mg/kg 200	kg/h 0,43	kg/h 14,47	kg/h 14,47	% 98,72		
2nd Semester 2012																
	INPUT						OUTPUT						RETENTION EFFICIENCY**			
	RAW MEAL			COKE			RESIDUE		SUM OF INPUT MASS	CLINKER		HCl EMISSION*		CHLORINE MASS DIFFERENCE (IN-OUT)		
MASS(t/h)	136,42		8,17	9,38	153,97	87,6										
Cl'	mg/kg 794	kg/h 108,32	mg/kg 132	% 0,01	kg/h 1,08	mg/kg 3187	% 0,32	kg/h 29,89	kg/h 139,29	mg/kg 451	kg/h 0,01	kg/h 99,80	kg/h 99,80	% 99,99		
1st Semester 2013																
	INPUT						OUTPUT						RETENTION EFFICIENCY**			
	RAW MEAL			COKE			RESIDUE		SUM OF INPUT MASS	CLINKER		HCl EMISSION*		CHLORINE MASS DIFFERENCE (IN-OUT)		
MASS(t/h)	142,75		7,35	7,3	157,4	91,24										
Cl'	mg/kg 263	kg/h 37,54	mg/kg 26	% 0,00	kg/h 0,19	mg/kg 5222	% 0,52	kg/h 38,12	kg/h 75,85	mg/kg 1709	kg/h 0,16	kg/h -80,00	kg/h -80,00	% 99,79		

* HCl emission limit in SEMA N° 16/14 is 1,8 kg/h

** The minimum retention efficiency in SEMA N° 16/14 is 99%

Table 12 illustrates a noticeable variation in the chlorine content of the different inputs. In 2012, there was a maximum chlorine content in the raw meal attaining 108.3 kg/h compared to 14.2 kg/h in 2010. Besides that, the contribution of chlorine in the raw meal is sometimes even much higher than the SRF. The same variation was also observed in the fuel. However, the chlorine content in the fuel is highly negligible compared to the other inputs.

From the mass balance, it can be noticed that there is a large gap between the input of chlorine and the output measured in the clinker or as HCl emissions. In 2011, there is a difference of 14.44 kg of Cl and in 2012, the difference attains 99.8 kg of Cl. Unless there is a problem with the measurements, the missing chlorine is whether trapped in the kiln dust or accumulated in the kiln adding to the previous enrichment cycles. In this last case, chlorine stays inside the kiln whether in its volatile form or deposits in the form of encrustations when equilibrium is reached. However, in 2013, the output in the clinker is highly superior to the sum of the inputs. It may be inferred that the clinker incorporated chlorine from previous internal or external cycles. In this case, the clinker does not comply with the limit of 0.1 %.

Concerning the SRF, percentages from 0.22 % to 0.52 % were used during this period. Even though the SRF with the lowest chlorine content was used in 2011, the emission was the highest among all the other years. This explains that HCl emissions from cement kilns are mostly dependent on the operating conditions and the treatment efficiency of the exhaust gas. In 2010 and 2012, respective HCl emissions of 0.05 kg/h and 0.01 kg/h were measured. Compared to the standard of 1.8 kg/h, those values are very negligible, which reflects the kiln ability to destroy chlorinated compounds. Concerning the removal efficiencies of chlorine, only in 2011, the 99 % standard stated by the Brazilian legislation was not verified.

In conclusion, it was confirmed that the raw meal brings an important chlorine input that is sometimes even higher than the SRF contribution. In addition, HCl emissions showed a high variability. However, the amount of chlorine entering the cement kiln is not enough to justify the resulting HCl emissions. An important amount of chlorine accumulates in the kiln or leaves with the kiln dust. In both cases, it was not really destructed and should not be considered as a removal. Eventually, high amounts of chlorine will incorporate in the clinker threatening the quality of the cement product.

5 CONCLUSION

Chlorine is a highly influential volatile compound in the cement preheater-kiln system even before the use of co-processing. It is present at variable amounts in all the inputs, namely the raw meal, the fuel and the SRF. Chlorine is responsible mainly for technical problems inside the preheater-kiln system affecting the process stability and operation. High inputs of chlorine lead to the formation of sticky molten salts that glue to the walls of the kiln and crystallize. As a direct consequence of these encrustations, pressure loss across the system increases and the maximum kiln draft is restricted. In the worst cases, frequent kiln stops are to be expected leading to higher heat consumption and reduction of the maximum clinker production.

Chlorine is considered as a co-processing technical parameter and not as an environmental parameter like Mercury from the European committee of Standardization. Thus, each cement plant should consider their design and operating conditions and have a more detailed description of the SRF to decide upon which chlorine content to work with. Besides, the maximum amount of chlorine in the clinker is another restriction for cement plants. Therefore, they are obliged to control the chlorine in the clinker burning process to comply with the allowed percentage in the final product.

A general limitation of chlorine content in the SRF input is only hindering cement plants from using the full co-processing potential of their kiln systems. It is restricting the amount and composition of SRF that could substitute the fossil fuel. In Europe, some cement plants recovered SRF, which replaced fossil fuels with a level more than 80 %. In Brazil, the average thermal substitution rate reported by ABCP in 2016 was 9.7 %. Many of the non-recyclable waste fractions find easily their way to landfilling in the absence of a recovery possibility such as co-processing.

Hazardous emissions such as PCDD/F or HCl can be largely ruled out during the process of cement manufacturing. This is due mainly to the highly alkaline atmosphere inside the kiln. In addition, residence time and temperature distribution in rotary kilns offer particularly favorable conditions for such compounds to be destroyed. Several research studies showed that under good operation conditions, dioxin emissions remained below 0.1 ng TEQ Nm⁻³. Limiting the SRF chlorine content does not necessarily reduce HCl or PCDD/F emissions. It depends mostly on the kiln design,

the operation conditions, the presence of a by-pass system and the exhaust gas treatment installations.

By-pass installations are an efficient technique for cement plants to achieve higher SRF substitution rates and chlorine contents. It reduces the high internal recirculation of volatile compounds and thus prevents encrustations and reduces HCl emissions. However, higher power and heat consumption along with material loss are to be expected. Furthermore, the by-pass dust must be discarded as hazardous waste due to high chlorine and alkalis content. A new technology suggests extracting the enriching elements in the form of salts and reintroducing the rest of the dust to the cement kiln. However, this method also requires additional costs from the cement plant.

Brazilian Federal standards related to chlorine combustion emissions during co-processing are found in the Federal Resolution CONAMA N° 264 that dates from 19 years ago. Concerning HCl standards, cement plants should emit less than 1.8 kg/h or achieve 99 % HCl removal efficiency. In addition to being very high, the emission rate of 1.8 kg/h does not take into account the production capacity of the cement plant. Furthermore, the 99 % removal efficiency requires the integration of a by-pass system or very efficient treatment installation of the kiln exhaust gas. It also supposes that, chlorine accumulated in the kiln or leaving with the kiln dust is removed. In Paraná, the standards for HCl emissions from the state Resolution SEMA N° 16/2014 are following the Federal standard with an additional condition on chlorine content (1.8 kg/h or 99 % removal efficiency if the SRF chlorine content is more than 0.5 %). This condition is subject to a different interpretation from the environmental Agency of Paraná (IAP), which forbids for the time being using SRF with chlorine content superior to 0.5 %. The state of São Paulo in its Resolution SMA N° 038/2017 already chose to follow the stringent European norm set to 10 mg/Nm³ with 10 % O₂.

PCDD/F Federal emission standard is found in CONAMA N° 316/2002 and not mentioned in CONAMA 264/1999, it is set to 0.5 TEQ ng/Nm³ with 7 % de O₂, which is equivalent to 0.36 ng TEQ /Nm³ with 11 % de O₂. Compared to the European or American standard set to 0.1 ng TEQ /Nm³ with 11 % O₂ correction factor, the standard is high for such dangerous compounds. Some States like Paraná or São Paulo already moved a step ahead following the limit of 0.1 ng/Nm³.

Taking into consideration that:

- the chlorine quantity entering the cement kiln is restricted due to eventual technical problems and degradation of the clinker quality with excess chlorine content (maximum acceptable limit is set to 0.1 % (CEN, 2000));
- if the cement plant plans to insert input materials with high chlorine content, the process should be configured so that technical and environmental problems are avoided. For example, the use of technologies to control the internal enrichment cycles of chlorine in the preheater-kiln system (for instance, bypass installation);
- the international legislations are converging to a global standardization of atmospheric emissions limits;

It is suggested to:

- limit the chlorine emission standard expressed as HCl to one concentration of 10 mg/Nm³ with 10 % O₂ expressed as a daily average with continuous monitoring.
- limit the dioxins and furans emission standard to 0.1 TEQ ng/Nm³ with 11 % O₂. The monitoring could be annual. In this case, a burning test of every used SRF should be carried out.
- avoid a general limitation of the alternative fuel chlorine content. Each cement plant should be considered individually depending on the characteristics of the kiln-preheater system.

To conclude, the Brazilian Federal legislation concerning co-processing is old and needs to be updated as soon as possible. An inclusion of leading experienced professionals from the cement industry is very important to ensure realistic and unambiguous regulations.

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**ANNEX 1: CURRENT TOXICITY EQUIVALENT FACTORS FOR DIOXINS AND
FURANS FOR BRAZIL, GERMANY AND USA**

Dioxins/furans	TEF (Germany)	TEF (USA and Brazil)
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	0.5
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0003	0.001
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.03	0.05
2,3,4,7,8-PeCDF	0.3	0.5
1,2,3,4,7,8-HxCDF.	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF.	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0003	0.001

SOURCE: Adapted from CONAMA (2002), NESHAP (2017), 17th BImSchV (2013).