

SECTION 3 ENVIRONMENTAL ASPECTS OF SECONDARY MATERIALS CO-PROCESSING IN THE MAKING OF CEMENT

This section provides further details of the proposed activity, shows why waste materials can be combusted in cement kilns, and the outputs that may result from the addition of secondary materials. The applicable international legislation applied to regulate the use of waste materials in cement is also discussed. As waste materials have been used to supplement coal for the firing of the cement kiln for approximately three decades, international trends are therefore included in this section, as well as PPC's experience with secondary materials.

3.1 INTRODUCTION TO SECONDARY MATERIALS CO-PROCESSING

Many waste products contain energy. This energy can be recovered by the combustion of the waste materials (whole or in some other form) as additional fuel sources. It is considered accepted international practice in the cement industry to substitute some of the primary fuel (coal) with waste materials.

3.1.1 Why is the Cement Kiln Suitable for Co-Processing of Secondary Materials?

a) High Temperature, Long Residence Time and Effective Mixing

It is internationally accepted that the efficiency of thermal treatment of hazardous waste is dependent on the three T's:

- i) Temperature;
- ii) Time (i.e. residence time of the waste at the highest temperature), and
- iii) Turbulence (i.e. mixing of wastes and mixing of the waste with the surrounding air).

Temperature

To ensure the destruction of organic compounds, extremely high temperatures are required. Halogenated compounds (those containing compounds such as bromine, chlorine, fluorine or iodine) are destroyed at temperatures of 1,200°C; whereas non-halogenated compounds (those without bromine, chlorine, fluorine or iodine) require slightly lower temperatures of 1,000°C for complete destruction. Hazardous waste incinerators are designed to meet these requirements and operate at temperatures between 650°C and 1,260°C.

As noted previously, the material in the cement kiln reaches a temperature of 1,450°C in the Sintering zone, which requires a flame temperature of 2,000°C. Hence the kiln is operated at higher temperatures than those required to destroy both non-halogenated and halogenated organic compounds.

Time

A residence time of 2 seconds inside a waste incinerator is necessary to ensure complete destruction of these organic substances. Inside the cement kiln, they would be exposed to temperatures higher than 1,000°C for at least 5 seconds. These residence times are more than adequate for total destruction of organic compounds.

Turbulence

In addition, the kiln is constantly rotating, and is subject to a strong air current through the kiln thereby providing an environment of excess oxygen. Maximum mixing, therefore, of the waste with the raw materials, as well as between the waste and the air and provision of sufficient oxygen, are ensured for optimal destruction efficiencies.

b) Minimisation of Waste

When wastes are incinerated in a hazardous waste incinerator, further waste is generated in the form of ash. This ash is classified as a hazardous waste and must be disposed of in an appropriate manner – usually, it is transported to a hazardous waste landfill site.

The ash generated from the burning of coal and/or secondary materials in the cement process remains in the kiln (i.e. where the waste is burned) it is incorporated into the clinker. No solid waste is therefore generated during the cement manufacturing process as a result of the addition of secondary materials. Any other solid by-products that may be formed as a result of the secondary materials in the kiln are also incorporated into the clinker and then into the final cement product.

c) Thermal Stability

Because the cement kiln is a large manufacturing unit with a high heat capacity, the temperature remains relatively constant and brief temperature drops are not possible during normal operation. During upset conditions, it is an industry norm that the feed of secondary materials to the kiln is discontinued immediately, with the kiln retaining its heat for sufficient time to destroy any remaining organic materials resident in the kiln. Thus emissions from partially combusted secondary materials are avoided.

The chemistry of the feed material and the kiln is alkaline and any acidic materials are effectively neutralised.

3.1.2 International use of Secondary Materials

In the 1970's, cement manufacturers and waste producers in the US and Europe began to investigate the possibility of the use of secondary materials in cement kilns. This was done to solve two problems: the waste producers were seeking an alternative to landfilling or incineration for the disposal of waste solvents, while the cement industry needed to reduce its energy costs.

Trials were conducted to identify any environmental issues that would arise from burning coal combined with a waste stream. The common practice was to replace 30 – 40% of the coal with waste. The preliminary investigations showed that burning secondary materials did not increase the impact of the emissions on the environment and public health. The process also offered the benefit of reducing the environmental impacts associated with landfills and incinerators. In the early 1980s, fears arose over dioxin emissions, and environmental groups began campaigning against the use of secondary materials in cement kilns. The US Environmental Protection Agency (EPA) responded by conducting more research on emissions and on the risks posed by cement kiln dust (CKD).

On the whole, international data has shown that there are sufficient advantages (from an environmental perspective) to warrant supplementing coal with secondary materials in cement kilns.

At present, the United States generates more than 5 million tons annually of organic hazardous waste that requires thermal treatment for destruction. The cement industry currently uses over one million tons of hazardous waste a year as an alternative fuel, which replaces expensive and non-renewable fossil coal resources. Companies currently using secondary materials and supplementary waste streams in Europe and the United States are listed below. These represent the major cement companies operating today in the world, outside of China.

- Ash Grove Cement (USA)
- Cementos Molins (Spain)
- Cemex (Mexico)
- Heidelberg Cement (Germany)
- Holcim (Switzerland)
- Lafarge (France)
- Secil (Portugal)
- Shree Cement (India)
- Siam Cement (Thailand)
- Taiheiyo (Japan)

- Italcementi (Italy)
- Lafarge (France)
- Secil (Portugal)
- Shree Cement (India)
- Titan (Greece)
- Uniland (Spain)
- Votorantim (Brazil).

The World Business Council on Sustainable Development acknowledges that the cement industry plays a key role in meeting society's needs for housing and basic infrastructure by supplying concrete. The industry employs about 850,000 workers in facilities in 150 countries, producing about 1.5 billion tons of cement a year. It has an estimated annual turnover of \$87 billion and has grown by nearly 4 percent a year over the past decade.

Cement production is energy-intensive - it accounts for 5 percent of global carbon dioxide emissions - and it touches on a wide range of sustainability issues including:

- Climate change;
- Pollution;
- Resource depletion, and
- Worker health and safety.

Selected hazardous wastes are being burned extremely successfully as fuels in more than 25 cement kilns in the USA. Our literature review identified the following quoted advantages to cement kilns over incinerators:

- a) The high temperatures (up to 1,450°C) that are reached in order to manufacture the cement clinker;
- b) The long gas residence times (up to 6 seconds);
- c) The automatic scrubbing of noxious gases such as hydrogen chloride from the gas stream by the alkaline conditions in the kiln;
- d) The savings in conventional fuel such as coal;
- e) Because they are existing facilities, there is usually less public opposition to their siting, and
- f) The capital expenditure required is only about 10% of that needed to build a dedicated chemical incinerator.

There are disadvantages, however, which include the following:

- a) Only limited amounts of certain hazardous substances, such as metals, sulphur, and chlorine, can be added;
- b) Pre-treatment of waste streams is often necessary due to the following:
 - i) Due to their effect on the operation of the kiln or on the quality of the clinker;
 - ii) Because of the increase in the cost of monitoring the stack gases, and
 - iii) Because the waste used in kilns should preferably have a reasonable calorific value.

Commonly utilized secondary materials at cement facilities worldwide are shown in Table 3.1. As can be seen, the majority of possible secondary materials can be classified as hazardous waste (which is defined as being a material which poses a potential threat to health or to the environment through one of the following outcomes:

- a) An explosion or fire;

- b) Chemical reaction, which could also lead to an explosion (some household cleaning agents or swimming pool chemicals are examples);
- c) Accumulation in food chains or persistence in the environment (accumulation of lead or mercury are examples), and
- d) Infection and toxicity (contamination of a drinking water supply – particularly an underground source – could occur through leaching from material dumped on the ground)).

Table 3-1: Typical Secondary Fuels in the manufacture of Portland Cement⁶

Solid Secondary Fuels		Liquid Secondary Fuels	Gaseous Secondary Fuels
Paper wastes	Wood wastes (bark, shavings, sawdust)	Tar	Landfill gas
Paper industry wastes	Rice chaff	Acid sludge	Pyrolysis gas
Petroleum coke	Olive kernels	Used oil	
Graphite dust	Coconut shells	Petrochemical wastes	
Charcoal	Household refuse	Paint industry wastes	
Plastics residues	Refuse-derived fuel	Chemical wastes	
Rubber residues	Shredding	Solvent wastes	
Old tyres	Oil-bearing earths	Distillation residues	
Battery cases	Sewage sludge	Wax suspensions	
Activated bentonite		Asphalt slurry	
Spent pot lining (also secondary fuel)		Oil sludge	

3.1.3 International Trends

In some countries, the cement industry provides a public or industrial service by disposing of wastes even though they contain little or no useful energy or mineral content⁷. This may be done at the request of national governments or in response to local demand. This is possible because a cement kiln provides:

- a) High temperatures;
- b) Long residence time, and
- c) A carefully controlled facility capable of high destruction efficiency.

This activity, i.e. accepting problematic waste streams on request from government, is not part of the normal fuel or raw material substitution process and is not part of this EIA application process.

Cement kilns have been used in this way for many years in countries such as Japan, Norway, and Switzerland, where there is little space for landfill sites. In Norway, PCBs have been disposed of in this way for more than ten years. More recently, modern kilns have been used for waste disposal in some developing countries where the lack of existing waste disposal and incineration infrastructure means that kilns are the most economical option. Even where good waste disposal infrastructure exists, it may be useful to increase local capacity through use of cement kilns.

⁶ Krefit, W.:Einsatz von Abfallstoffen als Energie- und Rohstoffersatz bei der Zementherstellung. TIZ, vol 112 (1988)No.2, pp. 123-127.

⁷ World Business Council on Sustainable Development: Guidelines to the Selection and Use of Fuels and Raw Materials in the Cement Making Process, Dec 2005

The substitution of fossil fuels and virgin raw materials with alternatives is a well-developed practice in a number of countries. Some countries have been co-processing secondary materials for almost 30 years, and some national governments actively promote this approach. In a number of countries this practice is well understood and highly developed (see Table 3.2 below.) Furthermore, in several instances, cement kiln disposal has been requested by governments:

- a) Disposal of ruminant by-product material infected with mad-cow disease in Europe and Japan⁸;
- b) 300,000 tonnes of contaminated soil was disposed to Holcim's kilns at Obourg and Rochefort following an oil spill from Erika, an oil tanker that crashed off France's coast in December 1999⁹, and
- c) The European Commission's Landfill Directive to ban the disposal of whole tyres to landfill by 2003, and shredded tyres by 2006. Some 450,000 tonnes of waste tyres are generated each year in the United Kingdom. Accordingly, more reuse, material recycling and energy recovery options are needed. To this end, the use of tyres as a fuel in cement kilns is an important outlet for waste tyres in the U.K. The Directive notes that burning tyres in cement kilns often has a net environmental benefit when compared to conventional fuels, which are usually coal and petroleum coke¹⁰.

The types of fuel substitution that were occurring in 2001 are listed in Table 3-2. Types of Alternative Materials reported by the WBCSD as in use in 2002 include:

- a) Blast furnace slag;
- b) Fly ash (coal ash);
- c) By-product gypsum;
- d) Steel manufacturing slag;
- e) Nonferrous slag, and
- f) Coal tailings, dirt, sludge, etc.

The total tonnage used in Japan is given in Table 3-4.

Table 3-2: Recent patterns in use of alternative fuels

Country or Region	% Thermal Substitution
Netherlands	83
Switzerland	47.8
Austria	46
Norway	35
France	34.1
Belgium	30
Germany	42
Sweden	29
Luxembourg	25
Czech Republic	24
EU (prior to expansion in 2004)	12
Japan	10
United States	8

⁸ Green Source, 1/23/2006

⁹ <http://www.holcim.com/CORP/EN/id/51567/mod/gnm50/page/editorial.html>

¹⁰ WMCSO : *Industrial Ecology in the Cement Industry*, March 2002.

Country or Region	% Thermal Substitution
Australia	6
United Kingdom	6
Denmark	4
Hungary	3
Finland	3
Italy	2.1
Spain	1.3
Poland	1
Ireland	0
Portugal	0
Greece	<1%

Table 3-3: Types of Alternative Fuels (2001) according to the WBCSD

Type of Fuel	Quantity in kT
Solid fuels (80%)	3,532
Meat and bone meal & animal fat	890
Other wastes	788
Tyres	554
Plastics	210
Paper/cardboard/wood	180
Impregnated saw dust	167
Coal slurries/distillation residues	112
Sludge (paper fiber, sewage)	107
Fine/anodes/chemical cokes	89
Refuse derived fuels	41
Shale/oil shales	14
Packaging waste	12
Agricultural and organic waste	11
Liquid fuels (20%)	841
Waste oil + oiled water	402
Solvents and others	266
Other hazardous liquid fuels	173

Table 3-4: Alternative Fuels and Raw Materials in the Japanese Cement Industry (thousand tons)¹¹

Item	1999	2000	2001	2002	2003
Blast furnace slag	11,449	12,162	11,915	10,474	10,173
Coal ashes	4,551	5,145	5,822	6,320	6,429
By-product Gypsum	2,567	2,463	2,568	2,556	2,530
Waste tires	28	323	284	253	230
Waste oil	250	239	204	252	238
Waste plastics	58	102	171	211	255
Wood chips	0.0	2	20	149	271
Others	6,423	6,923	7,077	7,023	7,438
Total	25,584	27,359	28,061	27,238	27,564

3.1.4 Specified limits on Secondary Material Inputs

Since the inception of the utilization of secondary materials in cement kiln in the 1970's, various limitations on the limits of elements and compounds in these material has been established, both self-regulatory or by national legislation.¹²

For example, all the Polish cement plants owned by Lafarge have the following specific requirements of secondary materials imposed upon them:

- Calorific value of over 14 MJ/kg (weekly average) and 11.7 MJ/kg (daily average),
- Chlorine content of less than 0.5%,
- Sulphur content of less than 2.5%,
- PCBs (polychlorinated benzenes) content of less than 5 ppm, and
- Metal content of less than 2,500 ppm (mercury less than 10 ppm, cadmium + thallium + mercury less than 100 ppm).

When a plant is being supplied with an alternative fuel, whether liquid or solid, it is also very important to observe other factors such as: self-ignition point, humidity content, ash content, grain composition, etc.¹³ Table 3-5 illustrates legislative limits for some developed countries in Europe.

Table 3-5: Example Limits on Compounds for Secondary Materials in Cement Kilns

Parameter	Unit	Spain ¹⁴	Belgium	France	Switzerland ¹⁵
TOC	mg/kg	2%	5000	5000	-
Total halogens (as Cl)	%	0,25	0,5	0,5	-
F	%	0,1	-	-	-
S	%	3	1	1	-
Hg	mg/kg	10	-	-	0.5
Cd	mg/kg	100	-	-	0.8

¹¹ Yoshito Izumi, Ph.D., Japan Cement Association & Taiheiyo Cement Corporation, Dec. 1, 2005

¹² Various sources per Annex 8-Guidelines on Co-processing Waste Materials in Cement Production: L Timberlake 2003

¹³ Mokrzycki E., et al. Alternative fuels for the cement industry Wydawnictwo IGSMiE PAN, Kraków 2004.

¹⁴ Limit values set by authorities for individual permits for specific cement plants in Spain, Belgium and France

¹⁵ Limit values for alternative raw materials, BUWAL 1998. Guidelines Disposal of Wastes in Cement plants, Table 1

Parameter	Unit	Spain ¹⁴	Belgium	France	Switzerland ¹⁵
TI	mg/kg	100	-	-	1
Sum Hg + Cd + TI	mg/kg	100	-	-	-
Sb	mg/kg	-	-	-	1
Sum Sb+As+ Co+Ni+Pb+ Sn+V+ Cr	mg/kg	0,50%	-	-	-
As	mg/kg	-	-	-	20
Co	mg/kg	-	-	-	30
Ni	mg/kg	-	-	-	100
Cu	mg/kg	-	-	-	100
Cr	mg/kg	-	-	-	100
V	mg/kg	-	-	-	200
Pb	mg/kg	-	-	-	50
Sn	mg/kg	-	-	-	50
Mn	mg/kg	-	-	-	-
Be	mg/kg	-	-	-	3
Se	mg/kg	-	-	-	1
Te	mg/kg	-	-	-	-
Zn	mg/kg	-	-	-	400
PCBs	mg/kg	30	-	-	1
Br+I	mg/kg	-	-	-	-
Cyanide	mg/kg	-	-	-	-

3.1.5 Use of Secondary Materials at PPC

In South Africa, PPC was the first cement company to investigate the feasibility of the use of secondary materials including waste material as a fuel supplement. Feasibility and Environmental Impact studies were carried out at the Jupiter cement manufacturing plant in Johannesburg in the 1990s and are discussed in more detail in Sections 9.8 to 9.12. Trial burns with chemical waste were also conducted and these showed that the addition of these secondary and waste materials had no negative effect on the stack emissions or on the health risk to the surrounding community. These trials also showed that the quality of the cement was not compromised. However, PPC did not continue the use of secondary materials at the Jupiter kiln due to temporary closure of the Jupiter kiln operation, due to low market demand.

The Jupiter factory was re-commissioned for production in 2006, but has not continued the use of secondary materials and is not included in this EIA. PPC does, however, use spent pot lining (SPL) as a secondary material in some of its kilns.

3.2 EMISSIONS TO ATMOSPHERE

The emissions leaving the process are the largest potential source of environmental impact from the process for the following reasons:

- a) The reactions occurring in the kiln consume fuel;
- b) These reactions cause a change in the chemical structure of the raw materials at high temperatures; and
- c) The physical removal of particulates occurs only after the kiln (i.e. no chemical treatment of the emissions occurs).

The emissions from cement plants that are of significance are nitrogen oxides (NO_x), sulphur dioxide (SO₂) and dust. Other important emissions include carbon dioxide (CO₂), carbon monoxide (CO), volatile organic compounds (VOC), dioxins (PCDD's), furans (PCDF's), and metals.

The environmental effects of these emissions are of two principal categories:

- a) Community Health Effects: respiratory impacts and possible toxic and carcinogenic effects may be related to the emissions of dust, CO, metals, VOC's and dioxins and furans.
- b) Environmental Effects: Emissions such as NO_x and SO₂ will contribute to acid deposition (also known as acid rain) in the regional context, and CO₂ to climate change in the global context. VOC's contribute to photochemical smog (subject to ultraviolet radiation degradation), which with dust, will also contribute to a visual impact if dispersion is poor. A minor degree of soil and surface water contamination may occur from dust settling out from the atmosphere. Current dust emissions result predominantly in an insignificant increase in pH of soil and surface water and possible increase in suspended solids in surface water courses. For dust, there may be an increase in metals accompanying the dust and an increase in the dioxins and furans possibly absorbed into the dust. This may result in toxicological (cancer and non-cancer) risks to receiving flora and fauna and the community.

The emission values depend mainly on input materials (raw material and fuel), the temperature profile across the kiln system and the oxygen content during the combustion process. In addition, kiln emissions can be influenced by flame shape and temperature, combustion chamber geometry, the reactivity of the fuel, the presence of moisture, the available reaction time, and the burner design.

Extensive tests, trials and surveys have been conducted since the early 70's in countries such as USA, Japan, France, Belgium, the Netherlands, Germany, Austria and Switzerland to establish the effect on emissions due to the use of secondary materials. These will form the basis of the discussion in the following sections.

3.2.1 Inherent Combustion Gas Cleaning Capability

In all cement kiln systems, the finely ground raw material moves in counter current flow to the hot combustion gases. Thus, the kiln acts as an integrated multi-stage exhaust gas cleaning system very similar to the operating principle of a circulating fluidized bed absorber.

Components resulting from the combustion of the fuels or from the transformation of the raw materials remain in the exhaust gas only until they are absorbed by the fresh raw meal in counter-current flow.

The adsorptive capacity of the material varies with its physical and chemical state. This in turn depends on its position within the kiln system. For instance, material leaving the calcination stage of a kiln process has high calcium oxide content (i.e. alkaline conditions) and therefore has a high absorptive capacity for acid species, such as HCl, HF and SO₂, as well as metals.

Wet kilns and long dry kilns (such as that at PE) provide intimate contact between gas and solid particles mainly at the kiln inlet with chain systems for heat exchange. Suspension preheater kilns with 4 to 6 cyclone stages are especially well suited to achieve a "multi-stage" scrubber effect, particularly when operating together with the raw mill (compound operation). At least 4 scrubber stages operate in series at different temperature levels between 300 and 800° C. This is, however, not the case at the PE factory where no preheater exists.

3.2.2 Nitrogen Oxides (NO_x) Formation

Due to the very high temperatures in the main flame of the rotary kiln, nitrogen oxides are formed by oxidation of molecular nitrogen in the combustion air ("thermal" NO_x¹⁶). Thermal NO_x formation is strongly dependent on the combustion temperature with a marked increase above 1,200° C. "Hard" burning required by certain raw mixes – i.e. at a higher temperature – increases NO_x formation.

¹⁶ NO_x: sum of nitrogen oxides. In cement kiln exhaust gases, NO and NO₂ are dominant (> 90% NO, < 10% NO₂).

While thermal NO_x is the dominant contributor to total NO_x generation, a smaller contribution may also result from nitrogen compounds contained in the fuels which are oxidised in the flame as well (“fuel NO_x”). In the main burner flame, the contribution of fuel NO_x is much lower than that of thermal NO_x.

Natural raw materials such as clays or shale may also contain nitrogen compounds. Part of these compounds may be released and oxidized upon heating in the kiln system and thus contribute considerably to the total NO_x emissions (“raw materials NO_x”). Table 3-6 illustrates the sources of NO_x in a cement kiln.

Table 3-6: Sources of NO_x in a Cement Kiln

Origin	Mechanism
Thermal NO _x	Oxidation of molecular nitrogen in combustion air at T > 1,200° C
Fuel NO _x	Oxidation of organic nitrogen in fuels
Raw Materials NO _x	Oxidation of (in)organic nitrogen in raw material minerals

NO_x formation is reduced if fuel is burnt in a localized reducing atmosphere with low oxygen content in the presence of CO. Operation under reducing conditions is limited due to process requirements of excess oxygen in order to maintain good clinker quality and undisturbed kiln operation.

NO_x emissions in cement kilns (expressed as NO₂) typically vary between 500 and 2,000 mg/Nm³. The formation of nitrogen oxides is an inherent mechanism in a high temperature combustion process such as cement production. It can be influenced to a limited extent only by:

1. Primary reduction measures:
 - a) reduce flame temperature;
 - b) reduce N content in the fuels;
 - c) reduction of primary air in main burner; or
 - d) the introduction of reburning whereby combustion occurs in O₂ starved zones in the presence of CO; and
 - e) Pre-calciner technology.

2. Secondary reduction methods:
 - a) selective non-catalytic reduction (using NH₃); and
 - b) catalytic reduction.

According to MES’s investigations, the impacts of the introduction of secondary materials to a kiln will affect the three NO_x generation mechanisms as follows:

1. The thermal NO_x, i.e. that which is generated in the main flame in the rotary kiln, is reduced if the secondary material utilized has an elevated moisture content or needs a higher excess air factor for optimized combustion. This is the effect of flame cooling.

Cases of increasing thermal NO_x formation with secondary materials were not discovered by MES in a detailed literature survey. Although high temperature at the main burner is the main contributor to the formation of thermal NO_x, this heat is also required to completely destroy unwanted organic substances which may be present in the input material.

2. An increase in fuel NO_x is only possible in cases where the secondary material carries more fuel nitrogen than the conventional fuel.
3. The third factor, raw materials NO_x, only makes a small contribution to the total and the influence of the fuel type is negligible.

PPC's Policy at this stage is not to implement any additional NO_x reduction methods on their existing kilns. For proposed new kilns, such as that at Dwaalboom, international best practice will be implemented by means of low-NO_x calciner technology. This entails the introduction of coal into an oxygen-starved zone in the calciner, before the introduction of hot air (21% O₂) from the cooler. This creates a localised reducing environment conducive to reducing NO_x back to N₂.

Such modifications are not considered feasible for the existing kilns in the PPC Group, i.e. those included in this EIA application such as Port Elizabeth. It is therefore proposed that NO_x reduction is beyond the scope of this EIA, unless the nitrogen content in the fuel is increased significantly. PPC's commitment, however, is to continue with the Secondary Materials project only if the current NO_x emissions levels after introduction of SM are maintained or reduced. In addition, frequent studies have shown that NO_x reduction is normally achieved by the introduction of SM due to the enhanced calorific value of the secondary materials over that of coal (as explained above).

3.2.3 Carbon Monoxide (CO) Formation

Carbon monoxide is an indication of incomplete combustion and is a function of excess air volume and temperature. It is therefore carefully controlled by measurement of CO. Oxygen, CO and NO_x are measured continuously at the back end of the kiln to ensure an excess O₂ environment throughout the kiln for complete combustion of fuel (C+O₂ → CO₂). Kilns are generally run with excess oxygen, resulting in approximately 2% O₂ at the back end, thereby ensuring the availability of sufficient O₂ to complete any combustion reactions.

As a further control measure, the CO level at the back end is measured continuously. In the case of insufficient supply of air for combustion the oxygen level will drop and the CO level will rise due to incomplete combustion (C+½O₂ → CO). As CO is an explosive gas even at low concentrations, the risk with this scenario is that explosions may occur in the ESP's. Further risks of CO formation at the back end of the kiln relate to increased build-up in the back end of the kiln due to the need for O₂ for the formation of Alkali Sulphates and Alkali Chlorides.

As a matter of routine practice, therefore, electrical power to ESP's is cut when CO levels reach around 1% at the back end of the kiln. This then purges the system of the excess CO, but also results in the excess particulate discharges seen from the main stack. Such situations normally last for 2 – 3 minutes. A high combustion efficiency is of primary importance to the thermodynamics and economics in cement manufacture, as well as from a safety perspective (to prevent the build up of CO). The combustion efficiency (CE) is calculated as follows:

$$\frac{\text{CO}_2}{(\text{CO}_2 + \text{CO})} \times 100 = \text{CE}$$

and should be in excess of 99.9%.

The CO concentration is therefore a process-regulated control parameter and can be measured for each kiln, with a curve similar to that in Figure 3-1. The O₂ concentration in the exhaust gases (measured at the back of the kiln) is normally controlled between 1 and 3% at optimal flame temperatures.

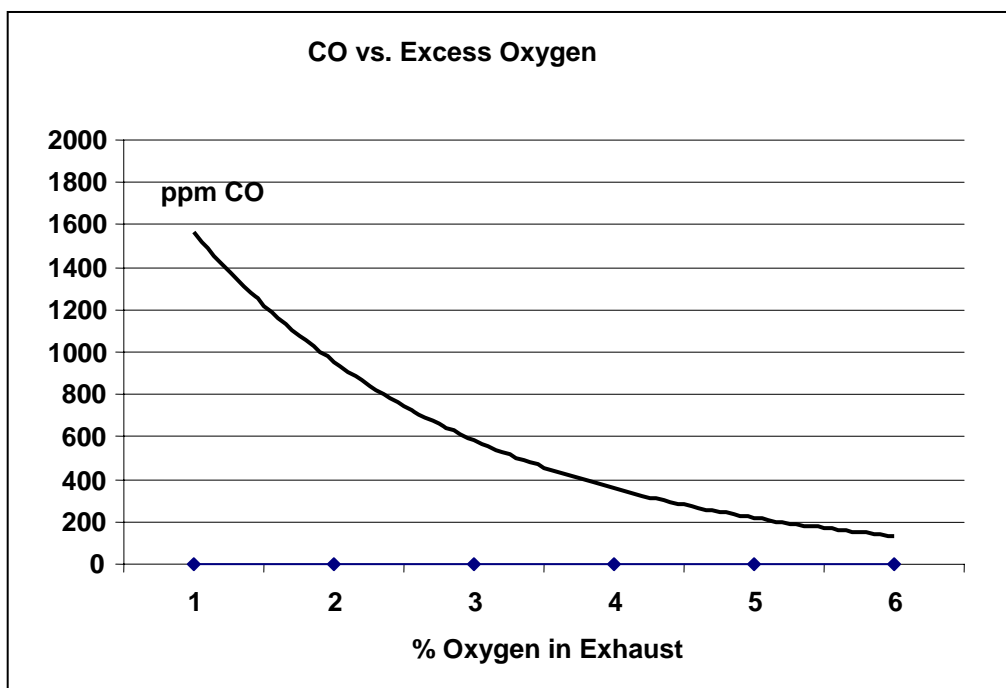


Figure 3-1: Relationship between CO and Excess Oxygen¹⁷

The addition of secondary materials is not expected to change the combustion characteristics of the kiln, and the generation of CO is therefore expected to remain unchanged. As this is a parameter which is measured on a continuous basis, PPC will detect any changes immediately as they occur. Due to the fact the PE plant operates with an ESP, the risk of explosions in the ESP will be controlled as described above, and therefore secondary materials introduction will be adjusted to keep CO levels to acceptable levels.

3.2.4 Organic Compounds

Organic matter introduced to the main burner will be completely destroyed due to the high temperatures and the long retention time of the combustion gases. However, natural raw materials such as limestone, marls and shale may also contain organic matter (“kerogene”) – depending on the geological conditions of the deposit. A large part of this organic matter may be volatilized in the kiln system even at moderate temperatures between 400 and 600° C. This is important in that the presence of organics at these temperatures, together with the presence of chlorides, under isolated process conditions, may lead to the generation of dioxins and furans which are carcinogenic gases.

Kiln tests with raw meals of different origin have demonstrated that approximately 85 to 95% of the organic matter in the raw materials is converted to CO₂ in the presence of 3% excess oxygen in the kiln exhaust gas, and 5 to 15% is oxidized to CO. A small proportion – usually less than 1% – of the total organic carbon (“TOC”) content may be emitted as *volatile organic compounds* (“VOC”) such as hydrocarbons¹⁸. The emission level of VOC in the stack gas of cement kilns is usually between 10 and 100 mg/Nm³, with a few excessive cases up to 500 mg/Nm³. As a result of incomplete combustion in the heating stages, the CO concentration in the clean gas can be as high as 1,000 mg/Nm³, even exceeding 2,000 mg/Nm³ in some cases. This is again due to carbon loading in the raw material, and not in the fuels.

Hydrocarbon contents in the stack of cement kiln systems are essentially determined by the content of organic matter in the raw materials. This is an important point to consider when applying secondary materials in that the organics introduced by secondary materials, as in the case of

¹⁷ Kiln Operation. Eric R. Hansen 2002: Please note that this graph is kiln dependent and the specific relationship will be unique to each kiln.

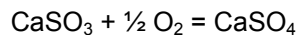
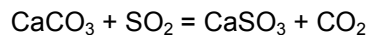
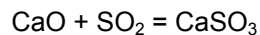
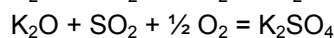
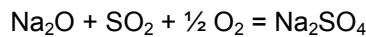
¹⁸ Cembureau: Best Available Techniques for the Cement Industry, Dec 1999

organics introduced with coal, are combusted entirely within the kiln if introduced to the kiln where the temperature is sufficiently high (i.e. 1,450 °C).

3.2.5 Sulphur Compounds

Sulphur compounds enter the kiln system either with the fuels or with the raw materials. Sulphur compounds in raw materials are present mainly as sulphates (for example, calcium sulphate CaSO₄) or as sulphides (i.e. pyrite or marcasite, FeS₂). Sulphates in the raw materials are thermally stable up to temperatures of 1,200° C, and will thus enter the sintering zone of the rotary kiln where they are decomposed to produce SO₂. Part of the SO₂ combines with alkalis and is incorporated into the clinker structure. The remaining SO₂ portion is carried back to the cooler zones of the kiln system where it reacts either with calcined calcium oxide or with calcium carbonate thus being reintroduced to the sintering zone ("*chemical SO₂ absorption*").

Chemical Reactions with SO₂:



Inorganic and organic sulphur compounds introduced with the fuels will be subjected to the same internal cycle consisting of thermal decomposition, oxidation to SO₂ and reaction with alkalis or with calcium oxide. With this closed internal cycle, all the sulphur which is introduced via fuels or via raw material sulphates will leave the kiln chemically incorporated in the clinker, and will not give rise to gaseous SO₂ emissions.

On the other hand, pyritic sulphur (sulphides) entering the kiln via raw materials are decomposed and oxidized at moderate temperatures of 400 to 600°C to produce SO₂ when the raw materials are heated by the exhaust gases. At these temperatures, there is insufficient calcium oxide available to react with the SO₂.

During direct operation – i.e. with the raw mill off – most SO₂ entering with the raw materials is emitted to the atmosphere. During compound operation – i.e. with the raw mill on-line – typically above 90% of the remaining SO₂ is additionally adsorbed on to the freshly ground raw meal particles in the raw mill ("*physico-chemical absorption*"). This depends entirely on if there is pyritic sulphur present in the raw materials. If the raw materials have low sulphur, the SO₂ emissions are very low, if not negligible.

In long dry and long wet kilns, the chemical absorption capacity for SO₂ is generally lower due to the reduced contact between kiln exhaust gas and raw materials. In these kiln systems, all kinds of sulphur input may partially contribute to SO₂ emissions, and the general emission level may be higher than in preheater kilns.

Gaseous emissions such as SO₂ or VOC are to a large extent determined by the chemical characteristics of the raw materials used, and not by the fuel composition. Emissions are lowest with raw materials which are low in volatile components.

3.2.6 Behaviour of Volatile Components

Volatile components such as *alkalis, sulphur and chlorine*, introduced with raw materials and fuels, may give rise to problems in kiln operation when present in high concentrations. Formation of rings in the rotary kiln inlet zone may lead to reduced kiln availability and productivity. Thus, the input of these volatile components is carefully controlled for process reasons. Input control is also required to achieve and maintain the required quality of clinker and cement.

Depending on their volatility, alkalis, sulphur and chlorides evaporate in the sintering zone of the rotary kiln and re-condense at cooler parts of the system, either on the raw meal particles or on the surrounding walls. With the raw meal, they are reintroduced to the sintering zone again thus establishing a permanent "*internal cycle*" of volatile "circulating" elements (see Figure 3-2).

After reaching equilibrium between input and output, a major part of the volatile components will finally leave the system incorporated in the clinker. Part of the volatile components may, however, form new compounds such as alkali chlorides or alkali Sulphates and other intermediate phases which will then contribute to the build-up phenomena mentioned above by producing a "sticky" raw meal which adheres to the walls of the cyclones, the ducts or the kiln tube lining. A small part only, of the circulating elements, leaves the kiln with the dust in the exhaust gas stream and is precipitated in the de-dusting device of the system.

With excessive input of volatile elements, the installation of a kiln gas bypass system may become necessary in order to extract part of the circulating elements from the kiln system. This *bypass dust* which is usually enriched in alkalis, Sulphur or chlorides is cooled and passed through a dust collector before being discharged. No bypasses exist at any of PPC's kilns, or any kiln in South Africa.

With dry process kilns, the dust is usually blended into the raw meal for reintroduction, or part of it is fed directly to the cement mill ("external cycle"). In some cases, for reasons of control of the alkali level in clinker or excessive input, it is not possible to recycle the dust completely to the process again. In these cases, part of the dust is sent to controlled landfills or, with or without further treatment, sold as a binder for waste stabilization, or as fertilizer.

The behaviour of *metals* in the kiln system has been described earlier. The only metal that may be released through the kiln stack with gaseous emissions is mercury. Therefore, the input of mercury with raw materials or fuels is carefully controlled. All the other metals are either incorporated with the clinker or captured with the kiln dust in the de-dusting units. The cement manufacturing process is susceptible to the input of components which are easily volatilized in the kiln system. For simple economic reasons, this input is carefully controlled.

3.2.7 Evaporation and condensation in the kiln system (circulation) –

Upon approaching the burning zone in the rotary kiln, a fraction of the volatile components will evaporate depending on the degree of volatility of the component and be transported with the kiln gas back to the colder zones in the kiln system. Here the components will condense on either the surrounding relatively colder surfaces or on the raw meal and re-enter the burning zone with the raw meal where a fraction re-evaporates. This repeated evaporation and condensation results in an *internal circulation* where the concentration of some components can be increased in the kiln material up to fifty times the input concentration.

When an equilibrium state is reached, the output of the volatile components is equal to the total input by the raw materials and the fuels.

3.2.8 Affinity between the Volatile Components

The volatility of the different compounds differs greatly, and with it the volatility of the individual elements in the compounds. For instance, potassium combined with chloride as KCl will evaporate nearly 100% in the burning zone while potassium combined with sulphate as K_2SO_4 , to a large extent, will leave the kiln with the clinker.

Chloride reacts primarily with the alkalis, forming NaCl and KCl. Any chloride in excess of alkali will combine with calcium to form $CaCl_2$. A part of the alkalis in excess of chloride combine with sulphur to form Na_2SO_4 , K_2SO_4 and double salts such as $Ca_2K_2(SO_4)_2$. Alkalis not combined with chloride or sulphur will be present as Na_2O and K_2O embedded in the clinker minerals.

Sulphur in excess of alkali combines with CaO to form CaSO₄. Strictly speaking, the SO₂ and gas that is liberated in the kiln does not condense.

3.2.9 Potential for Evaporation

Chloride compounds KCl, NaCl and CaCl₂ are seen to have a high evaporation factor. At approximately 800 °C these compounds are melted and at 1200-1300°C they are almost entirely evaporated.

Sulphate compounds with alkalis such as K₂SO₄ and Na₂SO₄ will in general be more stable than CaSO₄, which is the form that sulphur in excess of alkalis assumes. Alkali sulphates have lower evaporation. It is desirable that all sulphur is combined with alkalis, instead of with Ca to the widest extent. This can be investigated by looking at the molecular ratio of sulphur to alkalis.

3.2.10 Molecular Ratio of sulphur and Alkalis

The concentration of sulphur and alkali may increase to a point where it affects kiln operation by causing build-ups. Both overall quantity and relative proportions may be the cause. Individually they are more damaging to kiln operation than their sulphate compounds, K₂SO₄ and Na₂SO₄, as K₂SO₄ has such a high evaporation temperature, that it enters the clinker without evaporating. The same applies to approximately half the Na₂SO₄, despite the fact that this sulphate begins to split into Na₂O and SO₃ at temperatures as low as 900 °C. Sulphur in excess of alkalis will form the more volatile CaSO₄ which has a high evaporation factor in the kiln burning zone.

3.2.11 Ammonia (NH₃)

All NH₃ emissions from cement kiln are from thermally volatile, natural or secondary raw material components. Some natural raw materials (particularly clays) may contain NH₃ which is partially roasted-off at material preheating, producing N₂ and water. All evidence shows that NH₃ emission levels are very low (< 5ppm) and that secondary materials have very little, if any, influence on NH₃ emissions. As such, no limits have been set internationally for ammonia emissions from cement kilns.

3.2.12 Halogens (Cl and F)

Literature reviews showed that HCl and HF are typically emitted at maximum levels of 10 to 20 % of the emission limit values of the EU standard. In the case of high Cl and F values in the raw materials, increased emissions of HCl and HF may result, but are not expected to be significant. As a rule of thumb, PPC will not introduce a secondary material stream with a chlorine concentration of greater than 0.5% (by mass). This will, however, be reviewed subject to emissions monitoring results during trial burns and commissioning.

Both Cl and F levels in clinker are monitored by PPC as part of their Quality Assurance program to ensure compliance with quality aims (external and internal). For chlorides, a limit of 0.1% by mass has been set for cement by the standard EN197-1. This regulation is based on the need to prevent potential corrosion of reinforcing steel in concrete. For fluorides, there is no formal specification limit. PPC, however, applies an internal standard of 2000ppm (maximum) in clinker for F. At higher concentration levels, the presence of F in cement may affect setting times and, ultimately, the cement strength. Thus, it is in PPC's interest to regulate the Cl and F introduced into the kiln from a quality assurance point of view.

3.2.13 Metals

Trace elements such as metals are naturally present in low concentrations in the raw materials and fuels (including coal) used for the manufacture of cement clinker. The behaviour of these metals in the burning process depends largely on their volatility. *Non-volatile* metals remain completely

within the product and leave the kiln system fully incorporated in the mineral structure of the clinker – similarly to the main elements. Most of the common metals are non-volatile.

Semi-volatile elements such as cadmium and lead may be partially volatilized with the high temperature conditions in the sintering zone of the kiln system. These condense on the raw materials in cooler parts of the kiln system and are reintroduced to the hot zone. A major part of cadmium and lead will be incorporated in clinker; while the remaining part will precipitate with the kiln dust and be collected in the gas cleaning systems.

Volatile metals such as mercury and thallium are more easily volatilized and condense on raw material particles at lower temperatures in the kiln system (thallium at approximately 300-350°C, and mercury at 120-150°C). Whereas thallium is nearly completely precipitated on to the kiln dust particles, only part of the mercury will be collected in the filter system. Volatile metals are retained in the clinker minerals to a very small extent only.

As it is the only metal which can be emitted with the clean gas in gaseous form, the input of mercury with raw materials and fuels has to be carefully controlled.

Metals are present in all cement kiln input materials, including coal. Semi-volatile and volatile metals are evaporated and condense (predominantly) on the fine dust fraction. A portion of the volatilised metals, however, will pass through the dedusting equipment and into the atmosphere. Efficient dedusting equipment and limitation of mercury inputs in feed materials are therefore the most important control parameters to ensure compliance to emission standards for metals. Corrective raw materials, such as ash and iron ore, are analysed at PPC for the above trace components before being accepted for regular supply.

Non-volatile metals are, via direct incorporation in clinker or via addition of filter dust to the cement mill, practically insolubly embedded in concrete.

Table 3-7 demonstrates an emission comparison of metals when using fossil fuel or a secondary fuel source. Please note that this is based on data from US kilns, and that PPC's kilns will differ, albeit slightly, from these results.

Table 3-7: Metal emissions and Retention¹⁹ for kilns in the US. Note: PPC kilns will have slightly different values and these figures are included for reference purposes only.

Metal	Contribution to Emission (mass %)	Typical retention within Kiln System (% of input retained)
Cr	0.128	99.8553 ± 0.3990
Pb	0.167	99.8531 ± 0.2003
Ba	0.03	99.8781 ± 0.2939
Cd	0.44	99.5550 ± 0.4418
As	0.022	99.8863 ± 0.2916
Be	0.114	99.8681 ± 1.3278
Se	0.298	95.4002 ± 1.7779
Ag	0.163	99.8420 ± 0.1839
Ni	0.048	99.9574 ± 0.0103
Sb	0.266	99.7690 ± 0.0785
Zn	0.22	99.7869 ± 0.2598
V	0.004	99.9922 ± 0.0007

¹⁹ Emission testing of a cement kiln at Louisville, EPA 530/SW-91-016, Office of Solid Waste, Washington D.C.

3.2.14 Dioxins and Furans

Any chlorine introduced to the kiln system in the presence of organic material may form polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in combustion processes under certain conditions. The common name for these substances are dioxins and furans and they represent a possible risk to this project in they can be generated by the incineration of waste and have carcinogenic (i.e. cancer-forming) health effects. An introductory document published by an independent research group on dioxins has been included in the Environmental Technical Review, Appendix D1.

Dioxins and Furans, however, refer to a group of similar toxic chemicals. In order to derive an overall toxicity value for a mixture of dioxin and furan congeners, the concept of toxicity equivalency factors (TEFs) was introduced. TEFs are estimates of the toxicity of dioxin-like compounds relative to the toxicity of 2,3,7,8-tetrachloro-p-dibenzodioxin (TCDD), which is assigned a TEF of 1. 2,3,7,8-TCDD is the most toxic congener, and most scientific studies have focussed on the toxicology and health effects associated with this compound²⁰ & ²¹. The 2,3,7,8-TCDD toxicity equivalent (TEQ) for a mixture of dioxins and furans is determined by multiplying the concentrations of the individual congeners with their TEF values, and summing the products.

Flame chemistry in incineration systems involves the formation of many organic products of incomplete combustion, including chlorinated species such as polychlorinated biphenyls (PCB), dioxins and furans (hereafter referred to as dioxins). Because the latter are of environmental concern, a great deal of research has been expended on understanding their formation. There are two temperature windows in which they can form: the “homogeneous” route between 500 and 800°C and the “heterogeneous” one at 200 to 400°C²². Because of the features of a cement kiln (high temperature, long residence time and good mixing), full combustion of organics is expected. Extremely high destruction rates are confirmed both by PPC studies (see Sections 9.8 to 9.11) and literature. For this reason, as well as the temperature profile of the gases exiting the kiln, the latter phenomenon represents a risk of dioxin formation²³ & ²⁴. Heterogeneous formation, also known as *de novo* synthesis, is a catalysed reaction, which can take place on the ash or soot particles present in combustion systems if ALL of the following conditions are true:

- Chlorine and hydrocarbon precursors are available in sufficient quantities
- Sufficient Oxygen is present for the reaction to take place
- Sufficient time is available for the reaction to take place.
- Sufficient moisture is available.

Regarding *de novo* synthesis, it is important that, as the gases are leaving the system, they are cooled as rapidly as possible through this temperature range. According to PPC management, ducts at PPC plants are normally designed for a gas velocity of about 20m/sec. From the kiln exit at PE, given the short distance between the kiln exit and the ESP, the gas will typically take 0.5 - 1 second to reach the ESP at approximately 400 °C. As there is no conditioning tower, air bleed or in-line raw mill at PE, the temperature will remain within the *de novo* temperature window until leaving the ESP, thus presenting a possible opportunity for dioxin generation. However the low Oxygen concentration at the back end of the kiln, together with the low moisture content of the gases limit the risk of dioxin formation.

²⁰ USEPA, 1989. *Interim Procedure for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs and CDFs) and 1989 Update*. Risk Assessment Forum, EPA/625/3-98/016. NTIS, Springfield, VA; PB90-145756.

²¹ USEPA, 1994. *Estimating Exposure to Dioxin-like Compounds*. EPA/600/6-88/005, Office of Research and Development, Washington DC, US Environmental Protection Agency.

²² B.R. Stanmore: “The formation of dioxins in combustion systems”, *Department of Chemical Engineering, University of Queensland, Qld 4072, Australia, Combustion and Flame* 136 (2004) p 398–427

²³ *Formation and Release of POP's in the Cement Industry; Cement Sustainability Initiative March 2004*

²⁴ *Dioxin Emissions - Cement Kiln Operations, R Schreiber and W Winders, Proceedings of the International Specialty Conference for Waste Combustion in Boilers and Industrial Furnaces, Kansas City MO, March 1995*

In Europe, cement production has rarely shown to be a significant source of PCDD/F emissions. The USEPA has stated, in a comprehensive report on dioxin generation, that “[considering] hazardous waste burning cement kiln and non-hazardous cement kiln burning data, because both sets of data are adequately representative of general dioxin/furan behaviour and control in either type of kiln, our engineering judgement [is that] waste burning does not have an impact on dioxin/furan formation, [as] dioxin/furan formation is formed post-combustion.”²⁵

According to the most exhaustive review on dioxin generation in specifically cement kilns²⁶, the reported data (more than 1,700 dioxin and furan recent measurements from leading cement companies in the industry representing more than 100 countries) indicates that kilns generally can comply with an emission concentration of 0.1 ng TEQ/Nm³, which is the limit value in the European legislation for hazardous waste incineration plants (Council Directive 94/67/EC). German measurements at 16 cement clinker kilns (suspension preheater kilns and Lepol kilns) during the past 10 years indicate that the average concentration is about 0.02 ng TEQ/m³.²⁷

Indeed, Karstensen concludes his paper (ref. 23 above) by stating: “**The use of hazardous waste to replace fossil fuels does not seem to affect dioxin emissions.**”

Dioxin emissions from cement kilns are due to post-combustion formation reactions where the concentration of precursor materials, the time available for reaction and the temperature for the system are all important factors in dioxin formation. That the feeding of hazardous waste is not longer thought to influence the emissions of dioxins in cement kilns is clearly demonstrated by recent publications, for example the UNEP Toolkit, which differentiates between type of kiln and the ESP temperature, not by feeding of hazardous waste. Compared with the other industrial source categories covered by the Stockholm Convention, cement kilns in general are among the lowest contributors.”

The generally very low emission level of PCDD/F is due to the thermal conditions in the cement clinker burning process which are inherently unfavourable to PCDD/F formation. Limits to chlorine input are therefore required more from a process operation and product specifications (and possibly corrosion considerations) point of view than because of the emissions of PCDD/F.

As mentioned in 3.11, it is important to note that there is a natural and inherent control process with regards to certain pollutants which may otherwise contribute negatively to the emissions profile. Both Cl and F levels are monitored in the product to ensure compliance with quality aims (external and internal). For Cl there is a limit of 0.1% in cement, in line with the requirements of EN 197-1. This regulation is based on the need to reduce the potential for corrosion of reinforcing steel in concrete.

The Stockholm Convention on Persistent Organic Pollutants (POPs) lists cement kilns burning hazardous waste as a potential source of PCDD/F emissions, whereas HCB and PCBs can be disregarded as insignificant.

However, the Stockholm Convention Expert Group on BAT and BEP (Best Available Technology and Best Environmental Practice) for the cement industry has acknowledged that, although there are exceptions, PCDD/F emissions from cement kilns range normally from undetectable to less than 0.1 ng I-TEQ/Nm³ whether secondary materials are used or not.

UNEP and the WBCSD have also performed a comprehensive study of POPs and co-processing²⁸. The study found that:

- a) Cement kilns, with a few exceptions, do not emit PCDDs/Fs in any significant amounts²⁹;

²⁵ USEPA Federal Register, 40 CFR Part 60, et al. NESHAPS: Final Standards for Hazardous Air Pollutants for Hazardous Waste Combustors; Final Rule, Sept 30, 1999.

²⁶ Karstensen, K.H.: Formation and Release of Dioxins in the Cement Industry, A Review, The Foundation for Scientific and Industrial Research (SINTEF), P. O. Box 124, N-0314 Oslo, Norway, March 2005

²⁷ Integrated Pollution Prevention and Control (IPPC): Reference Document on the Best Available Technology in Cement and Lime Manufacturing Industries, 12/2001

²⁸ Formation and Release of POP's in the Cement Industry; World Business Council for Sustainable Development (WBCSD) Cement Sustainable Initiative (CSI) ;31 March 2004

- b) PCDDs/Fs from kilns are not a product of incomplete combustion of fuels; combustion is complete down to small amounts of remaining CO;
- c) If PCDD/F emissions are produced, they are reaction products from organic compounds in the raw materials, volatilized from the raw meal;
- d) Long wet and dry process kiln technologies (such as that at PE) are somewhat more susceptible to PCDD/F emissions than modern cyclone preheater/calcliner technology in cases of raw materials containing unfavourable organics (both natural and alternative); and
- e) PCDD/F emissions are independent of the use of secondary materials if the general principles of good process control are observed. Figure 3-2 demonstrates the non-dependence of dioxins emissions to the fuel or material source for a sample kiln. The horizontal red line represents the EC limit value for dioxin/furans.

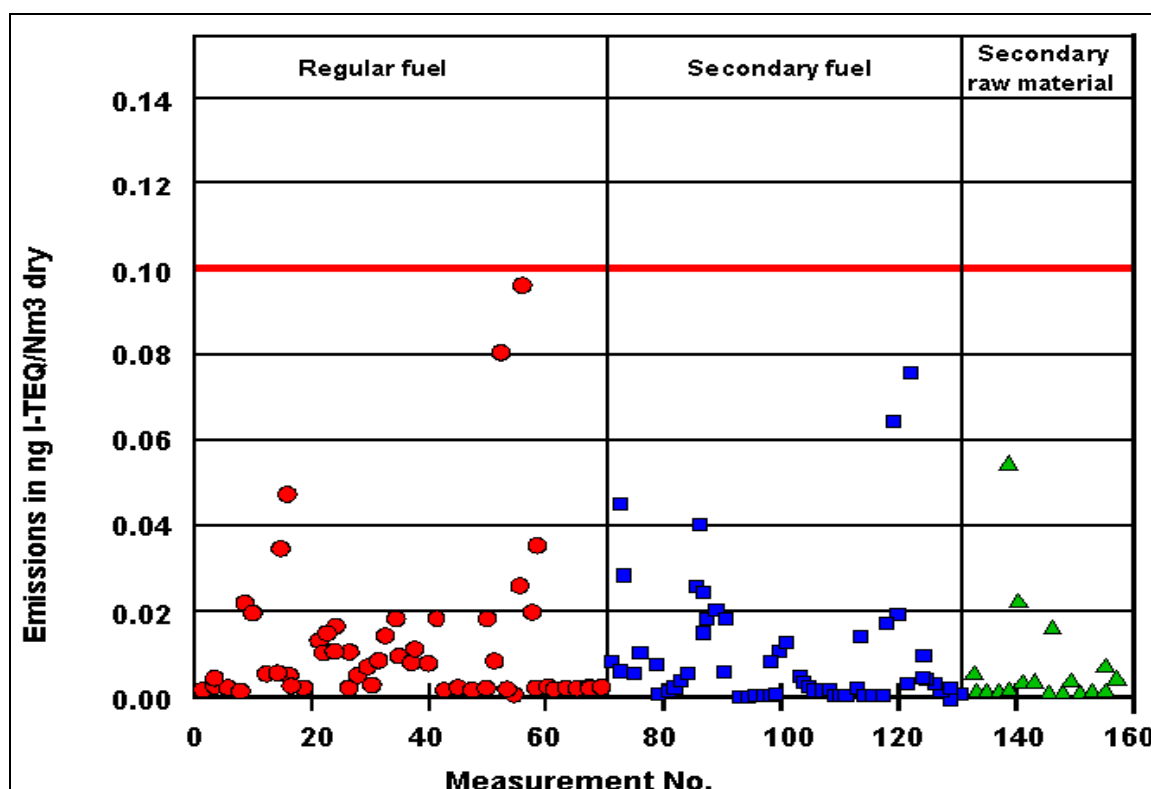


Figure 3-2: Concentration of Dioxin as a function of Fuel Type³⁰

On the other hand, Figure 3-3 shows an example of previous work on a single kiln in Austria, where a general increase of PCCD/F concentrations is observed as a function of chloride input into a kiln but the absolute values are so small that it may be deemed insignificant. PPC would need to establish, through means of trial burns, the effects of the intended waste streams on dioxin/furan formation, and develop an understanding of such relationships as presented in Figure 3-3 for each kiln.

Materials high in chloride content should therefore only be used in preheater/calcliner kilns to ensure low PCDD/F emissions. A suitable limit for Cl into long dry kilns would be 310 mg total input (fuel and raw materials) per kg clinker produced³¹, although the effect of this on dioxin/furan formation would need to be verified during the proposed trial burns. This figure will be adjusted depending on emissions results from trial burns and commissioning monitoring (see Sections 11.3

²⁹Alternative Fuels Fact sheet; 2004; <http://www.cement.org.au/industry.htm>

³⁰VDZ; CEMBUREAU BAT Reference Document

³¹Personal communication: PPC Management May 2007 according to FLS technical documentation

and 11.5). It is further recommended that over 95% of the total chlorine input from secondary materials be fed to the flame side of the kiln.

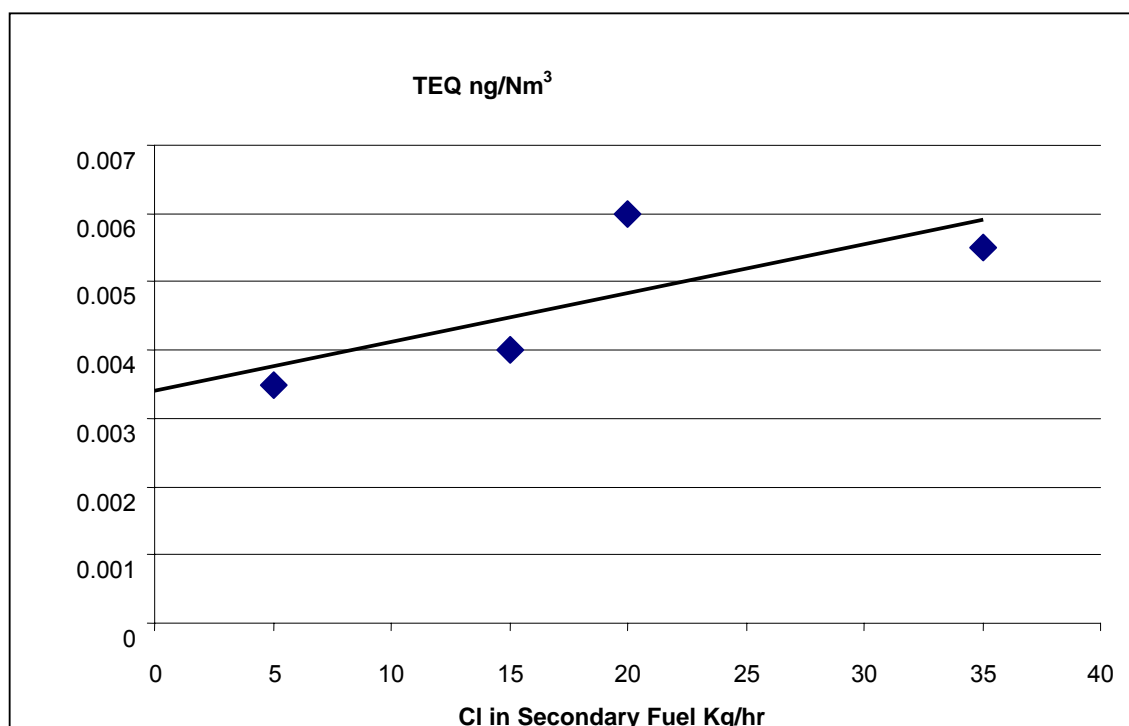


Figure 3-3: PCCD/F in Clean Gas as function of Cl Input³² for kiln in Austria

3.2.15 Dust

Kiln dust containing essentially the same minerals as the raw materials and/or clinker (and its intermediate products) is usually returned into the process – either to the kiln system or to the cement mill. In rare cases, it is not possible to recycle kiln dust or bypass dust completely in the process. This residual dust is disposed of on site (or in controlled landfills) or is treated and sold to other industries, i.e. as binder for waste stabilization or even as fertilizer. It is standard procedure on all PPC kilns for the kiln dust to be returned to the kiln, either directly or via the raw meal blending system.

As described above, metals arising from both conventional raw materials and fuels, and from secondary raw materials and fuels from industrial sources, will mainly be incorporated in clinker or – to a lesser extent – in kiln dust. The final product in all applications however, is concrete and mortar which acts as a “multi-barrier system” for metals for the following reasons:

- a) Chemical and structural incorporation in the clinker minerals;
- b) Chemical and structural fixation in the hydration products; and
- c) Physical encapsulation in the dense structure of concrete/mortar.

The cement manufacturing process is a closed-cycle process where all mineral input – including toxic components such as certain metals – is incorporated into the product leaving almost no residue for disposal.

Dust is released from cement production processes either as point source dust (from process exhaust stacks: kiln and raw mill, cooler, coal mill and cement mill) or as fugitive dust (dispersed from stockpiles, material transfer points, and road transportation). Most of the dust consists of pulverized raw material together with some clinker and cement dust.

³² Dioxin-Emissionen bei der Verwendung von Erztstbrennstoffen in der Zementindustrie. F.Wurst. T. Prey, Wien/Austria

There should be no change in the dust emission from a kiln equipped with either a bag filter or electrostatic precipitator (such as that at PE) due to the addition of secondary materials. Fugitive dust can arise from material spills from inadequately de-dusted and/or worn out material transfer points/material feeding points, material storage areas, dusty transport roads, etc. with subsequent wind erosion/dispersion. Mitigation techniques should include preventive and quick reactive maintenance, wetting of stockpiles, roof covering of stock piles, vacuum cleaning systems, etc.

3.3 CONSERVATION OF NATURAL RESOURCES

Cement production has high energy requirements, which can account for 30- 40% of cement production costs (excluding capital costs). Traditionally, the primary fuel has been coal, but a wide range of other fuels is also used, including petroleum coke, natural gas, and oil. In addition to these fuels, various types of waste are used as fuel.

The most energy efficient technology for the production of cement clinker is a dry process kiln with multi-stage suspension preheating and pre-calcination. Modern cement plants have an energy consumption of 3,000 – 3,300 MJ per ton of clinker, whereas the wet process, with long kilns, can consume up to 6,000 MJ per ton of clinker. As mentioned in Section 2.1, PPC's average per kiln is 4,500 MJ per ton of clinker.

Similar to the previous section, one of the main positive impacts from the proposed secondary materials project is the recovery of the energy value from the waste, which would otherwise have been lost should the waste be disposed of to landfill. One may argue that the energy value in the waste stream would be more appropriately recovered through a recycling initiative rather than combusting the waste, but this depends on each waste stream.

MES have performed a Waste Disposal Study in which cement kiln incineration is compared with landfill disposal and recycling. The results of this study are discussed in Section 9.7 of this report. The results show clearly that cement kiln disposal does not provide a financial disincentive to recycling, but rather presents an environmentally-favourable alternative until recycling opportunities become commercially feasible in the market.

Table 3-8 gives typical examples of common waste streams and their calorific values. It is clear from this table that many potential waste streams have a higher energy value than the low-grade coal currently being burnt in South Africa.

In addition to replacing fossil fuels, secondary materials can also replace raw materials. The mineral part of secondary fuels (ashes) as well as non-combustible industrial residues or by-products can be used to substitute part of the natural raw materials such as limestone, clay, etc. All components are effectively incorporated into the product, and no residues are left for disposal. Until the market responds with more economically efficient means of recovering the value from the waste streams, cement kiln disposal provides an efficient means of recovering 100% of the energy and mineral value of waste streams for which there are currently no other feasible recycling alternatives in South Africa. This is particularly true of hydrocarbon wastes and tyres, where the predominant quality of the waste stream is its high calorific value per ton.

Table 3-8: Typical Heating Values of Secondary Materials

Secondary Material	Calorific Value (MJ/kg)	Example Source
Pure Polyethylene	46	Plastic bags
Light Fuel Oils	42	Diesel
Heavy Fuel Oil	40	Used in boilers
Tar	38	By product of petroleum industry
Pure rubber	36	Waste from tyre manufacturing

Secondary Material	Calorific Value (MJ/kg)	Example Source
Anthracite	34	High grade coal
Waste Oils	33	Used engine oil
Petroleum Coke	33	Coke produced during petroleum refining
Scrap Tyres	32	Motor industry, Municipal waste collection service
Waste Pitch	31	Synthetic Fuels industry
Waste Solvent	26	Printing Industry
Chlorinated Hydrocarbons	24	Various Industries
Bituminous Coal	23	Lower grade coal produced in South Africa
Spent Pot Lining	20	Carbon and Refractory Waste from Aluminium Smelters
Landfill Gas	19	60% methane gas
Paint Sludge	19	By product from paint industry
Palm nut shells	19	From production of vegetable oils
Lignite and Peat	18	
Fuller Earth	17	A natural clay used to filter vegetable oils
Dried wood / sawdust	16	
Rice Husks	16	
Refuse Derived Fuel (RDF)	15	Sorted domestic waste
Cardboard/paper	15	
Dried Sewage Sludge	10	Sterilized sludge
Domestic Refuse	9	Sorted domestic waste
Contaminated Soils	2	Contain hydrocarbons or other organic contaminants
Waste Minerals	0	Contain no combustible organic material

3.4 LIQUID EFFLUENT

The cement production process does not produce liquid effluents. All water consumed (mainly for gas cooling purposes) is released to the atmosphere as water vapour. This situation will not change as a result of the introduction of secondary materials. Surface water quality might be impaired if storm water flushes large quantities of settled dust out of a dusty plant and directly into adjacent watercourses, but the risk of this occurring will not be affected due to the introduction of secondary materials.

3.5 POTENTIAL FOR SURFACE WATER, SOIL AND GROUNDWATER CONTAMINATION DURING TRANSPORTATION OF HAZARDOUS WASTES

The collection and transportation of waste from the generator of the waste to the PPC plant needs to be considered. Spills and accidents may occur during transportation wherein large quantities (up to 30,000 l per load) may be released to the soil and/or surface water bodies. Although the nature of these risks are the same as the risks of transportation of these waste streams to a hazardous landfill site, the risk may be amplified due to the longer transportation distances required to bring these wastes to PPC PE as opposed to the Aloes II hazardous landfill, for example.

The nature of the 5 waste categories, considered by PPC in this application do, to a degree, limit the impacts from such an incident. Paper, sludge pellets, plastic and tyre waste are considerably inert and may only present a litter/physical and visual impact on any sensitive receiving environment. Pulp and paper sludges (which are of high pH and corrosive nature) and hydrocarbons (containing toxic components (i.e. metals and possible PCB's), high chemical oxygen demand and flammable

properties) present a different risk and therefore require specific emergency response plans. Releases of these waste streams to the environment may result in the following:

- a) Soil contamination and possible sterilisation, resulting in a loss of biodiversity and visual impacts;
- b) Surface water contamination: changes in pH, conductivity, depletion of dissolved oxygen, and loss of biodiversity. Community health impacts may also result if this water is used for human use or irrigation of crops of cattle.
- c) Groundwater contamination: downstream water users who may abstract this water and use it for human or agricultural purposes may also be affected in terms of health impacts.

These will be compiled by PPC in accordance with the relevant SANS codes under the National Road Traffic Act (i.e. SANS 10232-1 to 3). Any contaminated soil arising from any clean-up exercises could be disposed of to the same kiln for which the waste load was originally intended (subject, of course, to the necessary approvals).

3.6 POTENTIAL FOR SURFACE WATER, SOIL AND GROUNDWATER CONTAMINATION ON-SITE

Although the volume of waste materials stored on-site will be minimised due to it being processed as it is received, the risk of spills, leaks, accidents and discharges of liquid and gaseous pollutants need to be planned for. The same effects as for spills during transport will be expected.

All dry material should be stored in protected bunkers and liquid material in engineered and bunded storage facilities. In particular, transfer of wastes from the transporter should occur within an enclosed or bunded area. Emergency Response Plans will be developed for any accidents and incidents, and spill kits should be maintained on-site. The storage areas of hazardous waste should be as close to the points of application to the kiln as possible, but far enough away to prevent being heated by the radiant heat from the kiln and to allow truck delivery access. Pumps and piping systems for liquid and sludge transfers should be able to tolerate varying viscosities and solid particles (or filters should be installed to remove such). Adequate maintenance of these pumping systems needs to be performed to prevent pipe bursts. Transfer of dry materials (especially paper, sewage pellets and plastic) should be enclosed to prevent wind-blown litter. PPE should be used by all staff exposed these waste streams (gloves, face shields for toxic waste streams and dust masks).

3.7 GENERATION OF SOLID WASTE

During the clinker burning process, all mineral input delivered by the raw materials – including both natural and secondary raw materials sources – is converted into the clinker phases (i.e. calcium silicates, aluminates and ferrites) at the high temperatures prevailing in the sintering zone of the rotary kiln (zero solid waste).

Combustion ashes from conventional and secondary fuels are also completely incorporated into the clinker minerals. Therefore cement kiln systems do not generate any ash from fuel combustion, which would normally require separate disposal. Consequently, the fuel ashes substitute part of the (natural) raw materials input. In order to maintain good clinker quality, the composition and contribution of the ash from the fuels has to be taken into account when designing the raw mix.

PPC has indicated though that only pre-sorted or waste that does not require separation on site will be accepted.

3.8 GREENHOUSE GAS REDUCTION

Producing 1 ton of clinker requires an average of 1.5 – 1.6 ton of raw materials. Most of the material loss from the process is from the calcination reaction ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$), which releases carbon dioxide to the atmosphere.

With the substitution of fossil fuels by (renewable) secondary fuels, the overall output of thermal CO₂ is reduced (“CO₂ neutrality”). A thermal substitution rate of 40% in a cement plant with an annual production of 1 million tons of clinker reduces the net CO₂ generation by about 100,000 tons. Figure 3-4 below illustrates this fact. This comparison assumes that the renewable fuel or waste is alternatively incinerated in a dedicated incinerator. The same basic principle would be valid when the waste should decompose in a landfill site or for instance digested in a biological treatment plant. The “greenhouse” gases would also include methane, for instance.

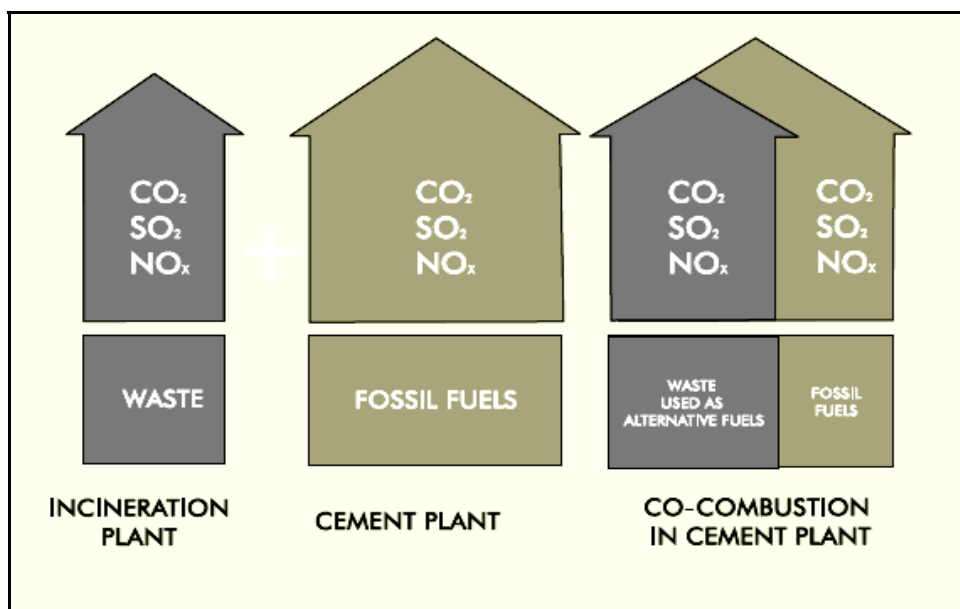


Figure 3-4: Reduction in overall emission by partial fuel replacement in cement kilns³³

Even more important is the substitution of clinker by secondary mineral additions as both thermal CO₂ from fossil fuels and CO₂ from the decarbonation of raw materials are reduced. Therefore, the use of secondary fuels, raw materials and mineral additions can contribute significantly to national schemes for the reduction of greenhouse gases.

3.9 REDUCTION OF WASTE SENT TO LANDFILL

Any waste management scheme or concept should consider the basic waste hierarchy as depicted in Figure 3-5. Whenever possible, waste should be avoided or used for energy and material recovery, as from the ecological and economical point of view this is the most appropriate solution for any country. Waste remaining after these measures must be disposed of in an environmentally-acceptable manner. Landfilling has been the traditional disposal option, but this poses a potential threat to groundwater, and is a legacy with which future generations must deal.

³³ Climate change, Cement and the EU. 1998

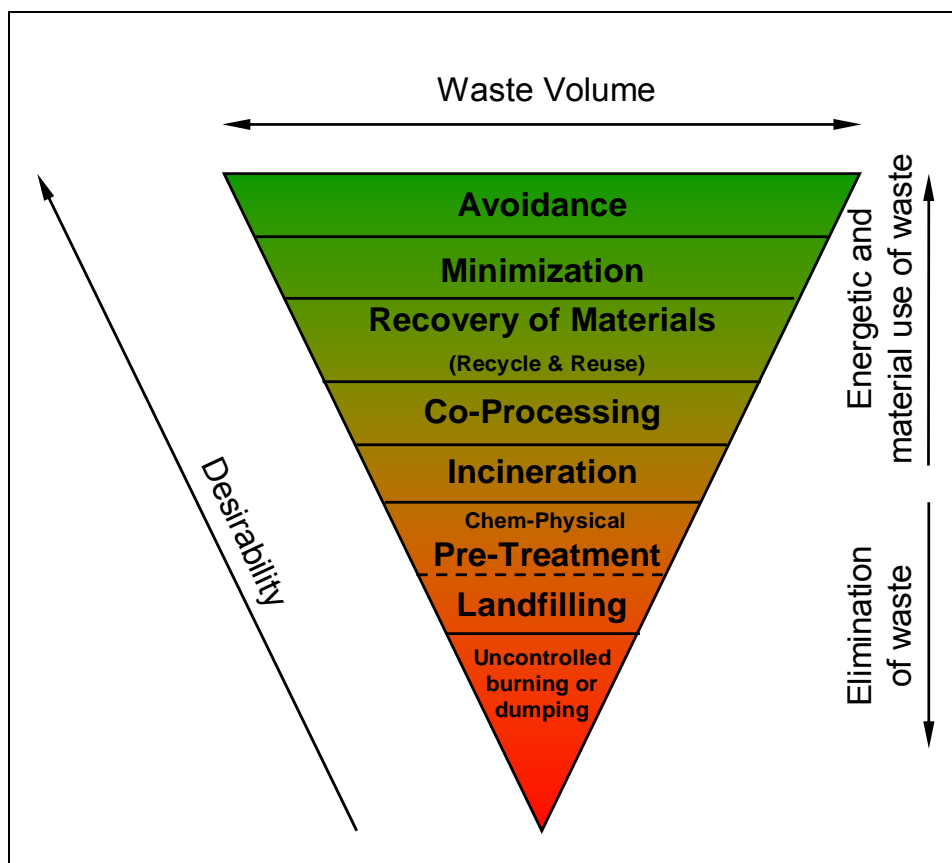


Figure 3-5: Waste Management Hierarchy

Many examples of problematic waste streams, however, exist for which re-use or recycling alternatives have not been developed on a commercially-feasible level. A common example is used tyres³⁴. Incineration is an option commonly utilised in Japan, for example, because of the limited availability of landfill area. With conventional incineration, a solid residue remains for disposal, usually by disposal to landfill. Strict control and monitoring of incinerator operation is required to ensure that the operation always conforms to permitted conditions. In addition, the considerable energy value of the tyre is lost as waste heat.

For the disposal of certain wastes, cement kilns offer an alternative option which is steadily gaining in importance. Thus co-processing of secondary materials in cement kilns is preferable to incineration, pre-treatment, landfilling or uncontrolled burning or dumping. Evaluation of the different disposal and treatment options (i.e. landfill, cement kiln or recycling) is an important part of the consideration of alternatives for a secondary materials program.

3.10 POTENTIAL IMPACT ON WATER QUALITY DUE TO USE OF CEMENT MADE FROM SECONDARY MATERIALS INCLUDING PRODUCT LEACHING

When water or other liquids come into contact with cement dust or hardened concrete, impurities may leach (i.e. dissolve) from the cement into the water stream. Exposure to the leachate may occur by ingestion of contaminated soils or waters, or by direct contact with the leachate. Assessments of the environmental quality of cement and concrete are typically based on the leaching characteristics of heavy metals to water and soil.

In an assessment of this risk, various exposure scenarios must be considered:

³⁴ www.ckrc.org & Tyre waste and resource management: A mass balance approach A B Hird, P J Griffiths

- a) Exposure of concrete structures in direct contact with groundwater ("primary" applications);
- b) Exposure of mortar or concrete to drinking water in distribution (concrete pipes) or storage systems (concrete tanks); (these are "service life" applications);
- c) Reuse of demolished and recycled concrete debris in new aggregates, road constructions, dam fillings etc. ("secondary" or "recycling" applications);
- d) Dumping of demolished concrete debris in landfills ("end-of-life" applications).

The leaching of trace elements from concrete within the environmentally relevant pH values (7 to 11) is a diffusion-controlled (i.e. extremely slow) process. The main results of the many leaching studies done to assess the environmental impacts of heavy metals embedded in concrete are as follows³⁵:

- a) The leached amounts of all trace elements from monolithic concrete (service life and recycling) are below or close to the detection limits of the most sensitive analytical methods;
- b) No significant differences in leaching behaviour of trace elements have been observed between different types of cements produced with or without alternative fuels and raw materials;
- c) The leaching behaviour of concrete made with different cement types is similar;
- d) However, leached concentrations of some elements such as chromium, aluminium, and barium may, under certain test conditions, come close to limits given in drinking water standards;
- e) Hexavalent chromium in cement is water-soluble and may be leached from concrete at a level higher than other metals; so chromium inputs to cement and concrete should be limited as far as possible;
- f) Laboratory tests and field studies have demonstrated that the applicable limit values (e.g. Groundwater or drinking water specifications) are not exceeded as long as the concrete structure remains intact (e.g. in primary or "service life" applications);
- g) Certain metals such as arsenic, chromium, vanadium, antimony, or molybdenum (so-called "oxyanions") may have a more mobile leaching behaviour, especially when the mortar or concrete structure is destroyed through crushing or other size-reduction processes (e.g. In recycling stages such as the use as aggregates in road foundations, or in end-of-life scenarios such as landfilling);
- h) As there are no simple and consistent relations between the leached amounts of trace elements and their total concentrations in concrete or in cement, the trace element content of cements cannot be used as environmental criteria.

One specific study done by NSF International (NSF)³⁶ (an independent and non-profit organization that provides third party services through programs which focus on public health and environmental quality) was performed by means of extensive tests at Southdown Dixie Cement Plant in Knoxville, Tennessee. The tests included organic, inorganic and specifically metals leaching characteristics of cement manufactured using fossil fuel (FF) and waste derived fuel (WDF) at various pH conditions.

Based on the data collected during this study, the NSF Special Studies Group recommended that drinking water products made with cement from the be accepted for evaluation under ANSI/NSF Standard 61. This recommendation was based on the fact that, for the compounds and elements of concern selected for this study, there was no statistical difference between fossil and waste derived fuels clinker and cement made at the Dixie Cement Plant.

³⁵ GTZ guidelines: March 2003

³⁶ A Comparison of Metal and Organic Concentrations in Cement and Clinker Made with Fossil Fuels to Cement and Clinker Made with Waste Derived Fuels: Mena Colucci, Paul Epstein, and Bruce Bartley NSF International 1993

The results of another study done by the construction Technology Laboratories on behalf of the US Portland Cement Association³⁷ are summarized in Table 3-9 below.

This table suggests that none of the metals in the extracts exceeded the health-based standards, and that the potential is minimal for large amounts of chemicals to leach from cement. This analysis suggests that the metals present in cement produced when burning only conventional fuel or a mixture of conventional and hazardous waste fuel are similar and would pose no increased threat to human health.

The conclusions regarding the leaching of toxic elements from the final cement product may therefore be summarised as follows:

- a) The potential for any additional negative environmental impact due to product leaching or direct water contamination when using secondary materials is not considered significant;
- b) The threat to human health due to leaching when using secondary or conventional materials is minimal and well within health standards;
- c) Special procedures are required for the handling, storage and transportation of secondary materials especially liquid waste, to prevent water and soil contamination; and
- d) In cases where the concentration of heavy metals exceeds the normal range found in cements made without secondary material, leaching tests should be conducted.

PPC monitors the Cr levels in cement on a regular basis although there exists no formal limit in terms of the SABS standards. The critical species is water-soluble Cr (6+), which is typically at ppm levels (less than 10ppm). According to PPC, the method used for determination has been validated and is accurate at these concentration levels.

Table 3-9: Metal Concentrations in Portland Cement Extracts

Metal	TCLP^a Extract Concentration Limit^b ppm	Average TCLP Extract Concentration^c ppm
Antimony	1	0.13
Arsenic	5	0.027
Barium	100	1.35
Beryllium	0.007	0.0005
Cadmium	1	0.002
Chromium	5	0.54
Lead	5	0.011
Mercury	0.2	0.0055
Nickel	70	0.11
Selenium	1	0.011
Silver	5	0.07
Thallium	7	0.01

a Toxicity Characteristic Leaching Procedure 40CFR 261

b EPA Standards 1991.

c US Portland Cement Association study 1991 on 97 Kilns burning hazardous waste and/or conventional fuels

³⁷ Burning Hazardous Waste in Cement Kilns: Environmental Toxicology International 1992

3.11 PROCESS CONTROL AND KILN STABILITY

One of the main advantages arising from the sheer size of cement kilns is the thermal stability of the kiln. Any material introduced to the kiln at the time of any interruption will be fully combusted without requiring the addition of any fuel or heat. This assumes that the feed of any secondary fuel will also cease at the same time as the cessation of coal feed, which is normally the case with power failures, for example. This is another major difference between cement kilns and other thermal incinerators of waste: interruptions to fuel feed in incinerators will result in incomplete combustion of the waste present in the incinerator system.

But this is not to say that cement kilns are without their problems: kiln instability is the most common challenge to any operator, and shutdowns are the most monitored parameter on any plant. Even without the addition of secondary materials, interruptions to production can occur due to any of the following:

- a) Mechanical or electrical failure of equipment;
- b) Instability of the raw meal feed quality or quantity;
- c) Instability of the fuel feed quality or quantity;
- d) Changes in airflow due to build-ups, wear etc, and
- e) Instrument failure and inaccuracy.

During stable processing, the kiln temperature remains above 1,450°C. Kiln instability may cause a reduction in the material temperature of 100°C, but seldom in the flame temperature. In extreme cases the kiln may become “cold” to such a degree that un-burnt material exists in the kiln as “raw feed”. During raw feed conditions, it is accepted practice that secondary fuels addition is therefore ceased, to avoid incomplete combustion.

Minor instability (e.g. small variations in the feed flow rate and quality of feed, gas flow variations due to build-up/drive failures, etc.) will not affect the combustion efficiency of the kiln, if the following are observed:

- a) CO at the back-end of the kiln is minimised;
- b) Excess O₂ is always maintained by measuring the O₂ at the back-end.
- c) Secondary fuels are only utilized if the kiln is operating above 70% of kiln rated production. (This limit is only an indication, and is different from kiln to kiln and will have to be established for each kiln independently.)

Typically, PPC has to stop their kilns 20 – 50 times per year for periods ranging from a few minutes to several days, depending on the nature of the problem. This is considered to be normal for the industry. A stop is defined as a cessation in kiln feed (fuel and raw materials).

Some examples may serve to provide further information on this important phenomenon:

- a) **Too little O₂:** If too little O₂ is available for combustion then the fraction of CO in the gas mixture will increase, indicating incomplete combustion. This brings with it a possible increase in the emissions of VOC gases. It is important to measure CO as accurately as possible at the back end (feed end) of the kiln to ensure that excess O₂ is available for complete combustion.
- b) **Mechanical/Electrical Failure of a part of the kiln system:** If the mechanical or electrical failure in a part of the system is small the period of instability will be minor. If large the result is normally a drastic reduction in the production rate of the kiln and a resulting cessation in the use of secondary fuel. The use of secondary fuel will only resume once the kiln system is back above the stated minimum production rate for secondary fuels usage.
- c) **Instability in raw meal feed quality or quantity:** Variations in feed quality and quantity can cause major kiln instability. In the event of minor variations the effect on the kiln is small and the operator will compensate to ensure that there is sufficient O₂ in the kiln

system to complete the combustion process. If the variations are such that the operator cannot control the kiln through major adjustments in fuel or airflow, the kiln production has to be reduced, stopping the use of secondary fuels if below the trigger level.

- d) **Power Failure:** A cement kiln has a large capacity to store heat in the equipment and materials. This means that, should a power failure occur, any secondary fuels that had been added to the kiln immediately before the power failure would still be completely destroyed. This can be confirmed by including the following process steps into the emergency shutdown procedure for the kiln:
- i) Ensure Excess O₂ in the kiln system at all times, and
 - ii) Rotate the kiln on Auxiliary Drive for at least 10 minutes after the emergency stop (to ensure good mixing in the kiln and to prevent physical bending of the kiln due to being stationary for too long).
 - iii) The following monitoring of kiln parameters relevant to secondary materials is therefore performed on a constant basis:
 - Gas analysis at kiln feed end, i.e. the back end (O₂, CO, NO_x);
 - Raw material and fuel addition rates (tph) and quality;
 - Temperatures and Pressures at the back-end of the kiln;
 - Shell temperature monitoring on the kiln shell (online, infrared eye positioned approximately 30 m from the kiln and surveys the entire kiln length);
 - Gas analysis at the kiln exit (O₂, CO);
 - Coal (daily CV, ash and loss on ignition (LOI));
 - Emissions monitoring (each kiln that will be processing secondary materials will have on-line OPSIS systems installed to monitor O₂, CO, NO_x, SO₂, HCl, VOC's, benzene, etc). For further details on this please refer to Section 10.1.2.
 - iv) It is therefore in the cement company's interest to avoid unnecessary disturbances to the kiln production due to the addition of secondary materials. This is an inherent control over the relationship between the input materials and the two outputs from a kiln system, namely: the emissions leaving the kiln stack, as well as the final product (clinker). The only caveat to this self-regulatory mechanism is that there may be ingredients in the secondary materials which will not affect either kiln stability or clinker quality, but which will present a risk to environmental and community health.
 - v) These substances, in our opinion, are limited to the following:
 - Volatile and semi-volatile metals, especially Mercury;
 - Dioxin precursors (organics and Cl) in the raw material (i.e. not fuels);
 - Sulphur compounds in pyritic raw materials (i.e. not fuels).
 - vi) The substances/factors listed in Table 3.10 are considered as detrimental to the kiln stability and clinker quality and will therefore be regulated inherently by the cement company.
 - vii) It is clear, therefore, that most substances which may result in an impact to the environment (either by themselves or due to secondary reactions) will be regulated by a cement company principally because they present a risk to the core business of the company, i.e. producing cement.

One of the key challenges with a secondary materials program is to ensure that other materials, namely volatile metals and raw material quality, are regulated before they enter the kiln and that appropriate emissions and clinker monitoring is performed to detect any unauthorised introductions of these materials.

Table 3-10: Constituents and Properties of the Secondary Materials and their environmental risks

Constituent or Property	Production Risk	Environmental Risk
Chlorides	Build-up in kiln system resulting in process blockages	HCl or dioxin emissions if introduced in raw material in excessive quantities, and in the presence of VOC's
Fluorides	Kiln instability due to lowering temperature required to achieve sintering	HF emissions
Sulphur in fuels	Build-up in kiln system resulting in process blockages	SO ₂ emissions
Non-volatile metals	Quality of clinker	None (absorbed in clinker)
Calorific Value of fuel	Too low – reduction of flame intensity	CO emissions (but fully oxidised in riser)
	Too high – overheating of kiln resulting in gas change at back-end	None
Moisture	Weak flame and gas flow changes	None (CO fully oxidised in riser)
Fuel particle size	Slow rate of combustion & incomplete combustion	CO emissions

It is nonetheless important to consider all the possible upset conditions that may result in a situation which can have environmental effects. Such situations may include explosions, fires, run-away reactions in the kiln, pipe blockages feeding the kiln, etc. The results of such events, if they occur, may result in large releases of dust, emissions and partially combusted gases to the atmosphere, large releases to ground (and if raining, surface water) of raw materials and secondary materials, thermal radiation, projectiles, fires in the plant, etc.

Such scenarios are normally considered as part of a Major Hazard Installation risk assessment through a Failure Modes Effect Analysis approach. PPC decided to approach this risk assessment through a HAZOP approach, which is considered as a simpler yet higher-level approach to such a study, and focuses more on identifying the mitigation actions rather than modelling the effects of such incidents.

3.12 SELF-REGULATION AND QUALITY ASSURANCE

When considering the burning of waste in cement kilns, it is important to note that the core business of the cement company is to produce cement of a required grade. One of the key challenges to the operator of the kiln is to therefore not compromise the quality of the clinker in the name of saving fuel or raw material costs. When operating a kiln, a balance is maintained between the feed rate (which is linked to kiln rotational speed), the fuel firing rate (coal, which may be partially replaced by selected secondary fuel materials), and the combustion air supply (which is drawn into the kiln by the ID (induced draught) fan).

Continuous analysis (for O₂ and CO) of the kiln exit gas stream is used to ensure that there is sufficient excess air present for complete combustion of the kiln fuel. Clinker of the correct quality will not be produced if this balance is not maintained, or if the required temperature profile over the kiln system is not maintained. At PPC, clinker quality is assessed by means of chemical testing on a two-hourly basis. The continuous monitoring of kiln operation effectively results in a continuous check on clinker quality.

In view of the process self-regulation, conditions under which complete combustion of secondary materials occurs, as well as utilization of the energy present in these materials, are maintained.

3.13 LEGISLATION APPLICABLE TO THE USE OF SECONDARY MATERIALS

Currently there is no legislation in South Africa that specifically controls the use of secondary or hazardous material in cement kilns. There is, however, other relevant legislation which regulates the handling storage and disposal of waste in South Africa, as follows:

3.13.1 Occupational Health and Safety Act (Act 85 of 1993)

This act provides for the health and safety of persons at work and to protect against the hazards posed by the use of plant and machinery. The Regulations for Hazardous Substances in this act prescribes rules and procedures for:

- a) Information and Training: Employers need to comprehensively inform and train employees about possible safety and health hazards that they may be exposed to.
- b) Assessment of potential exposure: Immediate assessment of the potential safety and health hazards must be performed before starting a new process or operation and thereafter follow-up assessments must be performed at least bi-annually. With the application of secondary materials at PPC, each new source of waste will have to be assessed.
- c) Air monitoring: A measurement program must be established to determine the airborne concentration of any hazardous chemical in the workplace. This program should include an air quality survey which is to be performed by an approved independent inspection authority in order to determine whether occupational exposure limits (OEL) are exceeded. The prescribed OEL's of substances is part of this Act under Regulations for Hazardous Chemical Substances, 1995
- d) Medical surveillance: Where employees may be exposed to potentially hazardous chemical substances, a comprehensive medical surveillance program must be established
- e) Respiratory zone: Where OEL's may be exceeded in the workplace, a clearly demarcated zone should exist where the use of suitable respiratory equipment is compulsory. This requirement would be of particular importance to PPC's secondary material program, as the composition of the possible waste to be used could vary considerably.
- f) Record keeping: Apart from the records of the previously mentioned required programs, i.e. training, air quality surveys and medical surveillance, a complete record of all material safety data sheets (MSDS) should be kept. The MSDS should contain the information as set out in Table 3.11. Where practical, PPC will have to obtain this information from the sources of secondary materials. This would emphasize the need to use reliable and trustworthy suppliers.
- g) Handling: Handling of hazardous waste should be done in accordance with Environmental Conservation Act 73 of 1989 (ECA) which will be discussed separately below.
- h) Control of exposure: The basic SHE control hierarchy as illustrated in Figure 3-6 should be followed to control exposure to hazardous chemical substances (HCS):
 - i) Limit the amount of HCS or the number of employees exposed to HCS;
 - ii) Introduce appropriate engineering controls such as automation, ventilation or enclosure;
 - iii) Clearly mark and demarcate areas where OEL levels of HCS might be high; and
 - iv) Introduce appropriate work procedures and training concerning operation, where any HCS is involved.
- i) Where it is not reasonably practical to adequately control exposure to HCS as above, workers must be provided with suitable personal protective equipment (PPE).

Table 3-11: ISO 11014 or ANSIZ400.1.1993 requirements for an MSDS

MSDS Information
Product and Company Identification
Composition (Information on Components)
Hazards Identification
First Aid Measures
Fire Fighting Measures
Accidental Release Measures
Handling and Storage
Exposure Control/Personal Protection
Physical and Chemical Properties
Stability and Reactivity
Toxicological Information Ecological Information
Disposal Considerations

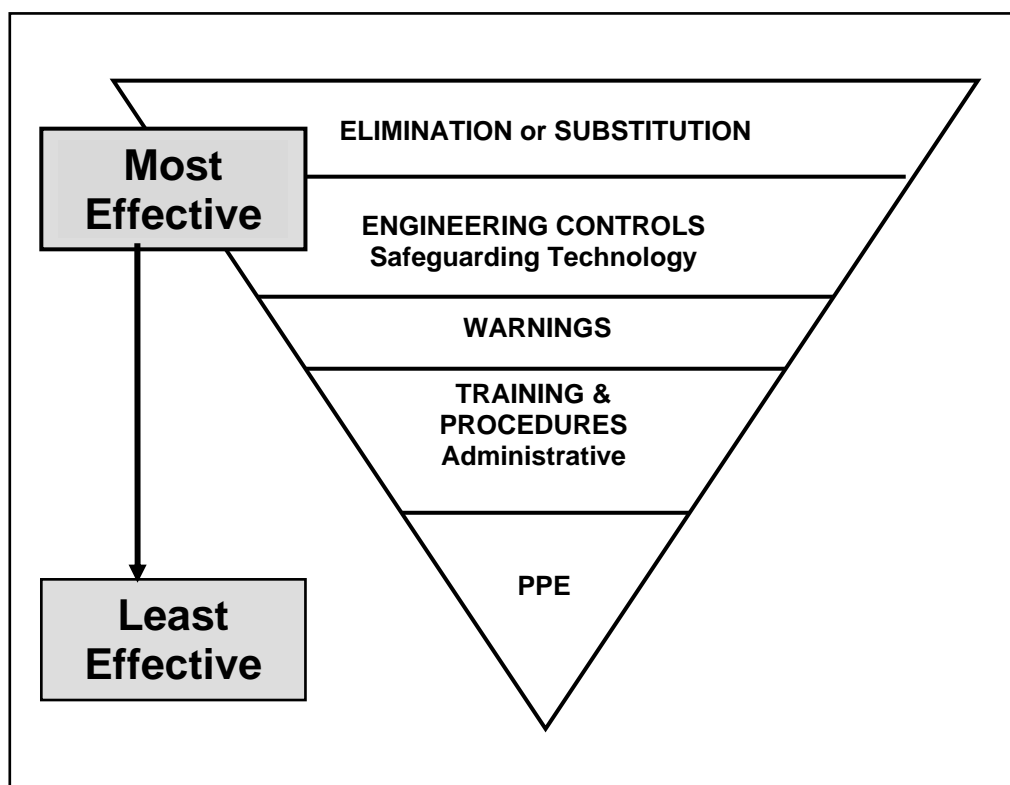


Figure 3-6: SHE Control Hierarchy

- j) Maintenance of control measures: All the control measures implemented, as discussed above, must be well maintained. At a frequency of at least once in every two years, an approved independent inspection authority should verify these actions.
- k) Labelling, packaging, transport and storage: Labelling, packaging, transport and storage of HCS derived from PPC’s secondary materials program should be done in accordance with the guidelines set out in Table 3-12 below.

Table 3-12: Classification of Hazardous Waste according to SANS 10228

Class	Description
1 Explosives	Unless the appropriate precautions are in place, and permission for acceptance of explosive waste for use as a Secondary Material—has been obtained from the Commissioner of Mines and other relevant authorities, explosive wastes should not be accepted or utilised as an alternative fuel source
2 Gases	The kiln offers a unique opportunity to utilise the energy derived from the processing of some flammable gases and non-toxic gases, such as the CFCs or hydro-chlorofluorocarbons, many of which are now banned in terms of the Montreal Protocol, United Nations (1993). The amount of these gases that could be available for use as Secondary Materials by the kiln would be very low, and is not expected to exceed 50 to 100 tons per annum.
3 & 4 Flammable Liquids & Solids	<p>These materials would form a significant portion of the alternative fuels used at the kiln due to their high calorific values. These flammable wastes are required to be handled carefully to avoid conditions which could cause them to ignite during transport and storage, but pose no higher risk than the management of fuels such as petrol, diesel and boiler fuels. Unless the appropriate handling and storage procedures are put in place, flammable solid wastes that fall into the following three classes should not be accepted at the kiln due to risks associated with the handling of these wastes:</p> <ul style="list-style-type: none"> - Self reactive and related substances and desensitized explosives. - Substances liable to spontaneous combustion - Substances that on contact with water emit flammable gases.
5 Oxidizers & Organic Peroxides	Stable organic peroxides would be acceptable for use/introduction into the kiln, but inorganic oxidizing agents, such as chromates and permanganates, should not be accepted.
6 Toxic and Infectious Substances	<p>Materials that are potentially toxic include petroleum-based fuels and many waste materials produced by the chemical, pharmaceutical and petroleum industries. These products can all be utilized as alternative fuel in a cement kiln. The acceptance procedure for these materials must determine if the toxicological, chemical and physical nature of the materials pose any significant threats to human health or the environment.</p> <p>Infectious waste and untreated medical waste should not be processed/accepted as an alternative fuel for a kiln because of the potential health risks associated with handling the material, and because it can contain surgical steel items that may not be completely destroyed in the kiln.</p>
7 Radioactive Substances	The kiln must not accept wastes that are radioactive. It is important that procedures are in place to confirm that a waste is not radioactive, both prior to acceptance and when it is received in the facility.
8 Corrosive Substances	The corrosive wastes that could be accepted at the kiln would be largely organic in nature, e.g. acetic acid (which is the main ingredient in vinegar). Mineral acid wastes such as Sulphuric, hydrochloric and nitric acid should not be accepted, as they could have a significant impact on process stability in the kiln
9	Miscellaneous Dangerous Substances

3.13.2 Environment Conservation Act, 1989 (Act 73 of 1989), National Water Act, 1998 (Act 36 of 1998) and the Water Services Act, 1997 (Act 108 of 1997)

- a) The Department of Environmental Affairs and Tourism (DEAT) is responsible for ensuring the correct management and disposal of waste in South Africa, in as much as it has an effect on the National water resource. This is because the DWAF is custodian of South Africa's water resources in terms of the National Water Act, 1998 (Act 36 of 1998) and the Water Services Act, 1997 (Act 108 of 1997) and is responsible for issuing waste disposal site permits (Environment Conservation Act, 1989 (Act 73 of 1989)). The Department, together with other government departments, has therefore set in place a waste regulatory system. This regulatory system includes:
 - i) The issuing of waste disposal site permits;
 - ii) A manifest system for the transportation of hazardous waste; and
 - iii) The registration of hazardous waste generators and transporters.
- b) The aim is to protect the environment and the public from the harmful effects of bad waste disposal practices.

3.13.3 Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste (DWAF, 2nd edition, 1998)

- a) Before a waste disposal site permit will be issued, minimum procedures, actions and information will be required from the permit applicant. These are termed "Minimum Requirements". The Minimum Requirements provide the applicable waste management standards or specifications that must be met in the absence of any valid motivation to the contrary. They also provide a point of departure against which environmentally acceptable waste disposal practices can be distinguished from environmentally unacceptable waste disposal practices.
- b) The objectives of setting Minimum Requirements are to:
 - i) Prevent water pollution and ensure sustained fitness for use of South Africa's water resources;
 - ii) Attain and maintain minimum waste management standards in South Africa, so as to protect human health and the environment from possible harmful effects caused by the handling, treatment, storage and disposal of waste;
 - iii) Effectively administer and provide a systematic and nationally uniform approach to the waste disposal process; and
 - iv) Endeavour to make South African waste management practices internationally acceptable.
- c) The Minimum Requirements of DWAF is a very comprehensive guideline that leaves very little margin for error in safe handling, transport and storage of hazardous waste. PPC will need to align plant operations and procedures with this guideline, especially because of the wide range of possible secondary materials which may be utilised.
- d) Table 3-13 below is an example guideline from the DWAF Minimum Requirements.

Table 3-13: Minimum Requirements for Waste Handling, Storage and Transportation³⁸

Subject	Minimum Requirement
Qualification as disposal site	If a waste is held at a storage site for a period exceeding three months, the site automatically qualifies as a Waste Disposal Site, and must be registered as such and meet all the requirements of a disposal site.
Temporary storage area	A temporary storage area must have a firm, waterproof base and drainage system. It must be so designed and managed that there is no escape of contaminants into the environment.
Identification of Waste	The transporter must be provided with accurate information about the nature and properties of the load.
Documentation	The transport operator must be provided with the relevant transportation documentation for the consignment.
Security of load.	The load must be properly loaded and secured on site
Hazchem placard.	The transport operator must be supplied with the appropriate Hazchem placards
Hazchem placard	The transport operator must ensure that the Hazchem placards are properly fitted to the vehicle.
Vehicle Roadworthiness	The Responsible Person must ensure that before the vehicle leaves the consignor's premises it is not overloaded or showing any obvious defect that would affect its safety
Escape of hazardous spillage at site	The Department and the Local Authority must be advised immediately, should it prove impossible to contain spillage of a Hazardous Waste on a site.
Protection against effect of accident	The Generator - or his representative, i.e., transporter - must ensure that adequate steps are taken to minimise the effect an accident or incident may have on the public and on the environment.
Spillage on site	The Generator must initiate remedial action to clean up any spillage remaining on a site after an accident.
Notification	All road accidents must be reported to the Department of Transport on the prescribed documentation.
Notification	In case of an accident, a full report, containing all the information listed in 10.8.2 must be sent to the Department

3.13.4 CAPCO Limits and Design Criteria

Currently there are no specific limits for emissions from cement kiln operating with secondary materials. The closest guide for emissions limits in South Africa is the Class 1 incinerator (Scheduled Process No. 39 (Waste Incineration) limits, in terms of the Atmospheric Pollution Prevention Act of 1965, or APPA). The discussion below discusses the registration requirements as they currently apply at the time of writing. Please note that, since the promulgation of the Air

³⁸Section 10.1 DWAF Minimum Requirements for The Handling, Classification and Disposal of Hazardous Waste

Quality Act No. 39 of 2004, an APPA Review Process is in process at DEAT, and these requirements are therefore expected to be updated or replaced.

These incinerators are classified by the Chief Air Pollution Control Officer (CAPCO) of the Department of Environmental Affairs and Tourism as “incinerators in which the waste serves as the fuel or supplementary fuel in an industrial process (e.g. the use of cement kilns or any other industrial boilers or furnaces for the disposal of noxious or hazardous materials)”.

The CAPCO guidelines further state the following design criteria for Class 1 incinerators:

- a) “The standard for these incinerators will be in accordance with 'the best practicable means' as determined by the Chief Officer for each individual installation, taking into account the particular industrial process, combustion techniques and emissions.
- b) A destruction and removal efficiency (DRE) = 99.99% should be attained on each principal organic hazardous constituent (POHC) in the feed waste.

The relevant sections of CAPCO’s document, which provides the basis of issuing Registration Certificates for incinerators in South Africa, are provided in full as follows:

- a) Feeding
 - i) Controlled hygienic, mechanical or automatic feeding methods have to be used which will not influence the air supply and temperature in the primary and secondary chambers of the incinerator negatively; and
 - ii) No waste is to be fed into the incinerator:
 - At start up and until the minimum combustion temperatures have been reached;
 - Whenever the minimum combustion temperatures are not maintained;
 - Whenever the previous charge has not been completely combusted in the case of a batch loader; and
 - Until such time as the addition of more waste will not cause the design parameters of the incinerator to be exceeded.
- b) Primary Combustion
 - i) The primary combustion chamber shall be accepted as the primary combustion zone and should be equipped with a burner/s burning gas or low Sulphur liquid fuel. Other combustion methods will be judged on merits. Primary air supply is to be controlled efficiently.
- c) Secondary Combustion
 - i) The secondary combustion chamber shall be accepted as the secondary combustion zone and should be fitted with a secondary burner/s burning gas or low Sulphur liquid fuel or any suitable fuel. Secondary air supply is to be controlled efficiently. Flame contact with all the gases should be achieved;
 - ii) The residence time in the secondary chamber should be not less than two (2) seconds;
 - iii) The gas temperature as measured against the inside wall in the secondary chamber, not in the flame zone, should be not less than 1100°C;
 - iv) The oxygen contents of the emitted gases should be not less than 11%; and
 - v) Both the primary and the secondary temperatures should be maintained until all the waste has been completely combusted.
- d) Chimney
 - i) The chimney should have a minimum height of nine (9) metres above ground level and clear the highest point of the building by not less than six (6) metres for flat

roofs or 3 metres for pitched roofs. (Refer to Circular 7 of 1994 Department of Health). The topography and height of adjacent buildings (i.e. closer than 5 times chimney height) should be taken into account;

- ii) If possible the chimney should be visible to the operator from the stoking floor;
- iii) The addition of dilution air after combustion in order to achieve the requirements of these guidelines is unacceptable;
- iv) The minimum exit velocity should be 10 metres/second;
- v) The stack shall be insulated to maintain the maximum outlet temperature; and
- vi) **Point for the measurement of emissions shall be provided.**

e) Instrumentation

- i) Temperature:
 - The temperature should be determined against the inside wall of both the primary and secondary combustion chambers. Care should be taken not to measure the burner flame temperature; and
 - An audible and visible alarm should be installed to warn the operator when the secondary temperature drops to below the required temperature.
- ii) In addition to the above the following instruments may also be required:
 - A carbon monoxide and/or oxygen meter/recorder;
 - A smoke density meter/recorder;
 - A gas flow meter/recorder;
 - A solid particulate meter/recorder; and
 - Any other instrument or measurement that the Chief Officer considers necessary.

f) Siting

- i) Should be sited in accordance with the relevant town planning scheme, the topography and be compatible with premises in the neighbourhood; and
- ii) It should be housed in a suitably ventilated room.

g) Emission Limits

- i) The total particulate emission should not exceed $180 \text{ mg/m}^3 @ 11\% \text{ O}_2$, for Class 2 and 120 mg/m^3 for Class 1 incinerators, as measured at 0% moisture;
- ii) Opacity of the smoke should not exceed 20%;
- iii) All the emissions to air other than steam or water vapour should be odourless and free from mist, fume and droplets;
- iv) The Chief Officer may require that the certificate holder have tests carried out by an accredited person or body to determine stack and/or ground level concentrations of the following substances:
 - All pollutant concentrations should be expressed at 0°C and $101,3\text{kPa}$, dry gas and 11% oxygen;
 - Emission concentrations for Class 1 and Class 2A incinerators:
 - Max. of $0,05 \text{ mg/m}^3$ (as measured in the chimney) for:

<i>Cadmium and compounds as</i>	<i>Cd</i>
<i>Mercury</i>	<i>Hg</i>
<i>Thallium</i>	<i>Tl</i>
 - Max. of $0,5 \text{ mg/m}^3$ (as measured in the chimney) for:

<i>Chromium</i>	<i>Cr</i>
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<i>Beryllium</i>		<i>Be</i>
<i>Arsenic</i>		<i>As</i>
<i>Antimony</i>		<i>Sb</i>
<i>Barium</i>		<i>Ba</i>
<i>Lead</i>		<i>Pb</i>
<i>Silver</i>		<i>Ag</i>
<i>Cobalt</i>		<i>Co</i>
<i>Copper</i>		<i>Cu</i>
<i>Manganese</i>		<i>Mn</i>
<i>Tin</i>		<i>Sn</i>
<i>Vanadium</i>		<i>V</i>
<i>Nickel</i>		<i>Ni</i>

(Refer Official Journal of the European Communities
No.C130/121/5/92)

<i>Chloride</i>	<i>as</i>	<i>HCl <30 mg/m³</i>
<i>Hydrofluoric acid</i>	<i>as</i>	<i>HF <30 mg/m³</i>
<i>Sulphur dioxide</i>	<i>as</i>	<i>SO₂ <25 mg/m³</i>

Any substance that the Chief Officer may consider necessary e.g. polycyclic hydrocarbons, benzene etc; and

- The average dioxin and furan concentration in the emissions of Class 1 and 2A should not exceed 80 ng/m³ total dioxins and furans if measured for a period of 6 to 16 hours or 0,2 ng International Toxic Equivalent (I-TEQ/m³) or result in an excess cancer risk of 1:100000 on the basis of annual average exposure.(ng = nanograms).

h) Operation

- i) Materials destined for incineration should be of known origin and composition and may only be incinerated in a furnace that is registered for the incineration of that particular type of waste;
- ii) Record should be kept of the mass and/or volume, the type and origin of the waste to be incinerated;
- iii) The incinerator should be preheated to working temperature before charging any waste;
- iv) Overloading of the incinerator should be avoided at all times;
- v) The incinerator should be kept in good working order at all times and should not be used if any component fails. Any malfunction should be recorded in a log book and reported to the relevant control authority;
- vi) It should be supplied complete with full operating instructions. The incinerator operator and all relevant staff should be trained to the satisfaction of the relevant control authority;
- vii) A list should be displayed at or near the control panel which identifies all trained operators;
- viii) The incinerator and its surrounds should be kept in a clean and neat condition at all times; and
- ix) In cases where noxious or offensive gases are emitted that cannot be destroyed by secondary combustion, additional control equipment e.g. scrubbers, bagfilters or electrostatic precipitators will be required.

3.14 INTERNATIONAL EMISSIONS LIMITS

- a) Internationally, there are legislated emissions limits for the cement industry. The following table shows the emissions limits for the cement industry in various countries, as well as the limits set out in PPC's Policy for Secondary Materials. The limits that PPC have committed to are based on the European Community Limits for the cement industry, the exceptions are:
- i) Total dust – this is set according to PPC's APPA permit; and
 - ii) NO_x – there is no South African legislation for this pollutant, PPC will adhere to current NO_x emission rates. Typical rates for PPC plants currently are 800 – 1300 ppm.
- b) Dust and Nitrogen Oxide emissions are independent of material use, but are related to the efficiency of the pollution control device and kiln combustion efficiency, respectively.

Table 3-14: Comparative Emission Limits for Cement Kilns

Country	SA ²	Brazil ³	China ³	EU ⁵	USA ⁴	Australia ³	PPC Policy
Total dust	120	77	100	30	25	100	As per each APPA permit
CO					98.1		Note ⁷
HCl	30	1.8 kg/hr		10	110	200	10
HF	30			1			1
NO _x				800/500 ⁸	714	940	Note ⁷
SO ₂	25			50	76		50
TOC				10	77.1		10
Cd +Tl	SUM = 0.05			0.05	0.14		SUM = 0.05
Hg		0.04		0.05	0.044	3	
Sb,As, Pb,Cr,Co,Cu, Mn,Ni + V ¹⁰	0.05 ⁶			0.5			0.5
TEQ ⁹	0.2	0.1		0.1	0.2	0.11	0.1

Notes to Table

1. Units mg/Nm³ except TEQ= ng/Nm³ and others indicated in table
2. DEAT Limit Class 1 incinerator
3. Source Battelle, 2002
4. New Plants-Waste Utilization & Environmental Considerations-FL Smidth
5. European Community Directive 2000/76/EC of 4 December 2000
6. Limit Value for each individual element
7. No SA legislation, however PPC is committed to reduce NO_x and CO to internationally accepted standards with its on-going kiln upgrading program and will adhere to current NO_x emission rates in the interim. Typical rates for PPC's plants range between 800 – 2000 ppm for NO_x, depending on the type of kiln.
8. New plants
9. Dioxins toxic equivalence
10. Sum of the individual elements.