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Production of Persistent Organic Pollutants from Cement Plants

Flávio Aparecido Rodrigues

*Universidade de Mogi das Cruzes, Laboratório de Materiais e Superfícies (LABMAR)*

*Brazil*

1. Introduction

In 2001, The United Nations Environmental Programme (UNEP), during the Stockholm Convention (UNEP 2001) listed the so-called “dirty dozen” chemicals, the persistent organic pollutants (POPs). The agreement was amended in 2009, including new classes of compounds. This agreement was ratified by 150 countries. Table 1 lists the POPs regulated by UN.

<table>
<thead>
<tr>
<th>Persistent Organic Pollutants</th>
<th>Pentachlorobenzene, Hexabromobiphenyl, Hexabromodiphenyl ether and heptabromodiphenyl ether</th>
<th>Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin, Chlordane, DDT, Dieldrin, Endrin, Chlordecone</td>
<td>Tetrabromodiphenyl ether, pentabromodiphenyl ether</td>
<td>Polychlorinated biphenyls (PCB)</td>
</tr>
<tr>
<td>Heptachlor, Hexachlorobenzene (HCB), Mirex, Toxaphene</td>
<td>Perfluoroctane sulfonic acid and its salts</td>
<td>Perfluoroctane sulfon fluoride</td>
</tr>
<tr>
<td>Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane, Lindane</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Persistent organic pollutants according to Stockholm convention agreement (2009)

The term persistent organic pollutant was used much before 2011 (Rantio, 1996) in scientific literature. However, it is important to recognize that UN convention was a significant step in order to bring many countries together with a unified goal: elimination and/or restriction of POPs.

The list presented in Table 1 comprises all chemicals considered persistent organic pollutants. It shows that persistent organic pollutants, in fact, constitute a diverse class of chemical compounds with specific physical-chemical characteristics. On the other hand, it is important to note that there are many important differences among these chemicals. For instance, alpha and beta hexachlorocyclohexane were completely banned and can not be produced under any circumstances, for commercial use. It can be produced however for research purposes. On the other hand, the production of DDT (1,1,1-trichloro-2,2-bis (4-chlorophenyl)ethane) is restricted and its use should be limited. DDT is still used to
control malaria in specific regions (Karakus et al., 2006). Other POPs, such as polychlorinated dibenzo-
\textit{p}-dioxins and dibenzofurans (PCDD/PCDF) are not intentionally produced; rather, they are generated as a result of combustion processes from industrial activities (Abad et al., 2002). From the chemical viewpoint, there are hundreds of POP’s, when considering congeners within a specific family of compounds (Jones & de Voogt, 1999). For instance, the term dioxin includes 75 PCDD and 135 PCDFs (Srogi, 2008). There are many differences between these compounds in terms of toxicity or degradation in the environment; however, it is much more convenient to use the “general” name, rather than describe each component individually.

Historically the large-scale utilization of most POPs grew faster after the World War II, especially as insecticide. DDT is perhaps the most “popular” organic pollutant. Table 2 lists the utilization of DDT in 10 countries, around the world.

<table>
<thead>
<tr>
<th>Country</th>
<th>Agricultural use (kTon)</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>590</td>
<td>1947-1972</td>
</tr>
<tr>
<td>Former Soviet Union</td>
<td>320</td>
<td>1952-1971</td>
</tr>
<tr>
<td>China</td>
<td>260</td>
<td>1952-1983</td>
</tr>
<tr>
<td>Mexico</td>
<td>180</td>
<td>1953-2000</td>
</tr>
<tr>
<td>Brazil</td>
<td>106</td>
<td>1947-1998</td>
</tr>
<tr>
<td>India</td>
<td>75</td>
<td>1947-1990</td>
</tr>
<tr>
<td>Egypt</td>
<td>66</td>
<td>1952-1972</td>
</tr>
<tr>
<td>Guatemala</td>
<td>60</td>
<td>1947-1985</td>
</tr>
<tr>
<td>Italy</td>
<td>46</td>
<td>1948-1987</td>
</tr>
</tbody>
</table>

Table 2. Agricultural use of DDT in history

It is apparent from table 2 that large amounts of DDT were intentionally released in the environment. It should be pointed out that many other insecticides were produced and used in every continent. It is not surprising that UN is acting directly to minimize the harmful effects of these chemicals on the environment. The dissemination of POPs is also due to their large range of applications. For example, aldrin, chlordane, dieldrin and endrin were used as insecticides, hexabromobiphenyl is a flame retardant (Sjödin et al., 2006) and perfluorinated organic compounds are used as insecticide, lubricants and surfactants (Liu et al., 2007). Despite having chemical differences, POPs show common properties, making them harmful to the environment. Probably, the most important aspects associated to POPs are the toxicity, the slow degradation in the environment and their bioaccumulation. These aspects are briefly discussed in the following section.

1.1 Persistent organic pollutants and their toxicity

World Health Organization (WHO) listed the toxicity of several POPs as shown in Table 3. All of the listed organic pollutants are toxic and few of these are extremely lethal, even in very small amounts. For instance, the International Programme on Chemical Safety report (IPCS) presents the toxicity of the dirty dozen, using the concept of lethal doses, LD\textsubscript{50}. LD\textsubscript{50} is the concentration of the compound to kill 50% of animal species under evaluation.
On the other hand, Schecter et. al (2006) compared the toxicity of dioxins, using toxic equivalent factor (TEQ). In this scale, the number 1 was assigned to the compound 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the most toxic among dioxins. Table 4 present a list of toxicity of dioxins using TEQ scale. As it can be seen, toxicity is dependent on chemical structure of compounds, and some dioxins present low toxicity.

There is not a comprehensive scale of toxicity, able to correlate all persistent organic pollutants. On the other hand, there are many studies dealing with toxicity of POPs. For instance, polybrominated diphenyl ethers (PBDEs) act directly on the brain (neurotoxic) and may cause behavioral disorders, specially the HO-PBDE form (Dingemans et al., 2011). Lee et al., (2010) suggested that some POPs may be associated to type 2 Diabetes. Many other harmful aspects of POPs on human beings, are presented in literature, such as tumour promoter (Shin et al., 2010), pancreatic cancer (Hardell et al., 2007), cardiovascular diseases (Lind et al., 2004) and neurological problems (Weiss, 2011).

### 1.2 Degradation in the environment

Many POPs were initially used as insecticide and deliberately spread over soils, rivers and air. Their use started in 1940 and for many years, thousands of tons were freely dispersed in
Table 4. Comparative toxicity of dioxins. Toxic Equivalent Factor (TEQ) = 1 for compound 2,3,7,8-tetrachlorodibenzo-p-dioxin, the most toxic substance.

<table>
<thead>
<tr>
<th>Compound class</th>
<th>isomer</th>
<th>TEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxins</td>
<td>2,3,7,8-Tetra-CDD</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1,2,3,7,8-Penta-CDD</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1,2,3,4,7,8-Hexa-CDD</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1,2,3,6,7,8-Hexa-CDD</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1,2,3,7,8,9-Hexa-CDD1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1,2,3,4,6,7,8-Hepta-CDD</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>OCDD</td>
<td>0.0001</td>
</tr>
<tr>
<td>Dibenzofurans</td>
<td>2,3,7,8-Tetra-CDF</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1,2,3,7,8-Penta-CDF</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>2,3,4,7,8-Penta-CDF</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1,2,3,4,7,8-Hexa-CDF</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1,2,3,6,7,8-Hexa-CDF</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>2,3,4,6,7,8-Hexa-CDF</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1,2,3,4,6,7,8-Hepta-CDF</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>1,2,3,4,7,8,9-Hepta-CDF</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>OCDF</td>
<td>0.0001</td>
</tr>
<tr>
<td>Coplanar PCBs</td>
<td>3,30,4,40-TCB (77)</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>3,4,40,5-TCB (81)</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>3,30,4,40,5-PeCB (126)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>3,30,4,40,5,50-HxCB (169)</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>2,3,30,4,40-PeCB (105)</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>2,3,4,40,5-PeCB (114)</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td>2,30,4,40,5-PeCB (118)</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>20,3,4,40,5-PeCB (123)</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>2,3,30,4,40,5-HxCB (156)</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td>2,3,30,4,40,50-HxCB (157)</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td>2,3,30,4,40,5,50-HxCB (167)</td>
<td>0.00001</td>
</tr>
<tr>
<td></td>
<td>2,3,30,4,40,5,50-HpCB (189)</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

many parts of the world. Of course, at that time, there was no complete evidence that these chemicals could be so harmful to the environment. Nowadays, even considering restrictions or banning of POPs they can still be found in different regions. There are indications that some POPs are still in use (Minh et al., 2007). The understanding of the behavior of a chemical in the environment is in fact, a very complex task. For instance, when a pesticide is spread over an agricultural area many phenomena may have place. Part of the insecticide may be simply volatized, remaining in the air. In this case, it can be immediately spread over a much larger area. In this case, atmospheric conditions will be important, such as wind intensity, the occurrence of rain, and even local temperature may dictate the fate of these components. When the pesticide contacts soil, it may interact with organic material and be held for an indefinite period of time. It can be degraded or remain stable for long periods. Also, it can be leached and reach rivers or the sea. A particular threat in the case of
POPs is the relatively slow degradation process. This is also a multifaceted development. Chemical degradation of POPs can take years or even decades to be completed. For example, technical chlordane (a mixture of more than 140 components) may persist in soil for more than 20 years (Mattina et. al, 1999). Lindane was found in many areas of France, even in regions without agricultural use (Villanneau et al., 2009). Similar observations and results can be found in the literature (Carlson et al., 2010), dealing with diverse situations, such as latitude and population, all around the world (Liu et. Al, 2009; Kurt-Karakus et al., 2006; Shuthirasingh, et. al., 2010). This behavior is observed under different environmental conditions, such as water, atmosphere or soils (Ramos et. al, 2001; Schwarzenbach et al., 2010; Pozo et al., 2011). Therefore, this degradation kinetic poses an additional and important threat. These substances can be spread over very long distances (Brzuzy and Hites, 1996). Also, the transport mechanism can be very complex and many variables are involved (Mackay and Arnot, 2011).

Perhaps the best way to understand the risks posed by POPs is to consider Polar Regions, Antarctic and Artic. At first glance, these areas could be considered remote and free from deleterious human activities. Unfortunately, this is not the case. Contamination in Antarctic continent was first reported in 1966 (Corsolini, 2009). Many POPs are relatively volatile under environmental conditions. These chemical may present a liquid-gas transition and be transported by the wind, according to seasonal conditions. This process (phase transition) may occur several times since the degradation is very slow. More important, when POPs reach cold climate like in Polar Regions, they tend to be trapped, due to very low temperature. For instance, there are many researches dealing with contamination in Arctic and Antarctic regions (Bargagli, 2008; Tin et al., 2009). (Wania, 2003). In this sense, even unintentional production of POPs is not a localized problem; rather, it should be treated as a global concern. It is very usual to say that POPs are subject to long-range atmospheric transport (Shuntirasingh et al., 2010).

1.3 Bioaccumulation

From the chemical viewpoint, all these organic pollutants are very hydrophobic and these chemicals will minimize contact with water, tending to migrate to organic matter. For example, when these chemical reach soils, they will be preferentially adsorb on bioavailable organic components, such as humic substances (Wu et al., 2011). Also, they can be absorbed by plants and living organisms. This is an example of how POPs may enter in the food chain and will be assimilated by animals, for example. They will preferentially migrate to fatty tissues. For instance, a recent study (Kim et al., 2010) indicates that the concentration of POP’s is much higher in obese individuals. Once again, since the degradation is very slow, they will be accumulated over the years. In a similar way, POPs are easily transported by atmosphere. When in contact with water they also will be transported to planktonic organisms, entering the food chain. POPs were found as contaminants in birds (Chen and Hale, 2010; Vorkamp et al., 2009), penguins (Corsolini et al., 20060, fish (Ondarza et al., 2011; Hardell et al., 2010), sea lions (Alava et al., 2011), among others.

2. Unintentional production of POPs

From the perspective presented so far, it seems that POPs should be banned from any industrial or commercial activity, in order to preserve the environment. However this is not a simple task. Many POPs are unintentionally produced; they are, in fact, a result of industrial activities. These chemical, polychlorinated dibenzo-p-dioxins and dibenzofurans
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(PCDD/PCDF), polychlorinated biphenyls (PCB), can be released into atmosphere as a sub-product. The following is the original text issued by UNEP.

“Hexachlorobenzene, pentachlorobenzene, polychlorinated biphenyls, and polychlorinated dibenzo-p-dioxins and dibenzofurans are unintentionally formed and released from thermal processes involving organic matter and chlorine as a result of incomplete combustion or chemical reactions. The following industrial source categories have the potential for comparatively high formation and release of these chemicals to the environment:

a. Waste incinerators, including co-incinerators of municipal, hazardous or medical waste or of sewage sludge;
b. Cement kilns firing hazardous waste;
c. Production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching;
d. The following thermal processes in the metallurgical industry:
   i. Secondary copper production;
   ii. Sinter plants in the iron and steel industry;
   iii. Secondary aluminium production;
   iv. Secondary zinc production.

Hexachlorobenzene, pentachlorobenzene, polychlorinated biphenyls, and polychlorinated dibenzo-p-dioxins and dibenzofurans may also be unintentionally formed and released from the following source categories, including:

a. Open burning of waste, including burning of landfill sites;
b. Thermal processes in the metallurgical industry not mentioned in Part II;
c. Residential combustion sources;
d. Fossil fuel-fired utility and industrial boilers;
e. Firing installations for wood and other biomass fuels;
f. Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil;
g. Crematoria;
h. Motor vehicles, particularly those burning leaded gasoline;
i. Destruction of animal carcasses;
j. Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction);
k. Shredder plants for the treatment of end of life vehicles;
l. Smouldering of copper cables;
m. Waste oil refineries”

As it can be seen, there are many different activities able to unintentionally generate some POPs. Of course, some activities do not generate significant amounts of persistent organic pollutants, while others, due to massive production, may pose a high risk to environment. Here we will focus only on cement production. This industrial area may be very useful to represent the challenges in our modern society, regarding economic needs and environmental concern.

3. Cement production: Background and economic aspects

Cement is produced in almost all countries in the world. Concrete is a composite material formed by cement, sand, rocks and water. There are many kinds of cements and concretes.
Concrete is versatile material. It can be used under many environmental conditions, such as cold and hot climate, in the sea, under very high pressure and temperature. According to Meyer (2009) the world production of concrete is superior to 10 billion tons yearly. Table 5 lists the top-10 countries in cement production, in the period between 2004-2007, as well as world total manufactures. (US Department of Interior, 2005-2009; Rodrigues and Joekes, 2011).

<table>
<thead>
<tr>
<th>Country</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>934,000</td>
<td>1,040,000</td>
<td>1,200,000</td>
<td>1,350,000</td>
</tr>
<tr>
<td>India</td>
<td>125,000*</td>
<td>145,000*</td>
<td>155,000*</td>
<td>170,000*</td>
</tr>
<tr>
<td>USA</td>
<td>99,000</td>
<td>101,000</td>
<td>99,700</td>
<td>96,500</td>
</tr>
<tr>
<td>Japan</td>
<td>67,400</td>
<td>69,600</td>
<td>69,900</td>
<td>67,700</td>
</tr>
<tr>
<td>Russia</td>
<td>43,000*</td>
<td>48,700</td>
<td>54,700</td>
<td>59,900</td>
</tr>
<tr>
<td>Korea</td>
<td>55,900</td>
<td>51,400</td>
<td>55,000</td>
<td>57,000</td>
</tr>
<tr>
<td>Spain</td>
<td>46,800</td>
<td>50,300</td>
<td>54,000*</td>
<td>54,500</td>
</tr>
<tr>
<td>Turkey</td>
<td>38,000</td>
<td>42,800</td>
<td>47,500</td>
<td>49,500</td>
</tr>
<tr>
<td>Italy</td>
<td>38,000*</td>
<td>46,400</td>
<td>43,200</td>
<td>47,500</td>
</tr>
<tr>
<td>Brazil</td>
<td>38,000*</td>
<td>36,700</td>
<td>39,500</td>
<td>46,400</td>
</tr>
<tr>
<td>World</td>
<td>2,130,000</td>
<td>2,310,000</td>
<td>2,550,000</td>
<td>2,770,000</td>
</tr>
</tbody>
</table>

* estimative

Table 5. Cement production for different countries during the years 2004-2007

In a recent review (Rodrigues and Joekes, 2011) it was presented some implications and consequences of cement production. As it can be seen in Table 5, China produces about 50% of cement in the world. At a first glance, this massive production could be related to Chinese economic growth. Although this is a correct assumption, it does not explain the current situation in that country. There are many important aspects to be considered (Shen et al., 2005; Zhang and Zhao, 2000). China has experienced an unprecedented urbanization. It is estimated that urban population reached 456 million in 2000. In 1978, this population was 170 million. It is obvious that urbanization caused many different problems (He et al., 2008). However, in the context presented here, it is important to note that urbanization is the driving-force to production and consume of cement and concrete. In fact, the consumption of these materials is due to the lack of infrastructure. Concrete is used in sanitation, construction of buildings, roads, power plants and so on. Also, along with economic growth, people demand better living standards. Furthermore the mobility of population requires the construction of many kinds of new buildings (Shen et al., 2005).

It seems clear that cement will continue to play an important role in modern society. However, from the environmental viewpoint, cement production can be considered harmful, when the whole process is considered. For instance, for each ton of cement produced, it will render about 1 ton of carbon dioxide. (Worrel et al., 2001). It corresponds to about 5-6% of total CO₂ produced by man. Under the same conditions, it will consume around 60-130 kg of fossil fuel and 110 kWh (Morsli et al., 2007). In USA, cement production consume 0.6% of total energy produced in that country. Also, 1 ton of cement, demands 1.4-1.6 ton of raw-materials. (Horvath, 2004).
In order to understand the generation of POPs from cement manufacture it is convenient to describe cement composition and the manufacture process. Table 6 lists the major components of Portland cement and their proportion. It is also important to note, that chemical cement composition is variable, depending on many variables (Rodrigues & Joekes, 2011).

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>% (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate</td>
<td>Ca₃SiO₅</td>
<td>45-60</td>
</tr>
<tr>
<td>Dicalcium silicate</td>
<td>β-Ca₂SiO₄</td>
<td>15-30</td>
</tr>
<tr>
<td>Calcium aluminate</td>
<td>Ca₃Al₂O₆</td>
<td>2-15</td>
</tr>
<tr>
<td>Calcium ferroaluminate</td>
<td>4CaO.Al₂O₃.Fe₂O₃</td>
<td>5-15</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄.1/2H₂O</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 6. Major components of ordinary Portland cement type I

Calcium silicates are the most important components of Portland cement, although calcium aluminate, calcium ferroaluminate and gypsum are important in the hardening process. Usually, the synthesis of cement is accomplished at around 1500°C. Comparatively, cement is a low-cost material. Many efforts are conducted by cement industry to be competitive, such as location, reduction of energy consumption and distribution (Kendall et al., 2008; Newmark, 1998). Figure 1 presents a simplified diagram for the production of commercial Portland cement.

Cement production is far more complex than presented in figure 1. Specially, the heating of raw-materials may be accomplished in different ways. In order to better understand POPs emissions, two stages are presented here: primary and secondary heating. This division was adopted to simplify the discussion, although this is not the usual method to describe cement production.

The Stockholm convention on persistent organic pollutants (2001) listed the 4 major sources of unintentional production of POP’s: waste incinerators, production of pulp using elemental chlorine or chemicals, thermal processes in metallurgical industry and cement kilns.

4. **Persistent organic pollutants from cement plants**

Cement manufacture demands the use of very high temperatures. It means that energy is a relevant cost in this industry. Several attempts were made through the years to minimize energy consumption. Also, in terms of sustainability, the reduction of fossil or non-renewable fuels consumption is a very attractive option. In many plants, coal is the preferred fuel. European Union countries consume about the energy equivalent to 27 Mt of coal (Kookos et al., 2011) to produce cement.

Perhaps the most interesting approach to reduce the use of fossil fuels is the utilization of co-firing wastes to replace coal. Initially, from the environmental point of view this solution is very interesting, and many residues can be used, such as tires (Prisciandaro, 2003; Carrasco et al., 2002), sewage sludge (Gálves et al., 2007), carpet (Lemieux et al., 2004), among many others. For example, European Union countries dispose approximately 600.000 tons of waste tires each year (Aiello et al., 2009). Table 7 shows several alternative materials
Fig. 1. Major steps of commercial production of cement that can be incorporated into cement production. As it can be seen, cement production can also be an environmentally-friendly process.

According to Cembureau (The European Cement Association) alternative fuels are classified in five categories:

Class 1: gaseous alternative fuels (examples: refinery waste gas, landfill gas),
Class 2: liquid alternative fuels (low chlorine spent solvents, hydraulic oils)
Class 3: pulverized, granulated or finely-crushed solid alternative fuels (sawdust, dried sewage sludge, granulated plastic, animal flours, fine crushed tires),
Class 4: coarse-crushed solid alternative fuels (crushed tires, rubber/ plastic waste, wood waste, reagglomerated organic matter)
Class 5: lump alternative fuels (whole tyres, plastic bales).
Table 7. Alternative materials used by European Union (27) countries in 2005

According Mokrzycki & Uliasz-Bochenczyk (2003) a different classification of fuels to cement industry is presented below:

Solid fuels:
vegetable compounds or natural products (oil shale, peat, barks, sawdust, etc.),
synthetic products (used tires, rubber waste, waste plastics, etc.),
others (parts of shredded cars, fuels derived from rejects, household garbage, etc.).

Liquid fuels:
liquid substitute fuels – easily decomposed, slightly toxic (acid tar, oil residues, etc.),
liquid substitute fuels, stable toxic (polyaromatic hydrocarbons (PAH), polichlorinated biphenyl (PCB), etc.).

On the other hand, the utilization of so many wastes or alternative materials may bring undesirable consequences. Here we are concerned with the unintentional production of persistent organic pollutants. The formation mechanism of POPs is certainly very complex, since many compounds are possible. For instance, dioxins, PCDD/PCDFs were studied in the process of the burning of municipal solid waste (Lee et al., 2008). Some reactions involved in this process may be depicted.

The formation of these chemicals from cement kilns occurs by two major mechanisms: by the presence of precursor or de novo synthesis. In the precursor mechanism there will be the polycondensation of precursor. Usually these gaseous reactions will take place in the range between 300-600°C. In the de novo synthesis, carbon must be present at the solid phase; on the other hand, the presence of oxygen in the gas phase is also fundamental (Fujimori et al., 2010). Usually these reactions take place at 200-400°C.

A possible example of precursor synthesis may be described as follows, considering the utilization of aromatic solvents.

The conversion of HCl to chlorine, in the presence of a catalyst (CuCl₂):
Production of Persistent Organic Pollutants from Cement Plants

\[
2CuCl_2 + \frac{1}{2}O_2 \rightarrow Cu_2OCl_2 \tag{1}
\]

\[
Cu_2OCl_2 + 2HCl \rightarrow 2CuCl_2 + Cl_2 + H_2O \tag{2}
\]

Followed by direct transfer of chlorine by a ligand transfer oxidation mechanism

\[
ArH + CuCl_2 \rightarrow ArHCl^* + CuCl \tag{3}
\]

\[
ArHCl^* + CuCl_2 \rightarrow ArCl + CuCl + HCl \tag{4}
\]

As the reaction proceeds, will occur a sequential chlorination. The formation of PCDDs, PCDFs and PCBs, PAHs may occur during cement fabrication (van Loo, 2008).

It should be pointed out that engineering aspects such as the kind of kiln, the way how chemicals are used, rate, oxygen levels, etc, may inhibit or minimize the formation of pollutants (Prisciandaro, 2003).

5. Conclusions

Cement production shows interesting aspects regarding the balance between an industrial (pollutant) activity and environmental concerns. The unintentional production of POPs is, certainly, an important issue to deal with. However, it is impossible to imagine a limitation on cement manufacture, based on this consideration. Rather, cement industry and other organization, such as United Nations and governments, should work together to understand and minimize this (and other) problems.

Cement industry shows a high potential to be sustainable. The utilization of residues and wastes from other industrial activities, in fact, should be stimulated, since tons of hazardous components may be eliminated. The generation of persistent organic pollutants, a side-effect, needs a better comprehension. It is very possible that in few years cements plants will be able to operate in order to avoid POPs emissions.

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7. References


concentrations of organochlorines in adipose tissue. *Biomedicine & Pharmacotherapy* Vol. 61, No. 10 (December 2007), pp. 659-664 ISSN 0753-3322


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Nature minimizes the hazards, while man maximizes them. This is not an assumption, but a basic idea of the findings of scientists from all over the world. The last two centuries have witnessed the indiscriminate development and overexploitation of natural resources by man causing alterations and impairment of our own environment. Environmental contamination is the result of the irrational use of resources at the wrong place and at the wrong time. Environmental contamination has changed the lifestyle of people virtually all over the world, and has reduced the extent of life on earth. Today, we are bound to compromises with such environmental conditions, which was not anticipated for the sustenance of humanity and other life forms. Let us find out the problem and its management within this book.

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