Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 158 (2008) 585–592
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Organic and inorganic pollutants from cement kiln stack feeding alternative fuels

Juan A. Conesa*, Araceli Gálvez, Fernán Mateos, Ignacio Martín-Gullón, Rafael Font

Department of Chemical Engineering, University of Alicante, Ap. 99 E-03080 Alicante, Spain

Received 22 May 2007; accepted 31 January 2008
Available online 19 February 2008

Abstract

In this work, an analysis of the emission of different pollutants when replacing partially the fuel type used in a cement kiln is done. The wastes used to feed the kiln were tyres and two types of sewage sludge. The increasing mass flow of sludge is between 700 kg h^{-1} and 5500 kg h^{-1}1, for a total production of clinker of 150 t h^{-1}, whereas the fed tyres were in the flow range of 500–1500 kg h^{-1}. Dioxins and furans, polycyclic aromatic hydrocarbons (PAHs) and other hydrocarbons, heavy metals, HCl and HF, CO, CO_2, NO_x and other parameters of the stack were analyzed, according to the standard methods of sampling and determination, through more than 1 year in six series: one blank (no sewage sludge) and five more with increasing amount of sludge and/or tyres. The emission of PAHs and dioxins seems to increase with the amount of tyres fed to the kiln, probably due to the fed point used for this waste.

Keywords: Dioxin; Heavy metals; Sewage sludge; Emission; Cement kiln; Tyres; Waste; Co-combustion

1. Introduction

Cement is an important binding agent for construction industry and is produced world-wide in large amounts. In 2000, about 323 million tons were processed in Europe (Bundesverband der Deuschen Zemenindustrie [1]).

A central process step during the manufacturing of cement is the production of the intermediate product clinker. For this production, inorganic raw materials are calcined at temperatures in the range of 1000–1500 °C. In order to reduce the costs of this energy-intensive process, which has a high share in the manufacturing costs of cement, regular fuels like coal, petroleum coke, oil and gas are increasingly substituted by different types of waste.

Co-incineration of wastes to substitute regular fuels started more than 20 years ago with the use of waste oil and used tyres. In the last 10 years, use of alternative fuels in the cement is continuously increasing. The share of secondary fuels in the total use of fuels in cement plants is expected to increase further.

Chemicals emitted from a source into the environment could be directly transmitted to humans through air inhalation. However, these chemicals could also cross-environmental media boundaries, transferring to soils, vegetation, water, biota, etc. Consequently, human health can be also indirectly affected through different pathways such as drinking water or groundwater, skin absorption of the chemicals present in water, intake of contaminated foodstuffs and oral and skin absorption of chemicals from soils. Therefore, for accurate health risk estimation, the chemical concentrations in each of these environmental media must be determined [2].

The use of solid wastes as a supplementary fuel or raw material substitutes in cement kilns is one of the best technologies for complete and safe destruction of these wastes, due to the fact that there is a simultaneous benefit of destroying wastes and getting energy. Nevertheless, some wastes, such as those containing an important amount of Hg, should be carefully treated in the kiln. At the same time, substituting primary fossil fuels has environmental and economic advantages. The main benefits in using solids wastes in cement kilns include energy recovery, conservation of non-renewable fuels, reduction in cement production costs and the use of already existing facilities. Types of waste presently used by the cement industry as a supplementary

* Corresponding author.
E-mail address: ja.conesa@ua.es (J.A. Conesa).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.01.116

fuel include paint thinners, degreasing solvents, solvents from ink and printing industries, chemical byproducts from pharmaceutical and chemical manufacturing, waste oils, waste tyres, municipal solid wastes, sewage sludges and waste timbers. The feeding rates vary from country to country. For example, while in Spain the limit is 15% of the thermal energy required in the kiln, there is no limit in Switzerland. Although they are actually burned, the thermal decomposition of such wastes has not been in some cases studied from a scientific point of view until now.

Tyres in the cement industry can be used as a whole piece or scraped into pieces, depending on the requirements of the installation. Industrial tests indicate that the costs of using approximately 20% shredded tyre as a fuel substitute are similar to those using only petroleum coke.

In an incineration process, some chemicals are emitted as a consequence of the combustion process, and these chemicals could be directly transmitted to humans through air inhalation. However, these chemicals could also cross-environmental media boundaries, transferring to soils, vegetation, water, etc. Consequently, human health can be also indirectly affected through different pathways such as drinking water or groundwater, skin absorption of the chemicals present in water, intake of contaminated foodstuffs and oral and skin absorption of chemicals from soils.

One of the major hazards in the alternative fuels flue gas composition is the heavy metal (HM) content. Not all heavy metals are toxic and not all toxic heavy metals have the same toxicity. Therefore many countries differentiate between different toxicity classes:

- *class I*: Cd, Hg, Tl;
- *class II*: As, Co, Ni, Se, Te;
- *class III*: Pb, Cr, Cu, Pt, V, Sn, Pd, Sb, Mn, Rh.

The HM in class I are the most toxic and harmful, the HM in class III the least ones. The main sources of HM emissions from cement kiln stacks are either raw materials or fuels containing heavy metals. According to the behaviour of the HM in the kiln system, three classes can be distinguished:

- The non- or low-volatile HM (As, Be, Co, Cr, Cu, Mn, Mo, Sb, Se, Te, V and Zn) are incorporated in the clinker to almost 100%, and therefore do practically not appear as emissions. As a general rule the sum of the emissions of all non-volatiles HM of a preheater kiln is always much below 0.1% of the corresponding metal input.
- The semi-volatile HM such as Tl, Pb and Cd are not completely (Pb, Cd) to very little (Tl) incorporated directly in the clinker. The remaining part which is not incorporated in the clinker is expected to be almost completely adsorbed on the surface of the dust particles in the kiln exhaust gas system.
- Volatile HM cannot be efficiently controlled by dedusting of the kiln exhaust gas because a portion of the volatile HM always remains volatile (not attached to dust particles). The most prominent and only example of relevance to the cement industry is mercury (Hg). Hg is suspected to be emitted to a large degree in vaporous form and can be retained by carbon filters. The lower the exhaust gas temperature is at the filter inlet the higher is the proportion of Hg attached to dust particles that can be removed from the exhaust gas. The origin of Hg is the cement raw material as well as the fuels.

The present work has the main purpose of checking the amounts of pollutants emitted by a cement kiln in different situations. Two different wastes were fed to the kiln, as a part of an industrial project concibed to develop an efficient system to eliminate the wastes. Six series of sampling were performed in the stack of the factory. In the series, the composition of the fuels used to heat the furnace was changed.

Dioxins and furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), heavy metals, HCl, HF and volatile organic compounds (VOCs) are analyzed, according to standard methods of sampling and determination (details later). Tests in the cement kiln were performed through more than 1 year, because of the difficulty of the work done.

Heavy metals entering the kiln (with the fuels and with the raw materials) have three different ways to exit the system: they can exit with the cement clinker, emitted through the stack and can also be found in the filter dust cement. Levels of metals in this last material are surprisingly high [3], arriving at levels close to 300 ppm for As.

The use of sewage sludge as an alternative fuel has its advantages and drawbacks; among the advantages one can cite that is a cheap fuel that is considered as biomass, and then does not contribute to the total emission of CO_2 considered in the Kyoto protocol. But as a disadvantage, environmental regulations are generally more exigent and there is a necessity to adapt the installations.

2. Materials and methods

Characterization of the sludges and tyres was carried out. Table 1 shows the details of the analysis performed. Two different sewage sludges were used in the study period, due to the inability to get the same sludge continuously.

The methods used for sampling and analysis are the standard methods suggested by the spanish regulations for stack analysis. Specifically, methods used were

- *PCDDs/Fs sampling*: EPA Method 0023A, European Norme EN 1948-1 (isokinetic).
- *PCDDs/Fs analysis*: EPA Method 1613 (high-resolution gas chromatography coupled to a high-resolution mass spectrometer (HRGC/HRMS) with labelled congeners).
- *PAHs sampling*: EPA Method 0010 (no isokinetic needed).
- *PAHs analysis*: EPA Method 8100 (mass spectrometry, no high resolution).
- *VOCs sampling*: EPA Methods 0040 and 0031 (with TENAX resin).
- *VOCs analysis*: EPA Method 8260B (thermal desorption with mass spectrometry).
- *Heavy metals sampling and analysis*: EPA Methods 0060, 0029, 3051, 3015 (isokinetic sampling, analysis by inductively coupled plasma with a mass spectroscopy (ICP-MS)).