

Leaching Of Samples Contaminated With Toxic Metals Representing Cements Contaminated By Industrial Waste Burning

Luciane Pimentel C. Monteiro, Fernando B. Mainier, Bianca De A. Santos
Escola de Engenharia, Universidade Federal Fluminense, Niterói, RJ., Brazil

ABSTRACT: *In the past, cement plants depended on the burning of fuel oil in their industries to meet their energy needs. After the 80s/90s, the fossil fuels reduction and the incentives to use alternative fuels intensified the burning of organic farming waste (sugarcane bagasse, rice straw, twigs) provided these residues had the acceptable calorific value, such as waste from other industries and waste tires. However, the cement industry must be aware of how toxic such waste, when burned, can be to the human being and the environment. Depending on their origin, the environmental risks increase and may endanger the quality of the cement produced. The study, based on leaching experiments in laboratory is a warning to society of the environmental and human risks in the presence of those contaminants (heavy metal compounds) during the burning of these alternative fuels in their clinker kilns. Static leaching results indicated the presence of heavy metal traces in the leachate.*

Keywords: *cement, fuels, leaching, waste burning*

I. INTRODUCTION

Aiming at reducing the production costs concerning energy, the cement industry has expanded its willingness to incinerate industrial waste in rotary cement clinker kilns, replacing part of the conventional fuels by various types of waste generated in other industrial units [1,2,3]. The possibility of this energy substitution has been developed in recent years, considering, among other aspects, the preparation of blends consisting of different types of waste mixtures, seeking improved energy efficiency. In some cases, waste is processed for the sole purpose of replacing the inorganic components of raw meal, that is, alumina, silica or iron oxide, with no thermal power generation [4].

With regard to the thermal load, it is continuously necessary and it is of about one thousand tons of fuel for burning in smaller plants, and more than five thousand tons in larger plants. For processing 3600 tons of clinker, the main component of cement, in a single kiln per day, a larger capacity rotary kiln is required, which consuming only fuel oil, will consume about 300 tons of energy, that is, ten trucks tank.

In Brazil, the number of cement plants installed consists of 487 clinker plants and among them 30 co-process waste and have the environmental license to do so, consuming the equivalent to 39.48% of the final energy consumption of the country[5,6] .

Around 1979-1981, fuel oil had its price tripled because of the national dependence established on imported oil. There was, then, the creation of quotas for fuel oil supply to the industries, which should not exceed the 1979[7] consumption. Thus, incentives and subsidies to some alternative sources of fuel and thermal power were created through the signing of protocols for the use of domestic coal by the steel, cement, paper and cellulose industries[5]. In September 1979, the cement industries signed the "Protocolo de Redução e Substituição do Consumo de Óleo Combustível na Indústria Cimenteira" ("Fuel Oil Consumption Reduction and Replacement in the Cement Industry Protocol"), in which they pledged to reach, by the end of 1984, the total substitution of fuel oil consumed in their plants by national mineral coal and adopt energy conservation measures at plant level. Consequently, in 1985, the cement industry had already replaced about 95% of the fuel oil used before [5].

II. CEMENT PRODUCED FROM THE BURNING INDUSTRIAL WASTE

The most commonly used cement is composed of 96% clinker and 4% of gypsum plaster. The clinker is produced by the thermal treatment in rotary kilns at high temperatures from a rocky material usually containing 80% calcium carbonate (CaCO_3), 15% silicon dioxide (SiO_2), 3% aluminum oxide (Al_2O_3), and smaller amounts of other components such as iron, sulfur and others. Such materials are found in limestone deposits, located near the clinker production kilns. The raw material is mixed and finely ground, being subjected to a heating process that leads to the final production of the clinker [8].

The energy required for the drying, calcining and sintering of the clinker is obtained by burning a variety of fuels, of which the most commonly employed are mineral coal, natural gas and fuel oil [8].

According to Cavalcanti [9], alternative fuels are used such as old tires, waste paper, wood waste, residues of pharmaceutical industries, petroleum, petrochemical, and others, in the period before the 70's. This fact has not changed. However, rules are not always complied with for this purpose. Fig. 1, below, shows the layout of a typical waste- incineration kiln.

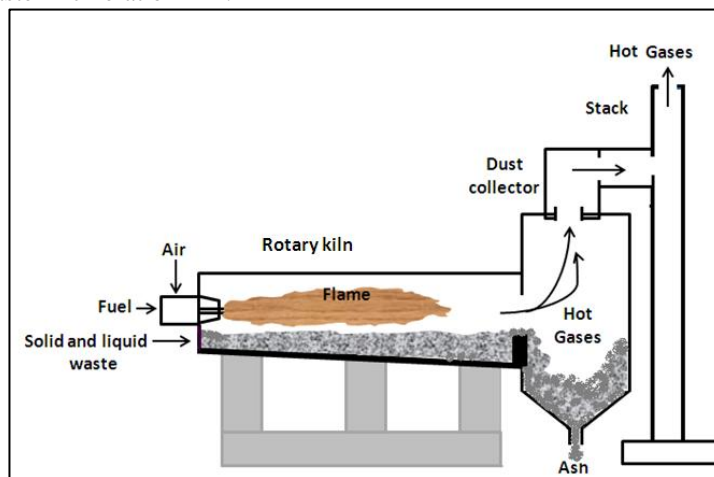


Figure 1: Layout of a typical rotary kiln for burning waste

By using those residues, in addition to a larger amount of elements as calcium, silicon, iron and aluminum, other elements are introduced with the fuel such as magnesium, sulfur, sodium, potassium, manganese, phosphorus and titanium, and trace elements such as chromium, lead, zinc, vanadium, nickel and many others [8].

Some types of waste should not be used in clinker kilns, often by environmental restrictions (legislation) as well as by the characteristics of the clinker manufacturing process [10]. Firstly, the aim of using the residue must be verified, whether for partial fuel replacement, partial raw material replacement, or both.

To be regarded as a fuel substitute, the residue must supply thermal power to the process in the combustion stage, and when considered partial replacement of the raw material, it must contain major components such as calcium, silica, aluminum and iron, which are mineralizing and/or flux materials of the cement production process. The environmental agency of the state of São Paulo (Brazil) -CETESB - defines a procedure for a residue to be used as a substitute fuel: it must have lower calorific value (lower heating value) on a dry basis higher than 2775 kcal/kg. When use is defined, its physicochemical properties should be assessed, for certain contaminants in the residue, when burned in the kiln, must have their amounts limited [11].

The maximum rate of waste supply to be burnt in the kiln is established by previously performed blank tests. This has the purpose to prevent that the emission limits set by law are exceeded, avoiding environmental impacts, not affecting safety and public health, not damaging facilities, equipment and the quality of the clinker/cement products [10].

As they want to please the environmental authorities as well as the interests of the industries, cement companies are even co-processing industrial waste. The materials most frequently used for this purpose are the carbonaceous residues that derive from different industrial processes such as oils, solvents, hydrocarbons and alcohols sludge. However, the chemical composition of oxidized materials and salts, which are used in the cement production, are not taken into consideration, since they generally contain heavy metals in their composition [3,12]. Yet, it should be emphasized that the specifications for the cement produced with the use of natural gas or industrial waste are the same, and society is not aware of the toxicity risks caused by the presence of contaminants within the cement [10, 14, 15].

III. EXPERIMENTS

3.1 Leaching Experiments

Leaching experiments were performed to obtain the contaminant ion levels of copper, chromium, cadmium and nickel in the leaching solutions of the white cement test specimens impregnated with salts of the respective elements to be analyzed [13].

Thus, the possibility of leaching salts of some heavy metals in the cement produced from industrial waste into the environment was shown.

3.1.1 Method

The equipment used in the leaching experiments consisted of plastic containers of 200 mL containing the test specimens fully immersed in the leaching solution. The preparation of the test specimens was carried out with 40 g of white commercial cement contaminated by the addition of 1 g of one of the salts containing a contaminant element (copper sulfate, potassium chromate, cadmium chloride or nickel chloride) and 10 mL of demineralized water, as Fig. 2, below, shows:



Figure 2: test specimens

The resulting mixture was then placed in conical polystyrene molds with the following measures: larger diameter: 5 cm; smaller diameter: 3 cm and 4 cm height, with a total area of 50 cm². A small shovel of plastic material was included to facilitate the entry and removal of the test specimens from the leaching containers.

The test specimens were then subjected to natural drying for two days and complementary drying in a laboratory incubator at 120° C for a two hours' period.

Next, the test specimens removed from the polystyrene molds underwent static leaching operation in periods of 14 and 28 days in 200 mL plastic containers fully submerged in volumes of 100 mL of sodium hydroxide solution 0.1 M or hydrochloric acid 0.1 M (prepared with demineralized water in a laboratory). pH control of the hydrochloric acid 0.1 M leaching solution was carried out, as alkali components of the cement matrix tend to increase this value. The corrections for leaching with hydrochloric acid 0.1 M were carried out with concentrated hydrochloric acid, searching for values between 4 and 5 in the pH range. Leaching with sodium hydroxide solution maintained pH values at about 12.

After the time limits established for the leaching operation, samples were taken from the leaching solutions in glass flasks suitable for spectrometer sampling and sent to be analyzed by emission spectrometry with inductively coupled argon plasma to quantify the leached contaminants. Fig. 3, below, shows the optical emission spectrometer with inductively coupled argon plasma.



Figure 3: Optical emission spectrometer with inductively coupled argon plasma

3.1.2 Experiments analysis

Experiments are commonly performed to demonstrate the possibility of certain contaminants leaching into the environment such as metal compounds, when they are present in the cement. Twenty sample test

specimens impregnated with copper sulfate, potassium chromate, cadmium chloride and nickel chloride, respectively, in curing times of 28 days (0.1M sodium hydroxide) and 14 and 28 days (0.1M hydrochloric acid) were analyzed. Curing times were determined by the temperature condition differences of the clinker kiln (about 1800°C); leaching experiments occurred at 25°C. The same is true for the pH, since the clinker kilns have specific oxidizing conditions, requiring more aggressive ones for the leaching tests simulation.

Importantly, this type of analysis can be performed for any toxic element, such as metals possibly present in the clinker/cement matrix, although the aim of the present work is to evidence that certain types of control can be carried out without major complications with respect to rules and legislation applicable to the cement manufacturing process. Tables 1,2,3 and 4 show the results for Cu²⁺, Cr⁶⁺, Cd²⁺ and Ni²⁺ ion contents found in the leaching tests.

1.1.3 Experiments results

Table 1: Cu²⁺ ions analyses results

Sample	Curing Time	Leaching Type	% initial weight of Cu ²⁺ ions	Cu ²⁺ ions content in the leachate (ppm)
CIM-Cu-1	28	NaOH0.1M	0.83	0.06
CIM-Cu-2	14	HCl 0.1M	0.69	0.02
CIM-Cu-3	14	HCl 0.1M	0.70	0.12
CIM-Cu-4	28	HCl 0.1M	1.02	0.03
CIM-Cu-5	28	HCl 0.1M	0.80	0.03

Table 2: Cr⁶⁺ ions analyses results

Sample	Curing Time	Leaching Type	% initial weight of Cr ⁶⁺ ions	Cr ⁶⁺ ions content in the leachate (ppm)
CIM-Cr-1	28	NaOH0.1M	0.57	288
CIM-Cr-2	14	HCl 0.1M	0.94	232
CIM-Cr-3	14	HCl 0.1M	1.26	25
CIM-Cr-4	28	HCl 0.1M	0.69	72
CIM-Cr-5	28	HCl 0.1M	0.55	61

Table 3: Cd²⁺ ions analyses results

Sample	Curing Time	Leaching Type	% initial weight of Cd ²⁺ ions	Cd ²⁺ ions content in the leachate (ppm)
CIM-Cd-1	28	NaOH0.1M	1.41	0.001
CIM-Cd-2	14	HCl 0.1M	1.06	0.002
CIM-Cd-3	14	HCl 0.1M	1.14	0.004
CIM-Cd-4	28	HCl 0.1M	1.16	0.001
CIM-Cd-5	28	HCl 0.1M	1.07	0.002

Table 4: Ni²⁺ ions analyses results

Sample	Curing Time	Leaching Type	% initial weight of Ni ²⁺ ions	Ni ²⁺ ions content in the leachate (ppm)
CIM-Ni-1	28	NaOH0.1M	0.78	0.002
CIM-Ni-2	14	HCl 0.1M	0.62	0.006
CIM-Ni-3	14	HCl 0.1M	1.01	0.022
CIM-Ni-4	28	HCl 0.1M	0.70	0.004
CIM-Ni-5	28	HCl 0.1M	0.54	0.005

IV. CONCLUSIONS

Based on the study, the following conclusions are considered as critical:

- laboratory tests using test specimens leached with white cement contaminated with heavy metal salts have shown that environmental contamination is possible from the cement produced, incinerating industrial waste in the kilns;
- the fact of not having quantitative control of what may be impregnated in the cement matrix, and that regardless its concentration it might become leached into the environment must be investigated by the competent authorities of the matter;
- most of the workers of the cement industry and surroundings do not question the burning of any of the residues in the kilns, they just live with this reality, and "businessmen's" major concern is the use, in a

sustainable way, of this annoying environmental waste that causes problems with the environmental legislation that controls them;

- burning waste tires in clinker kilns is not a recommendable alternative in environmental terms for the destination of this troublesome residue;
- cement kilns neither meet the necessary conditions to regulate the process of industrial waste incineration, nor have the effective control of contamination that occurs during this process, as there is no information that adjustments in the kilns are carried out to burn waste instead of conventional fuels;
- the sale of industrial waste with undeclared contaminants to its incineration in any industrial kiln becomes negligent and irresponsible;
- in face of the dangers related to the contamination of the cement produced from the use of industrial waste, its use without any additional control should be carefully avoided, and if responsible practice is not possible, only clean “fuels” should be used;
- these observations are not relevant only to the issues concerning the production of cement from industrial waste burning, but also for any environmental damage resulting from industrial processes that do not care about the used technological routes.

REFERENCES

- [1] F.Bagnoli, A. Bianchi, A. Ceccarina, R. Fucoco and S. Giannarelli, Trace metals and organic pollutants in treated and untreated residues from urban solid waste incinerators, *Microchemical Journal* 79, 2005, 291-297.
- [2] J. Péra, J. Ambrosie and M. Chabannet, Valorization of automotive shredder residue in building materials, *Cement and Concrete Research*, 34, 2004, 557-562.
- [3] P. H. Shih, J.E.Chang and L. C. Chiang, Reuse of heavy metal containing sludges in cement production, *Cement and Concrete Research*, vol.35, Issue 11, Nov/2005, 2110-2115.
- [4] T. M. Braga, *Risco e conflito ambiental sob o signo da (mono) indústria: um estudo sobre políticas ambientais na bacia do rio Piracicaba, Minas Gerais*. População e meio ambiente: debates e desafios/ Haroldo Torres e Heloisa Costa (organizadores) – São Paulo: Editora SENAC, São Paulo, 2000.
- [5] A.M.M. Santi and F. O. S. Seva, Resíduos renováveis e perigosos como combustíveis industriais. Estudo sobre a difícil sustentação ambiental da fabricação de cimento no Brasil, anos 1990, *VIII Congresso Brasileiro de Energia*, RJ, dez, 1999.
- [6] J. G. Silva, *Há emissões acrescidas na co-incineração de resíduos industriais perigosos em cimenteiras*, Universidade de Coimbra, Associação Nacional de Conservação da Natureza, QUERCUS, abril/2002.
- [7] D. Lemarchand, Cement kiln incineration associated to pretreatment, a viable waste management solution, *Congresso Brasileiro de Cimento*, 5, SP, nov/1999, Anais São Paulo, 1999.
- [8] A. F. Battagin, O Mundo do Cimento, www.cimento.org, accessed in 2012.
- [9] J. E. Cavalcanti, A década de 90 é dos resíduos sólidos. *Revista Saneamento Ambiental*, nº 54, nov-dez, 1998, 16-24.
- [10] A. M. M. Santi and M. S. Cremasco, Combustíveis e riscos tecnológicos ambientais na fabricação do cimento: avaliação contextualizada no município de Barroso, Minas Gerais, *III Encontro da ANPPAS*, Brasília, maio, 2006.
- [11] C. Mazzer and O. A. Cavalcanti, Introdução à gestão ambiental de resíduos, *Infarma*, v.16,n. 11-12, 2004.
- [12] R. Barna, Z. Rethy and L. Tiruta-Barna, Release dynamic process identification for a cement based material in various leaching conditions. Part I. Influence of leaching conditions on the release amount, *Journal of Environmental Management*, 74, issue 2, jan 2005, 141-151.
- [13] L. P. C. Monteiro, *Impacto Ambiental Associado à Queima de Combustíveis Alternativos em Fornos de Clínquer: Visão sob o Prisma da Educação Ambiental*. Tese de Doutorado, out/2007, UFF, RJ, Brazil.
- [14] X. D. Lin, C. S. Poon, H. Sun, I. M. C. Lo and D. W. Kirk, Heavy metals speciation and leaching behaviors in cement based solidified/stabilized waste materials, *Journal of Hazardous Materials*, v. 82, n. 3, April, 2001, 215-230.
- [15] EPA-Environmental Protection Agency, Test methods for evaluation solid waste, toxicity characteristics leading procedure (TCLP): Method 1311, Revision 0, 35 p. Physical /chemical methods. SW-846, 1992.