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Proposal for Reducing Emissions of SO_x in Cement Plants

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Abstract In the cement industry, emissions of sulfur oxides, nitrogen, carbon dioxide and water are inherent in the manufacturing process. However, there are limits to the amount of SO_x and NO_x emissions; the inhalation of such substances entails risks to human health, and their interaction with the atmosphere results in the formation of sulfuric acid and nitric acid, causing acid rain. These emission limits are even more severe when there is co-processing in the production process. SO_x emissions can be formed by burning fuel, but they can also be present in the raw materials used. The presence of sulfur-based compounds in the raw materials has a great impact on the cement industry, owing to the large amount of limestone used in the process, especially when the deposits have a high content of pyrite (FeS_2). One of the barriers encountered in the process of environmental licensing for co-processing is the high level of SO_x emissions. To decrease these emissions and to enable co-processing in a cement industry, tests were performed, using abatement with lime (CaO). By varying the conditions of the manufacturing process, it was possible to obtain a reduction of up to 90% of the SO_x emissions. With the implementation of this technique, SO_x emissions reached values that met the legal limits, which could enable the start of co-processing in the industry.

Keywords Cement industry, Sulfur oxide, Emissions, Environmental

1. Introduction

In Brazil, for the past ten years, there has been a large increase in civil engineering projects, from the construction of popular houses to large infrastructure works. The graph of the Brazilian production of Portland cement, presented in Figure 1, strengthens this scenario; however, in the environmental vision, large quantities of gases, such as CO_2, SO_x, NO_x, are generated as a consequence [1].

The construction of buildings, based on the cement industry, has a very important impact on the environment in terms of the volumes produced and its contribution to greenhouse-gas emissions. Currently, based on worldwide cement production, it is estimated to contribute 5–7% CO_2 emissions, and there is an average of 866 kg CO_2 per ton of clinker produced [2-4].

Currently, cement can be defined as the product of an integrated industrial activity that incorporates the extraction and processing of minerals (limestone, clays, sand), the use of siliceous slag from a blast furnace in steel manufacturing, using various types of fuel, its chemical and physical transformation in clinker, the addition of other relevant products and, finally, the grind, as this final product fits the technical specifications of a cement.

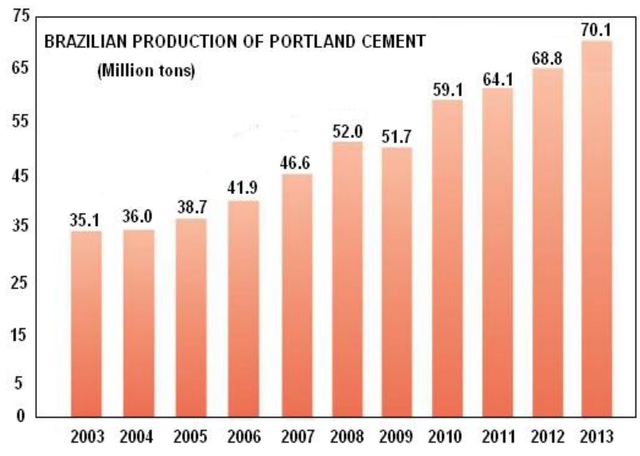

Figure 1. Brazilian production of Portland cement (2003-2013) [4]

The raw materials used in cement production are limestone, clay and sand, and the typical formulation has the following composition presented in Table 1.

Table 1. Composition of the mixture used for burning in rotary kilns

Composition of mixture	%
$CaCO_3$	80
SiO_2	15
Al_2O_3	3
Others	2

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The burning of this mixture, especially in rotary kilns, will generate large volumes of CO_2 as a function of the decarburization of limestone. Portland cement is a fine, grey powder that consists of a mixture of the tricalcium silicate ($3CaO.SiO_2$), dicalcium silicate ($2CaO.SiO_2$), tricalcium aluminate ($3CaO.Al_2O_3$) and tetracalcium aluminoferrite ($4CaO,Al_2O_3.Fe_2O_3$), to which one or more forms of calcium sulfate ($CaSO_4$) have been added.

In the step of mixed burning, other gases are generated in addition to CO_2, among them are the SO_x, and of these emissions, the main gas is SO_2. Usually small amounts of SO_3 are issued in conjunction with a chimney; therefore, SO_x is listed as the two oxides SO_2 and SO_3 in the cement manufacturing system, corresponding to the following steps:

- As a result of the chemical reaction that occurs in the oven in obtaining the clinker from the sulfur content contained in the form of pyrite (FeS_2) within the raw material employed for the reaction:

$$2\ FeS_2 + 11/2\ O_2 \rightarrow Fe_2O_3 + 4\ SO_2.$$

- From the burning of sulfur from the fuel used in the kiln.
- From waste typically burned in cement plants, which can contain organic sulfur compounds represented by the reaction:

$$R_1\text{–}S\text{–}R_2 + O_2 \rightarrow CO_2 + H_2O + SO_x,$$

where R_1 and R_2 are hydrocarbons.

Environmental acidification can be understood based on the predominant mechanism for the conversion of SO_2 in H_2SO_4, which consists of several sequential steps that are accelerated or reduced depending on the contaminants in the air, primarily from industrial complexes, pyrometallurgy of copper [5], petrochemicals, petroleum and cement plants associated with industrial waste co-processing.

According to Baird & Cann [6], if you add SO_2 to the hydroxyl radical ($OH^{\cdot}$), a new radical ($HSO_3^{\cdot}$) will form, which then reacts with oxygen (O_2) and water droplets, as shown in the steps of the following reactions:

$$SO_2 + (OH^{\cdot}) \rightarrow (HSO_3^{\cdot})$$

$$(HSO_3^{\cdot}) + O_2 \rightarrow SO_3 + (HOO^{\cdot})$$

$$SO_3 + H_2O \rightarrow H_2SO_4\ (g)$$

$$H_2SO_4\ (g) + \text{many}\ H_2O \rightarrow H_2SO_4\ (aq)$$

Other contaminants such as NO_x, ozone (O_3) and other oxidants or catalytic substances (Fe^{3+}, MnO_2, V_2O_5) can contribute to the formation of sulfuric acid and, consequently, acid rain. There is no doubt that both the emissions of SO_2 and acid rain create environmental problems [7-9].

Based on these facts, Table 2 presents human health indices for the SO_2 levels required to function outdoors, according to the EPA (Environmental Protection Agency) [10, 11].

Owing to the great power of SO_2 emissions from the cement industry, some techniques for their removal are presented in Table 3.

Table 2. Indices of SO_2 for quality of life

Concentration of SO_2, μg/m^3	Levels in terms of human health	Precautions
0 – 50	Good	------
51 - 100	Reasonable	------
101 - 150	Unhealthy for sensitive groups	Asthmatic people should limit physical exertion outdoors in these areas.
151 - 200	Insalubrious	Children, asthmatics and people with heart or lung diseases should limit physical exertion in outdoor areas.
201 - 300	Insalubrious	Physical exertion should be avoided in these outdoor areas for children, asthmatics, and people with heart or lung diseases. It is recommended that you also avoid physical efforts in these areas.
301-500	Very toxic	Children, asthmatics and people with heart or lung diseases should stay indoors; other individuals should avoid outdoor efforts.

Table 3. SO_2 reduction techniques applied in the cement industries

Operational techniques	Types of kiln where the application is possible	Reduction efficiency	Emission kg/t clinker
Adding absorbent	All	60-80%	0.8
Dry washer	Dry	>90%	<0.8
Wet scrubber	All	>90%	<0.4
Activated carbon	Dry	>95%	<0.1

The purpose of this study is to evaluate the SO_2 reduction technique by adding absorbent material in an industrial cement process to identify how the efficiency of this process can be increased.

2. Materials and Methods

Based on research and development aimed at reducing SO_x in cement plants, the method of injecting an absorbent material in the raw material feed, where the exhaust gases pass the counter flow of the material before they go to the fireplace, is proposed as outlined in Figure 2.

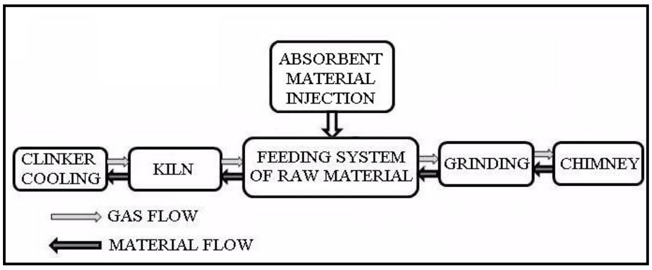

Figure 2. Schematic of the clinker manufacturing process

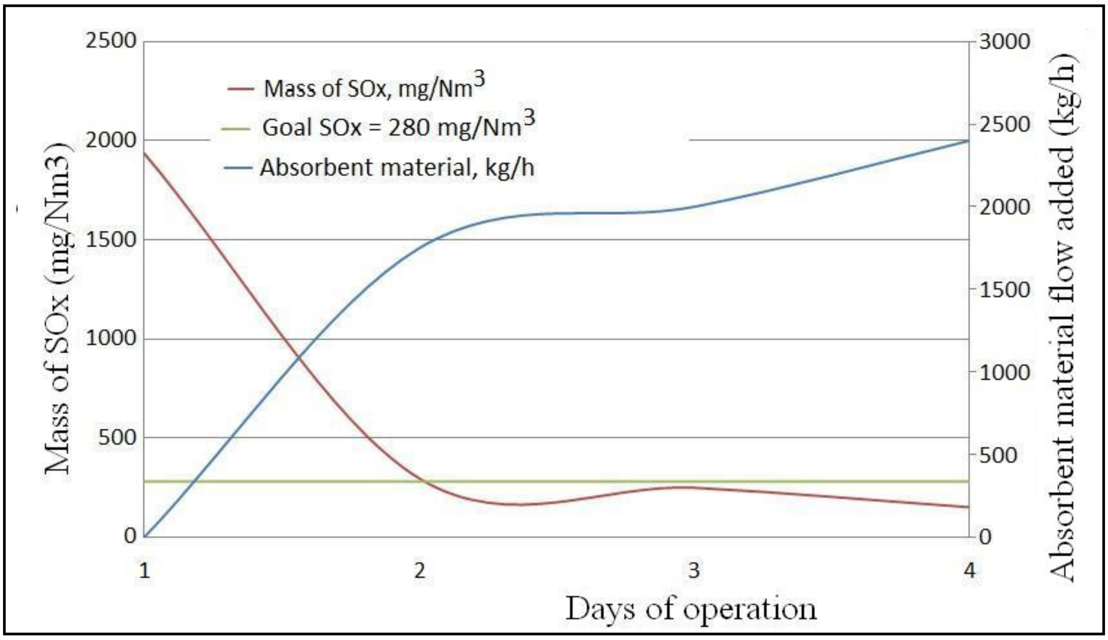

Figure 3. Emissions of SOx

The specific area of absorbent material injection was 12.499 cm^2/g and chemical analysis demonstrated that it contained 42.1% CaO and 52.7% $CaCO_3$; the remainder is made up of oxides (SrO, Fe_2O_3, SiO_2, Al_2O_3, MgO).

3. Results

The purpose of the CaO that is free in the absorbent material is to react with SO_2, SO_3 and to, consequently, be incorporated into clinker in the final product (cement), as the reactions [12, 13]:

$$CaO + SO_2 \rightarrow CaSO_3$$

$$CaSO_3 + ½\, O_2 \rightarrow CaSO_4$$

$$CaO + SO_3 \rightarrow CaSO_4$$

Another point that justifies special mention in this environmental proposal is the use of industrial waste resulting from an industrial route to raw materials (limestone), which is similar to cement production. Chemical analysis shows that such waste does not cause incompatibility in the final specification of the cement.

The industrial test was carried out by varying the flow of the absorbent material added to the raw material for 4 days, according to the cement flowchart (Figure 2), aiming to evaluate the variations that are inherent in the process upon this addition.

On the first day, the amount of SO_x issued without addition of absorbent material was held in order to measure it. On the second day, the absorbent material was added at a flow rate of 1750 kg/h. On the third day, the flow rate was increased to 2000 kg/h and, on the last day, further increased to 2400 kg/h. The test results can be found in Table 4 and the graph is shown in Figure 3. The addition of absorbent material is referred to in terms of kg/h of CaO.

During the test period, several analyses were carried out in order to determine the average emission of SO_x. In the Brazilian region, where it is located, this cement industry has a limit value for this emission of SO_x of 280 mg/Nm^3.

Table 4. Results of emission of SOx

Parameters	Days			
	First	Second	Third	Fourth
Absorbent material flow (kg/h)	0	1750	2000	2400
Mass of SOx (mg/Nm^3)	1935	296	249	151

The measurements carried out over these days show that the SO_x content was below the limit of 280 mg/Nm^3, meaning that there was a reduction of 1784 mg/Nm^3, with a yield of 92.20%.

4. Conclusions

Based on the study for reducing emissions of SO_x in a cement industry, it can be concluded that:

- The absorbent material, consisting of 42.1% CaO and 52.7% $CaCO_3$, with a specific area of 12.499 cm^2/g, provided a 92.2% reduction in SO_x emissions, thus getting under the SO_2 limits established by the environmental agency.
- The choice of absorbent material was based on the CaO content that was free to react with SO_x, as well as industrial origin and low cost.
- It is important to say that this industrial waste (from a plant for the production of CaO) does not exhibit any physicochemical incompatibility in the production of the cement.

REFERENCES

[1] SNIC, Sindicato Nacional da Indústria de Cimento (Brazil, National Union of Cement Industry), http://www.snic.org, accessed 30/05/2014, (in Portuguese).

[2] IEA, CO_2 emissions from fuel combustion. Paris: International Energy Agency; p. 512, 2008.

[3] UNSTATS, Greenhouse gas emissions by sector (absolute values). New York: United Nations Statistical Division; 2010.

[4] WBCSD, World Business Council for Sustainable Development, http://www.wbcsdcement.org, Accessed: 30/05/2014.

[5] F. Habashi, Copper metallurgy at the crossroads, Journal of Mining and Metallurgy, 43 B, p. 1–19, 2007.

[6] C. Baird and M. Cann, Environmental Chemistry, Macmillan, 2005.

[7] Sing, A. and Agrawal, M., Acid rain and its ecological consequences, Journal of Environmental Biology, 29(1), p.15-24, 2008.

[8] Wang, T. J., Jin, L. S., Li, Z.K., Lam, K.S., A modeling study on acid rain and recommended emission control strategies in China, Atmospheric Environment, 34, p.4467–4477, 2000.

[9] Xiea, S., Qia, L. and Zhoub, D., Investigation of the effects of acid rain on the deterioration of cement concrete using accelerated tests established in laboratory, Atmospheric Environment, 38, p. 4457–4466, 2004.

[10] J. M. Broder, E.P.A. Tightens Sulfur Dioxide Limits, The New York Times, 3 June, 2010, http://www.nytimes.com/science/earth, Accessed: 30/05/2014.

[11] S. J. Smith, J. van Aardenne, Z. Klimont, R. J. Andres, A. Volke, and Delgado Arias, Anthropogenic sulfur dioxide emissions,: 1850-2005, Atmospheric Chemistry and Physics, 11, p.1101-1116, 2011.

[12] Li, Y., & Sadakata, M., Study of gypsum formation for appropriate dry desulfurization process of flue gas. Fuel, 78(9), p.1089-1095, 1999.

[13] Ishizuka, Tomohiro, et al. "Initial Step of Flue Gas Desulfurization An IR Study of the Reaction of SO_2 with NOx on CaO. Environmental science & technology 34.13 p. 2799- 2803, 2000.