ASSESSMENT OF FLUE GAS CONTROL TECHNOLOGY: ISSUES FOR REGIONAL ENVIRONMETAL MANAGEMENT[1]

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ABSTRACT

The capacity to reduce potentially contaminating metallic-element emissions using control technology has been the object of much research. The evaluation of risks relating to human and environmental health in terms of atmospheric pollution is very complex when dealing with industrial emissions. Predicting this impact is difficult due to atmospheric conditions that may or may not encourage dispersion of the pollutants. This study aims at characterizing those materials that demonstrate the ability to retain potentially contaminating elements due to their structural characteristics. Among those studied were Brazilian limestone (both calcitic and dolomitic) and clay minerals considered best suited for use with this technology. Dolomitic limestone from São Paulo in southeastern Brazil and mineral clay (vermiculite) from the state of Piauí in the northeast of Brazil were selected. The study involved a series of tests designed to characterize the materials, which were submitted to experiments for SO_2 removal and to order potential contaminating elements associated with acid emissions.

Key words: Environmental and human health; control technology; sorbent materials.

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INTRODUCTION

Over the past 30 years we have seen a transformation in the behavior of society with respect to the environment. The industrialized countries and those in the process of industrialization have increasingly adopted quality standards for air and water and emission standards for industrial flue liquids and gases. However, most industries have only complied with environmental legislation when obliged to by the competent organs. Competitiveness and the environment were, then, completely antagonistic and the relations between industries, governments and society were of constant confrontation. This behavior is, however, becoming modified. Although Brazil still does not have a formal commitment to reducing its gas emissions, a number of initiatives have been taken that can be considered in that sense. Due to growing awareness from society as a whole, entrepreneurs have come to understand that it makes sense to invest in modifying their production processes and the government is giving emphasis to providing special initiatives in this area.

The problem of air pollution is not recent: one of the first episodes recorded in history was caused by the burning of coal in England in 1911, according to Braga *et al*. (2004). From this period until today the problem has only worsened: the burning of fossil fuels is still far from slowing down. Excessive emissions of pollutants have been causing serious damage to human health, such as breathing problems (chronic bronchitis and asthma), allergies and degenerative lesions in the nervous system or vital organs. In 1962, 4,000 people died in London from atmospheric pollution (smog). In Brazil there are records of episodes in the city of São Paulo. However, atmospheric pollution is very complex to control and if the construction of prospective scenarios is fundamental to learning about the dimensions of the environmental question, it is even more so for this type of pollution. Control technologies and materials have also been researched in order to minimize this problem. Based on the identification of critical situations, any decision taken will depend on options – on the part of governments, society and companies – to prevent and mitigate damage to the environment. It is this association of various segments that could give rise to a strategic environmental management.

Studies recently conducted by environmental organs have been defining the principal biomes (spatial units) for diagnosis and prospective analysis. The main vectors and impacts resulting from them have been identified, and historical and desired scenarios have been developed. The impacts and answers already identified begin to make sense when referenced to the biomes and local and regional scales. To allow the integration of ecological conditions with socioeconomic variables, we opted to use physiographic zones (groupings of municipalities with similar environmental characteristics) as the base territorial unit for defining the biomes.

Even having been identified and diagnosed over the past three decades as a relevant question for the effective implementation of environmental policies, until the 1990s few effective actions were undertaken to reduce the fragmentation of sectorial policies, be they environmental or of another nature. On the contrary, the various laws, agencies, plans and programs and other instruments created during this period at first contributed to increasing that segmentation (IBAMA, s/d). Thus the move to profile via biomes (be it for their integrative capacity or the potential to promote sustainable development) is a genuine advance in the Brazilian institutional framework. However, care should be taken not to issue conflicting environmental legislation.

Technological processes based on the need to control gas emissions are currently being developed, and searching for materials that have the capacity to trap compounds considered harmful to human and environmental health is part of that process. On the one hand, materials made of limestone are traditionally used to control the acidity offlue liquids and gases in various countries. In Brazil, however, they have still not been sufficiently characterized for the specific purpose of controlling gas emissions. With planning, they can be considered yet another control tool due to their low relative cost. Also, the proximity of deposits is an important aspect to be taken into account when considering environmental management. The use of clay as an absorbing material for treating flue gases is also a promising field to be explored, with broad usage possibilities (UBEROL; SHADMAN, 1991).

Energy production from fossil fuels, residue incineration and metallurgical processes all generate acid gas emissions that contain arsenic, chrome, lead, cadmium and mercury, among other noxious elements. The high volatility of these elements at the temperatures in which combustion processes take place makes the treatment of these flues a complex task. In general, the control of SO_2 emissions by modern industries consists of injecting particles of sorbent material into the flow of gas. Solid sorbents based on calcium compounds are widely used given their low cost and high sorption capacity. The use of limestone has the advantage that the byproduct of the process, anhydrite, is an insoluble compound in water, thus offering greater safety when disposing of the residue. It has the additional convenience of incorporating certain volatile metallic elements in its structure during the sorption process.

Flue gases contain a number of aggressive acid species such as SO_2, HF and HCl. The sorption of a volatile metallic element by any solid can take place through physical or chemical adsorption, a chemical reaction or even from a combination of these processes. In the case of capturing sulfur dioxide through the use of a limestone material, the following reactions will occur (ALVORS; SVEDBERG, 1992):

$CaCO_3$ (calcite) $\rightarrow$ $CaO + CO_2$ (1)

$CaMg(CO_3)_2$(dolomite) $\rightarrow$ $CaO + MgO + 2CO_2$ (2)

CaO (lime) $+ SO_2 + \frac{1}{2} O_2 \rightarrow CaSO_4$ (anhydrite) (3)

From reactions (1), (2) and (3) it can be verified that in the case of using dolomitic limestone as a sorbent (2), periclase (MgO) acts inert within the temperature band in which the process takes place (around 750-850°C at atmospheric pressure). That's because volatile metallic elements can be retained in the sorbents not only as a result of chemical reactions but also as a consequence of the condensation processes that occur on the surface of sorbent particles (SLOSS, 1992).

It is known that limestone rocks with high porosity have a greater capacity to react with SO_2. Dam-Johansen and Ostergaard (1991) showed that the retention possibility of sorbents is correlated to physical texture – which, in turn, demonstrated a strong relation to the geological age of the rock. For this a prior study was conducted on the porosity of the rocks, and based on those results the materials used in this work were pre-selected.

At first were studied clay minerals that operate together with limestone materials. In nature these occur in associations with other types of minerals and in the case of limestone of a sedimentary origin (the most appropriate for use with this type of technology), the presence of aluminum-silicates is very common. Of these, the most frequent are clay minerals like illite, montmorillonite and caulinite, among others. Either calcitic or dolomitic limestone can be used.

MATERIALS AND METHODS

Exploratory tests were conducted on a bench scale using a heavy fuel oil (ANP Classification 1A, 2-4% sulfur content) as the generating source of SO_2. This simulation is interesting due to the large number of small industries in Brazil that burn heavy oils in their processes. The combustion experiments were conducted with each of the sorbents chosen. The amount of limestone used was calculated on the base of previous reactions, assuming a minimum stoichiometric relation of 2:1 based on the content of sulfur in the fuel.

Sampling and analytical methods

The samples were submitted to stages of preparation that involved reduction in size, homogenization and quartering. The chemical analyses were conducted by the Institute of Radioprotection and Dosimetry (IRD – Rio de Janeiro – Brazil). The samples, after solubilization, were analyzed using Inductively Coupled Plasma– Mass Spectrometry (ICP-MS). Determination of the superficial area and the study of the porosity of the material were done with a Micromeritcs 2010 Accelerated Surface Area and Porosymmetry System (Asap) using the nitrogen adsorption/desorption technique. The mineralogical analyses were conducted at Cetem using a LEO S440 SEM/XDS (Scanning Electron Microscopy/X-ray Dispersive Spectroscopy) equipped with a Link ISIS L300 energy-dispersion microanalysis system with a Pentafet SiLi detector, ATW II ultrafine window and a resolution from 133 eV to 5.9 keV. The analyses were conducted with 20 kV of electron acceleration tension. To determine the mineralogical composition we used an x-ray diffractometer (XRD), Siemens AXS, D505 and the x-ray fluorescence technique (Phillips, model TW2400). The thermal analyses employed a thermal scale (Simultaneous DTA/TGA, TA Instruments, model SDT 2960), while a LECO SC -232 Model 781-400-100 was used to determine the sulfur.

Experimental apparatus

The experimental apparatus used for the static-bed combustion test consisted essentially of two tubular ovens with a system to allow passage of the gas and a coil, besides a filter and flasks for receiving the gas. The apparatus used for the adsorption experiments is shown in Figure 1.

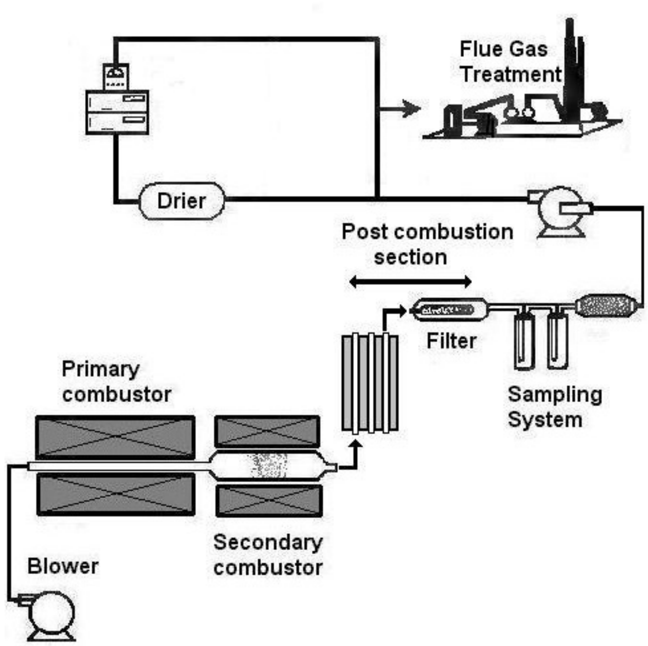

Figure 1: Diagram of the experimental apparatus

In Figure 1 it can be seen that in the first oven the fossil fuel is preheated and burned, liberating a gaseous chain to a second oven, which contains the reactor and the sorbent bed. To stimulate the greatest turbulence a quartz bed was used.

Result and Discussion

The oil that was used began showing an initial loss of weight at 319°C, with the greatest weight loss occurring at approximately 458°C. At 700°C it became completely decomposed, according to experimental verification in the reactor. In terms of analyzing the gases, the presence of methane, CO_2 and H_2S was verified, besides SO_2, which could be masked by the presence of water vapor.

Characterization of the sorbent materials

Initially a series of tests was conducted with different kinds of limestone in terms of geological age. Analyses of the porosity of the limestones are presented in Figure 2. Based on the results, the Irati limestone was selected.

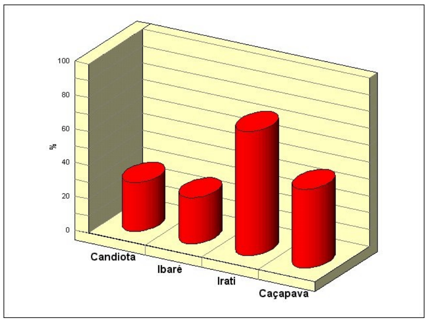

Figure 2: Porosymmetry studies made with limestones analyzed in the Asap.

The results obtained from the porosity study seem coherent with the appearance of the samples. The most crystalline specimens (Ibaré and Candiota) are the least porous and have a smaller specific surface.

At the Irati formation, a carbon-looking faces was mined that corresponded to a dolomitic limestone tabular bank with a thickness of 2 m to 4 m, topped by a rhythmic sequence of schists and silicificated limestone.

Thermal analysis of the sorbents

The reactivity of SO_2 with the solid sorbents has been related to their superficial area and the intrinsic porosity of the materials. In order to determine the bands for working temperatures, tests were conducted using differential thermal analyses (TGA/DTA). From the burning of the fuel results a gaseous chain that passes through the sorbent, transforming SO_2 into $CaSO_4$, as shown in reaction (3). The fact that these reactions took place at high temperatures led to the emergence of a porous structure in the sorbent that at the beginning was not well developed. The time required for the calcination stage (1) is very small when compared to that associated with the second reaction, sulphation (3).

Based on the initial results obtained, 650°C was chosen as the ideal temperature for minimizing the occurrence of residues resulting from the combustion of the heavy oil, since total combustion took place at around 550ºC. In relation to the limestone, it was observed that its transformation from $CaCO_3$ to CaO occurred at a temperature of around 760ºC.

The microphotographs showing the limestone residues obtained after the tests can be seen in the figures below.

(a) (b)

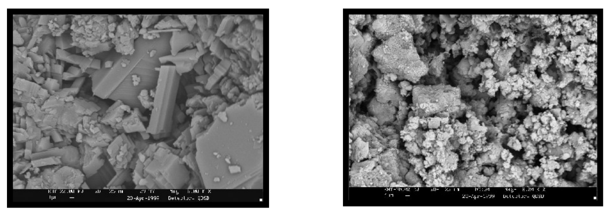

Figure 3 (a): Microphotograph of the raw limestone obtained with MEV; 3 (b) Microphotograph of the limestone residue.

Results of the adsorption tests

A greater concentration of some elements such as Co, Cu, Ge, Nb and U in the residues was observed under lower temperatures (300°C) than when high temperatures (850°C) were used. Based on the results obtained from this study, we can observe that the appropriate temperature for using natural limestone materials in sorption processes for potentially contaminating elements lies between 750°C and 850°C.

Under the test conditions, a volatilization of cadmium and arsenic was observed, even when using limestone material as a sorbent. The results obtained here contradict what has been observed by other authors, notably Ho *et al*. (1994), who emphasized the possibility of using materials of this nature for efficient capture/sorption of cadmium in gas flows at high temperatures. Molybdenum demonstrated a similar behavior to that observed for germanium; a fraction was captured by the sorbent materials. Some of the elements considered nonvolatile under the temperature conditions in the tests (copper, cobalt) could demonstrate volatile behavior due to their likeness to known volatile elements such as fluorine and chlorine. In this case, a combined treatment with activated coal that focuses on retaining these elements would be of great importance.

The results were, in general, quite satisfactory, bearing in mind that they were obtained by simulation on a laboratory scale. New tests would be necessary with changes in certain conditions – not only scale, but also in the combustion chamber and the granulometry of the material, for example. This would contribute to better understanding the adsorption process of trace metallic elements. One of the possibilities that should be considered is to also pre-treat the limestone material, especially to a temperature of 765°C, which results in a greater specific superficial area and the largest volume of micropores.

Effects of emissions of contaminating elements on human health

The trace elements considered of greatest interest to environmental study are: As, Cd, Cr, F, Hg, Ni, Pb and Se. They are followed by B, Be, Cl, Co, Cu, Mn, Mo, Sb, Sn, Th, Tl, U, V and Zn, which are considered to be of interest (SWAINE, 1994) although of less important from the point of view of contamination. However, even chemical elements essential for human health, when excessive, can become harmful. Furthermore, the impact of compounds involved in gaseous emissions is difficult to predict because they are usually complex mixtures of chemical substances. Upon contact with the atmosphere, primary pollutants develop into secondary pollutants through chemical reactions. This impact is even more difficult to forecast due to atmospheric conditions that may (or may not) disperse the pollutants. Under adverse conditions in the sub-adiabatic state, such as the phenomenon of thermal inversion, there could be a restriction on vertical dispersion, provoking potentially critical situations of air pollution (BRAGA *et al*., 2004).

The impact of genotoxic elements in the environment and their significance for environmental health, in turn, are also difficult to evaluate. Many indicators of health for biological systems have been tested in recent years. Each has sensitivity for different levels of degradation and different types of anthropogenic stress. However, the complexity of biological systems and the diversity of factors responsible for their degradation make it very unlikely that any measure will have enough effectiveness to be used under all circumstances. (KARR *apud* MORAES *et al*., 2002). The toxicological target of these elements is DNA, which exists in all types of living cells. Therefore it can be presumed that compounds which are shown to be reactive with DNA in one species have the potential to produce similar effects in other species. In general, disturbances of genetic material are harmful to an organism and can lead to severe and irreversible consequences for environmental health (HOUK *apud* MORAES *et al*., 2002).

Cadmium is an element of great interest because it causes a degenerative disease. Apparently some Ca^{+2} ions are substituted by Cd^{+2} ions, since their ionic rays are very close.

Limestone is a material traditionally used in SO_2 retention technology and is widely available in various regions of Brazil, as can be observed in Figure 4. Therefore it is a resource that could be of interest to environmental control processes.

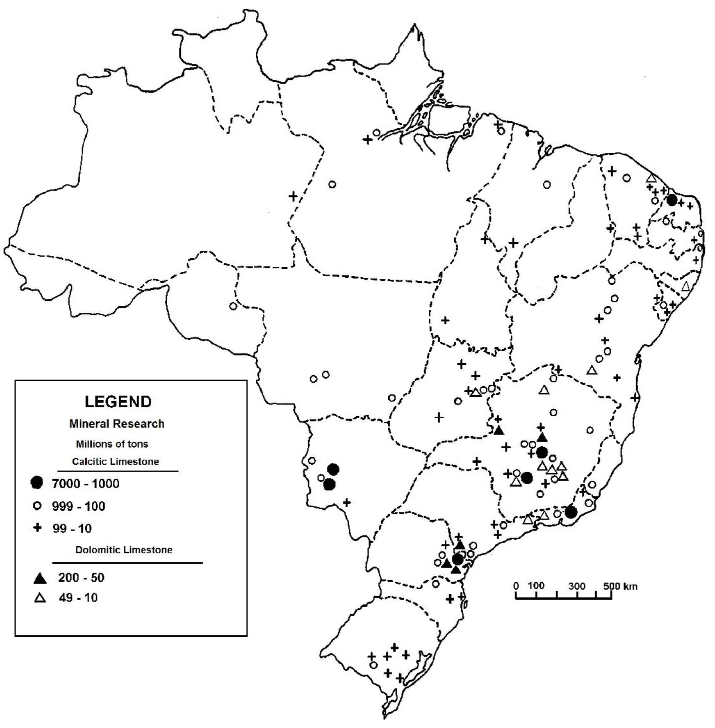

Figure 4: Map of calcitic and dolomitic limestone occurrences.
Source: CPRM (1995).

Possible alternatives are sought for the various scenarios resulting from thestudies conducted. In this way, via trend scenarios, a new configuration with a broader diffusion of information can be established for strategic environmental management. The search for resources available in the country is a goal to making such conditions more viable.

According to a document issued by the Brazilian Senate[1], the average price of limestone in 2000 was R$ 7 per ton at the mine for the sedimentary type used in agriculture. The price of limestone for producing lime (quicklime) is presented in Table 1. The least crystalline varieties like sedimentary limestone are the most appropriate for use as a sorbent material.

Basic Statistics - Brazil

Discrimination			**2002(r)**	**2003(r)**	**2004(p)**
Production:	Crude limestone	(10^3)t	10,745	10,910	11,406
	Lime	(10^3)t	6,500	6,600	6,900
Average price(c):		(R$/t)	136.63	157.67	146.06
		(R$/t)	177.11	203.67	208.27

Sources: MDIC/Secex, Brazilian Association of Lime Producers (ABPC), DNPM, Mineral Commodity Summaries – 2005.

Notes: (e) Production + imports - exports; (r) revised data; (p) preliminary data subject to revision; (c) FOB quote at processing plant.

Table 1: Prices of limestone and lime

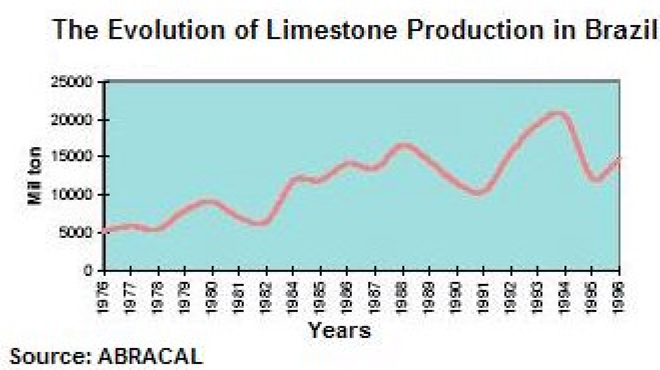

Figure 5: Evolution of limestone production.
Source: BNDES (1997).

[1] Available at : <http://www.senado.gov.br/web/senador/odias>.

CONCLUSION

Studies seeking to diagnose and propose a treatment for minimizing environmental degradation have increased substantially in recent decades. However, there are still no definitive solutions that can resolve the problems caused by burning fossil fuels. Far more than punitive measures, the development of environmental awareness is still the most effective manner for pressuring industries to adopt pollution control technologies suitable for each region. Profiling through biomes – be it for their integrative capacity or their potential to promote sustainable development – is an important advance in the Brazilian institutional framework. However, care should be taken to not pass conflicting environmental legislation. There are at least two challenges to an environmental strategy aimed at sustainable development. The first refers to interagency cooperation and second to the participation of broad segments of society in the decision-making process and in forums that allow discussion between different actors.

The gas emissions generated by industries have the capacity to influence areas very distant from their emission point (via atmospheric phenomena). This makes environmental management, as we have said, much more complex in the sense evaluating the consequences of these gases on, especially, human health. However, after studies have been made characterizing the sources and phenomena involved and with control based on the monitoring of biomes, it is possible to reach a level of sustainable development in the future.

As already mentioned, limestone is a relatively cheap mineral product in the market and quite commonly found around the country. The byproduct of the process of injecting limestone into the gas flow is anhydrite (or plaster), which, due to its insolubility in water, offers an advantage in terms of disposal, as mentioned. Thus its utilization can be justified in certain specific cases, such as when deposits are close to the factories that burn fossil fuels.

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