DEVELOPMENT OF A SOLID INORGANIC ADSORBER TO REDUCE FLUORIDE EMISSIONS IN THE CERAMIC INDUSTRY

E. F. Urano Carvalho [(1)], H.G. Riella[(2)]

[(1)] Instituto de Pesquisas Energéticas e Nucleares -ipen/cnen-SP
CEP 05508-900, São Paulo/SP - elitaucf@ipen.br
[(2)] Universidad Federal de Santa Catarina – Department of Chemical Engineering
University Campus, Florianópolis, CEP 88040-900.

After the Second World War, the development model of the Western world saw economic growth in a short period of time by the use of new productive processes and the intense exploration of energy and raw materials, whose sources were considered limitless. That model generated an impressive surplus of economical wealth, but it brought with its great social problems and the need for adaptation, and consequently economical problems.

The impact of an industrial activity in the environment can show itself in three ways: atmospheric contamination; liquid wastes and solid residues. Among the large quantity of gases emitted from the kiln, originated from the ceramic industries, fluoride is especially important, since it is associated with other contaminants. These gases are liberated during the firing of all raw materials containing aluminium and when they are subjected to temperature above 700ºC.

The European environmental legislation imposed extremely rigid restrictions in relation to the atmospheric concentrations and or ceramic factory emissions with regard to available evidence that such emissions have harmful effects in plants and surroundings close to factories, which are especially sensitive to fluoride, mainly in springtime when the production increases in the factories and a great amount of fluoride is liberated into the air in a short period of time.

After reviewing the evolution of the Brazilian ceramic industry, it was verified that in the beginning of the 1970s the production of ceramic coverings reached a continuous demand, thus causing the industry to raise production significantly, together with the appearance of new companies. For many years, that industry has occupied a prominence position in the international market, having been the second largest world exporter. In the last years, however, the participation of Brazilian products in that market is being reduced in favour of the leaders, China, Italy and Spain.

The Brazilian industry of ceramic coatings has consolidated itself as one of the principal ones, by surpassing the figure of half a billion square meters produced in the year. The production in 2002 was 508,3 million m^2. The sector developed a peculiar industrial park, in that a great part of production involves manufacturing combined with evaporation processes.

The fluoride compounds in gaseous form, even at lower concentrations, could result into sensible harms to the environment and to the human being. The fluoride could be assimilated to the human organism by ingestion, inhalation and/or absorption. However the hazard risks to the environment, not only depending on fluoride concentration, but also the type and composition of the vegetations, wind direction, dispersion and deposition.

The fluoride is present in minute quantities of 0.01 - 0.1% in the ceramic raw material. During firing the fluorine is partly released as hydrogen fluoride (HF) in the gases. The absolute volumes exhausted from a tunnel kiln , depending on its efficiency, are only of the order of 0,1 - 0,8kg F^-/h, i.e. compared with other industries, the heavy clay industry is only a very minor emitter of fluorine. The fluorine compounds however, even in very low concentrations, under unfavourable weather conditions, can result in damage to sensitive plants. Concentrations of 1-200mgF^-/N^3 have been recorded in the flue gases of kilns in the brick and tile industry. The degree of hazard not only depends on the F^- concentration in the exhaust gases, but also on a number of other factors, such as the type and composition of the vegetation, the wind direction and dispersion, and inclement weather conditions.

Recently a number of technologies have once again been offering equipment for the cleaning of the gases in the ceramic industry, being classified in groups in agreement with the applied mechanism and the present pollutant species.

Fluorine in the minerals oscillates from 150 to 1773 $g.g^{-1}$, existing minerals as phlogopite and tremolite with considerably higher, 3400 to 24000 $g.g^{-1}$. Variations have been registered in the fluorine in the several clays, in function of your geographical positioning, your mineral composition and texture.

This work has the aim at developing a solid inorganic adsorber able to block the liberated fluoride by chimney at ceramic industries. It was evaluated the fluoride content in the clay materials used as raw material, the mechanism of fluoride liberation, the fluoride adsorption kinetic in the hydrogen fluoride medium and the development of an adsorber on calcium ($CaCO_3$), with low cost and easy processing.

The raw material used as departure material for obtaining of the adsorber it consisted of the marine limestone or limestone of shells, produced by the company Cysy Mineração Ltd., located in the state of Santa Catarina, Brazil. The marine limestone or calcareous shell generates a product with high reactivity. Chemically the limestone of sea shells is formed by carbonate of calcium ($CaCO_3$) and composed inorganic. With the objective of obtaining a solid adsorber using a low cost technology, we have used the technique known as pelletizing.

In an industrial process for $CaCO_3$ conversion, it is suitable to use pellets less than 10 mm in size. The optimum value, determined in this work denoted the pellets should be between 5-8 mm in diameter.

The results obtained in the present work showed that it is more effective, to control fluorides gas emissions in the end of production line, instead of regulating the process during firing of ceramic mass.

The new technology developed in this work, could be well used to treat the fluoride gases using a dry sorption treatment process. Reaction occurs between the gas pollutants and the solid, which is able to react chemically with the pollutant without generating solid wastes or liquid effluent. However, the process obtain a new product (CaF_2), which could be incorporated into ceramic mass during the productive process or could be used in agriculture management for soil correction.