seres'09
I. INTERNATIONAL CERAMIC, GLASS, PORCELAIN ENAMEL, GLAZE AND PIGMENT CONGRESS
12-14 OCTOBER 2009

DEVELOPMENT OF A SOLID INORGANIC ADSORBER TO REDUCE FLUORIDES EMISSION IN THE CERAMIC INDUSTRY

E. F. Urano Carvalho [1]; H.G.Riella[2]

[1] Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN/SP
Av.Prof.Lineu Prestes,2242 CEP 05508-900, São Paulo/SP
[2] Universidade Federal de Santa Catarina UFSC/SC
Campus Universitário, Florianópolis, CEP 88040-900.

ABSTRACT

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 optimum value, determined in this work denoted the pellets should be between 5-8 mm in diameter. The new technology developed in this work, could be well used to treat the fluoride gases using a depuration dry sorption process. Once the reaction occurs between the gas pollutants and treated in the solid, which is able to chemically react 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.

Key words: Fluoride, Solid inorganic adsorber, Ceramic industry.

1. INTRODUCTION

After Second World War, the western world had as development model the economical growth obtained in short period by the use of new productive processes and the intensive exploration of energy and raw materials, whose sources were considered limitless. That model generated impressive surplus of economical wealth, but it brought with itself great social problems 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. A legislation on fluorine emission in Europe is diverse. Although each member state has their own legislative and controls, they will tend towards the harmonization, as the European Council has adopted a directive on Integrated Pollution Prevention and Control. The aim of this directive is to obtain a high level of protection of the environment as a whole, and will involve considering the best available techniques in issuing permits for industrial activity [1-3].

The Brazilian industry of ceramic was consolidated as one of the main industries when surpassing of billion of square meters half produced along the year. The section developed a peculiar industrial park, in that the road process it evaporates manufactures expressive part of your production.

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 gaseous. The absolute volumes thrown for 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 compounds fluorine compounds however, even in very low concentrations, can results under unfavorable weather conditions 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 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 dispersed inclement weather conditions. Recently a number of technologies have once again been offering equipments 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 [4,5].

Fluorine in the minerals oscillates from 150 to 1773 $g.g^{-1}$, existing minerals as flogophite 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 [6-12].

2. EXPERIMENTAL PROCEDURE

The marine limestone or limestone of shell has shown to be extremely interesting as a starting material for adsorber obtaining. It is a low cost product with constant chemical composition, easily available on a commercial scale**,** produced by the company *Cysy Mineração Ltda*., located in the state of Santa Catarina, Brazil. The marine limestone or calcareous shell was made by organic matter with

high reactivity. Chemically the limestone of sea shells is formed by carbonate of calcium ($CaCO_3$) and composed inorganic.

With the objective of the obtaining of a solid adsorbed using a low cost technology, we used the technique known as pelletizing. Pelletization process is the agglomeration of moisturized fines in a rotating disc. The use of a disc pelletizer, Eirich, model TR 04, was carried out with revolution speed and angle of pelletization disc's plane to the normal as well as the use of lubricants.

The formation of the ball through the movement of rotation of the material in combination with the ligant and water sprinkled on the material. The balls obtained with a defined form favoring good conditions of fluidity. The size of the sphere established by the position of the disc and of the amount of liquid introduced. For the rotation movement they obtained larger balls addressed automatically for the surface of the disc, doing with that they flowed outside in a continuous way segregating them for size. During the optimization study, firstly, the angle and revolution speed parameters were tried to be determined for the desired pelletization process. This was done by observing of pellets formation stages, the shape and apparent strength of fresh pellets. The formation of pellets occurred between 2 - 15mm.

Some agglutinants were tested and among them ES70, X3 and XP, of the *Agaesse Company*, were the ones that they demonstrated results for an industrial process. They were tested the cement Portland, CP-I and refractory cement CP-III aiming at to increase the resistance to the mechanical compression. In all the rehearsals, it was used as lubricant water. The agglutinants were used in a proportion from 0,25 to 1,5%, in weight. Being made use of the cement Portland, when the balls reached the wanted size, it was left for an additional time to improve the uniformity. During that period the surface of the balls was maintained humid sprinkling occasionally with water. The balls of uniform size were separate and they came back to pelletizing mixer rotating with constant speed an amount of cement was added gradually, sprinkling with water. The adsorption of the gas were accomplished with the objective of studying the influence of gaseous reactant dilution, the temperature, the height of the bed and the granulometry of the balls on the kinetics of the reaction between the hydrogen fluoride and the calcium adsorber. In that stage, the reactant used in the study they consisted of the hydrogen fluoride gaseous, purity of 99.98%, from Matherson -Tri Gas, and the nitrogen type U. Gas adsorption was measured by passing the test gas with air over adsorber sample enclosed in a monel vessel (adsorption chamber) and recording the change in gas concentration before and after the adsorption chamber as an indication of the extent of gas adsorption as presented in the TAB.1.

Table 1. Operations conditions for the adsorption experiments

Operating parameter evaluated	Range of variation	Number of experiments
Total gas flowrate (L/h)	4-14L/h	4
Reaction temperature (^oC)	70 - 600	7
Diluition of the reactant gas (%)	1,1 - 50	5

Pellet diameter (mm)	3 – 7,1	4

The furnace is of the type resistive with scale from 0 to 800^{0}C, total potency of 2kW. Digital controllers monitor the temperature. The adsorption chamber, composed by a in 400 monel of 30mm of internal diameter for 250mm of length. The inferior extremity is funneled for the entrance of the gases inside the adsorption chamber, and to superior was connected a system of wash of gases.

Thus before adsorption, activation of the adsorber was made by introducing water vapor(steam) into the adsorption chamber for a short time (3-5s) at a rate about 0.7l/min using vacuum, which was connected to a steam generator. After the selected time, the steam and vacuum disconnected, and the nitrogen-hydrogen fluoride was connected to the pressure filter vessel containing the adsorber. The gas was allowed to flow under vacuum for selected periods. Prior to the humidification and gas adsorption steps, the adsorber sample was evacuated and its weight was recorded.

3. RESULTS AND DISCUSSION

The resistance compression varied from 20 to 45N/mm to sample with cure process to vapor, from 12 to 25N/mm for roasted samples and from 10 to 4N/mm for samples only droughts to 150^{0}C. The difference observed among the balls with cement addition and with agglutinant it can be explained by the difference in the porosity and reactivity of the material. The conversion of CALCX3 and CAL X3A, CPI and CP III came much lower than CALC ES70- 1. In order to check that this, five experiments were performed with CALC ES70-1(medium size of 7,1mm of diameter) with a molar fraction of hydrogen fluoride of 1,1%, using nitrogen as the carrier gas. Figure 1 show that does not modify significantly the curve. The medium earnings, in weight, was of 18,1% with standard deviation of 1,44%. The results of adsorption of CALC ES70-1 were significant in refers to the reproducibility.

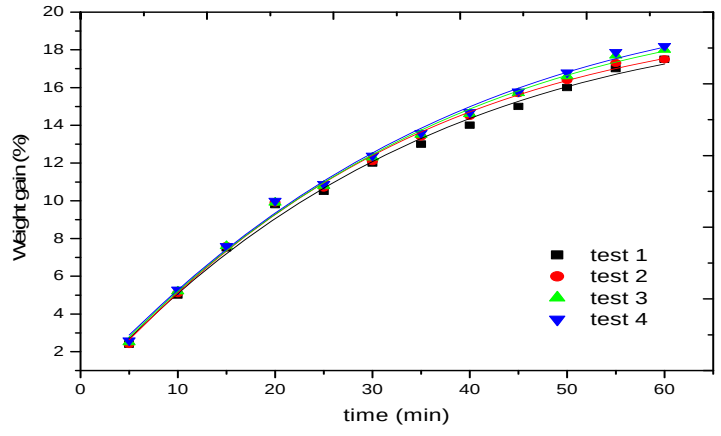


Figure 1. Experimental conversion data versus time

HF 1,1% , Temperature of 200^{o}C/h

The ligant denominated commercially Ligofor ES70, used in adsorber CAL ES70-1 obtaining, it consists of a lineal polymeric derived anionic of the starch and of the cellulose. It is a salt formed by units, anidroglycose, containing three groups hydroxile in your chain polymeric.

The adsorber CALCES70-1 it was obtained being used the gathering technique by pelletizing well as, being made use of a pelletizing mixer of the type plate with diameter of 40cm, angle in the order of 35-50, speed of 1000rpm, humidity of 12% and ligant ES70 to 1%. The formation of the balls happened between 6 and 9 minutes. The total time of pelletizing was determined after 20 minutes and with a strip granulometric very it narrows, about 81%.

The CALC ES70-1 adsorber, chemistry as characterized and physically, being used the techniques of X-ray diffraction patterns, scanning electron microscope, specific surface area (BET), X-ray fluorescence spectrometry and resistance compression and resistance to the compression. The characteristics physical-chemistries of the adsorber are presented in TAB.2.

Table 2. Physical and Chemical Characteristics of the Adsorbed - CALC ES70 -1

Composition	Substance		
$CaCO_3$ (%)	98,00	Form physic	Pellets/white
MgO (%)	0,17	Medium diameter (mm)	7,1
P_2O_5 (%)	0,023	Apparent density(g/cm^3)	1,06
B_2O_3 (%)	0,015	Porosity (%)	2,81
Cu_{total} ($\mu g.g^{-1}$)	5,00	Agglutinant (%)	1,00
Mn_{total} ($\mu g.g^{-1}$)	28,00	Humidity(%) (dry grain)	1,20
Zn_{total} ($\mu g.g^{-1}$)	11,00	Surface area (m^2/g)	1,5
Mo_{total} ($\mu g.g^{-1}$)	<14,00	Resistance (N/mm)	10 ± 2

In FIG. 2 presented a typical of the adsorber CALC ES70-1 that presents characteristic picks of carbonate of calcium. CALC ES70 -1 produced he comes more or less in the form of balls spherical with porous appearance and with white coloration and macroscopic sizes of the order of 7,1mm. A visual evaluation and for scanning electron microscope it indicated us a granular and porous structure as having presented in FIG. 4

The hydro fluorination tests were accomplished with the objective of studying the influence of gas flow, the influence of gaseous reactant dilution, the temperature and the size grain of the adsorber on the kinetics of fluorination of calcium with the hydrogen fluoride.

The way the reaction progress inside a pellet depends exclusively on the rate-controlling step(s) .The effect of the gas reactant in a bed of particles was studied due to the formation of a gaseous layer stagnated about of the solids, that in some processes can be constituted in the controlling stage of the reaction. When the reaction speed increases with the increase of the flow of gas, to a constant temperature, the mass transfer just controls the kinetics of the reaction when the

213 variation of the concentration of the gas reactant through the bed is minimum, in
214 other words, the increase of the flow of gas can increase the reaction speed due to

elevation of the medium concentration of the gas reactant, without any influence of mass transport.

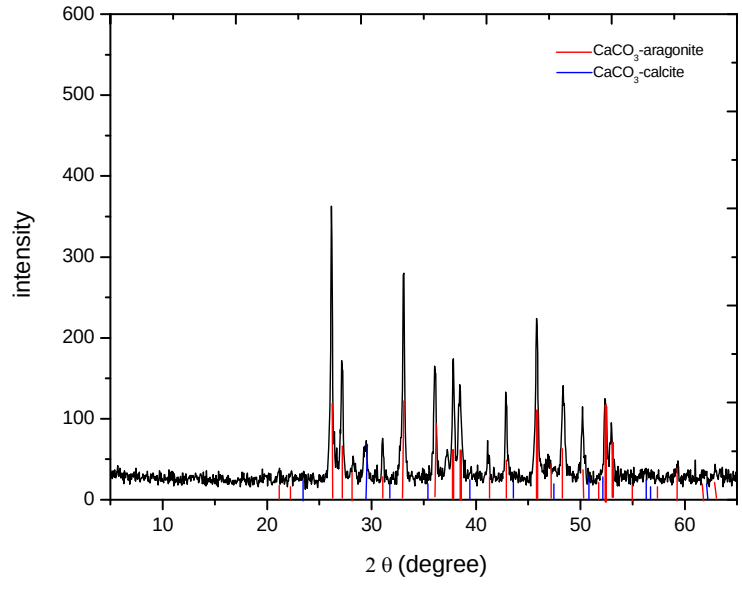


Figure 2. Typical XRD patterns the adsorber CALC ES70 -1

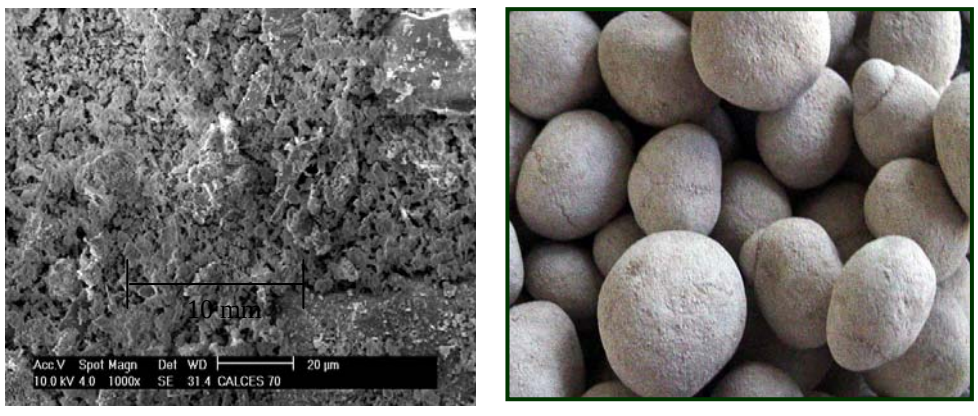


Figure 3. SEM micrographs and visual image of the adsorber - CALC ES 70 –1.

If the concentration of the gas reactant in the exit of the reaction camera differs considerably of the concentration in the entrance, the increase of the flow of gas can increase the reaction speed due to the elevation of the medium concentration of the gas reactant, without any influence of mass transport. It gave way, the probability exists of there being shortage of gas when you lower flow and deep beds are used. A series of tests was performed with variations in the total flow gas.

In Fig. 4 shows that an increase in flow of gas beyond 12L/h does not modify significantly the curve. External transport was considered not to be rate-controlling in these conditions and the remaining experiments conducted with a flow of gas of 12L/h. The flow of gas 12 and 14 L/h correspond practically to the double of the flow of HF used of industrial furnace, once the normal flow of gas corresponds to 7Nm3/Kg of mass with a medium substance 0,1% of HF. Therefore, that corresponds to 7L of HF/Kg mass.

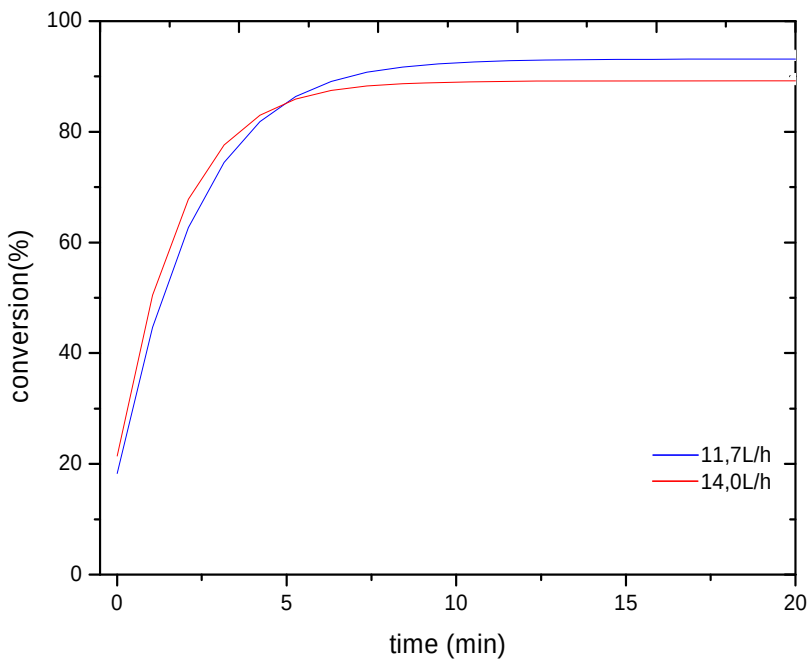
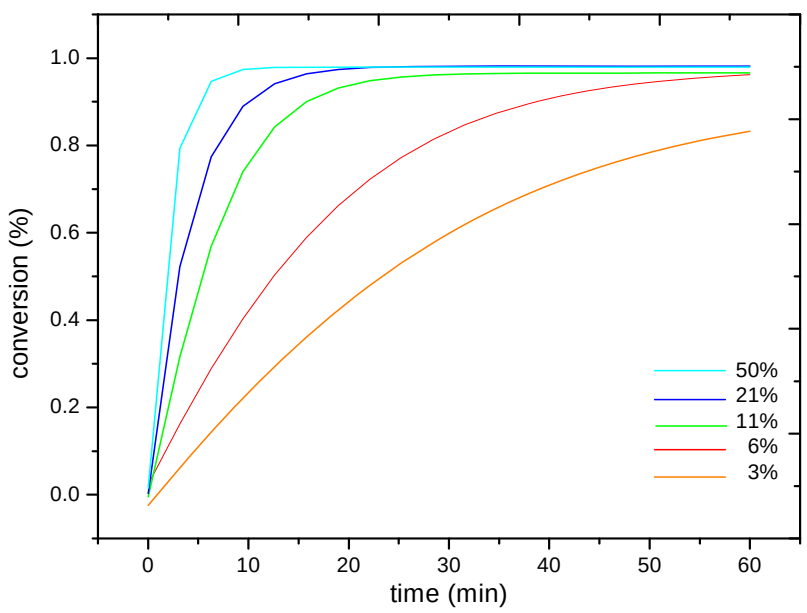


Figure 4. Influence of total gas flowrate

Pellets with size diameter of 7,1mm, Temperature = 300^0C, 14% HF

To determine the order of the kinetic reaction in relation to the gaseous reactant, a series experiments were performed with a molar fraction of hydrogen fluoride varying from 3 to 50% using nitrogen as the carrier gas. In FIG.5 shows the influence of the dilution on the conversion curves. We can observe that, for rates of dilution from 6 to 11% the necessary time of reaction for a conversion of 90% is of the order of 20 minutes. When the dilution rate is very low the retention system it requests a very long time, however they are cases that certainly don't occur in the industrial section.



269

270 **Figure 5.** Influence of the HF faction in the gas. Temperature 300°C, Pellets size
271 diameter of 7,1mm

272

273 The rate for unit of reaction of the area of surface of a heterogeneous chemical
274 reaction is usually expresses as:

275 $$\Re = kC_A^n \qquad (1)$$

276

277 where *k* is the constant rate and *n* it is the order of the reaction with respect to the
278 gaseous reactant *A*. For a first-order reaction , one has:
279

280 $$\frac{dX}{dt} \propto C_{AO} \quad \text{ou} \quad y_{AO} \qquad (2)$$

281

282 where *dX/dt* is the overall or apparent reaction rate and e y_{AO} the molar fraction of
283 A in the bulk gas. In FIG. 6 has been plotted for two conversion of degrees, x = 0
284 and x = 0,6, and shows that this relation is effectively to hydrogen fluoride is thus
285 equal to one.
286
287
288
289
290
291
292

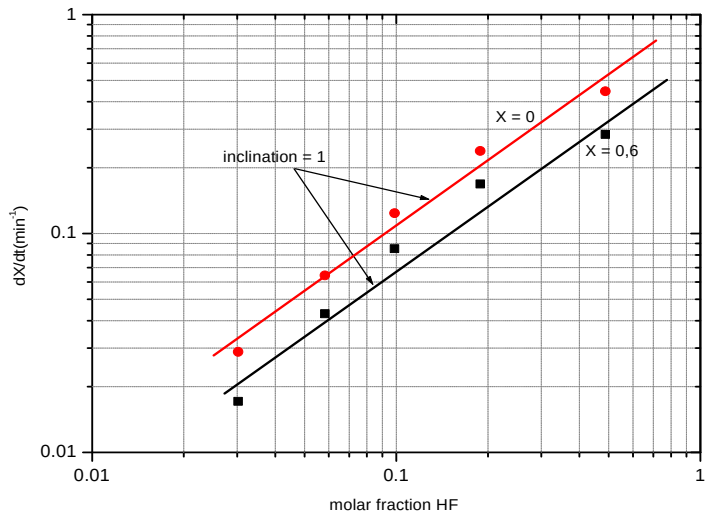


Figure 6. Determination of the order of the chemical reaction with respect to HF.

The influence of the temperature on the kinetics of the reaction is usually detected starting from the "Arrhenius equation" which contributes in the indication of the possible controlling mechanism of the reaction for the calculation of the energy of activation of the reaction. That activation energy is defined as the energy for the reactants to reach the unstable intermediate states, forming the activated complex calls that generate the final products of the reaction spontaneously.

The experiments were accomplished in the strips of temperatures of 70^0C-600^0C and in samples with diameter of 7,1mm. As the temperature it is characterized as one of the most important variables in than it plays to the elucidation and definition of mechanisms of kinetics of the fluorination reaction, your influence will be appreciated in more detailed experimental conditions. They were certain k, $D_{e,p}$, $D_{e,g}$ for each experiment accomplished in different temperatures. Where k, $D_{e,p}$, $D_{e,g}$ consists of the constant of speed of the chemical reaction (m/s), diffusion coefficient executes of " A " among the particles of a ball (m2/s) and diffusion coefficient executes inside of " A " of the particles of a pellet (m^2/s), respectively. The values obtained are given in TAB. 4 together with the associated values of σ_p^2 e σ_g^2. The value zero of σ_g^2 indicates that intra granulate diffusion is not a rate-controlling mechanism.

Table 4. Kinetic Parameters in function of temperature. 10% HF

Temperature (°C)	k(m/s)	$D_{e,p}$(m^2/s)	σ_p^2	$D_{e,g}$(m^2/s)	σ_g^2
70	1,21 x 10^{-5}	∞	0	∞	0
100	2,49 x 10^{-5}	7,86 x 10^{-6}	0,20	1,44 x 10^{-11}	0,16
200	3,19 x 10^{-5}	4,66 x 10^{-6}	0,43	∞	0
300	5,04 x 10^{-5}	5,51 x 10^{-6}	0,58	∞	0
350	4,63 x 10^{-5}	6,27 x 10^{-6}	0,47	∞	0
400	5,67 x 10^{-5}	8,11 x 10^{-6}	0,44	∞	0
600	4,84 x 10^{-5}	6,91 x 10^{-6}	0,44	∞	0

In this work a detailed study was not accomplished with respect the diffusion process, it was just preceded to the superficial evaluation, as presented in FIG. 7. an adherent layer is formed about of the particles forming a solid product, causing a reduction of the limestone nucleus and that should probably contribute to reduce the diffusion inter granulate of the gases of the surface to the nucleus. Therefore, that fact limits the size of the pellets, demonstrating that balls with great diameters are inefficient.

The influence of the pellet (ball) size was studied experimentally for series experiments with pellets diameter ranging from 2 to 7,1mm, with grain remaining constant. The influence of pellet and grain is related to the reaction regime. In the chemical regime, where the reaction is controlled by the displacement conversion is proportional to the grain diameter and independent of the pellet size. In the inter granulate diffusion regime, where the reaction is controlled by the diffusion of the gases between the grains composing the pellets, the time to complete conversion is proportional to the square of the pellet diameter independent of the grain size. In the intermediate regime,

$$t_x = 1\ \alpha\ d_p^{\alpha} \quad \text{e} \quad t_x = 1\ \alpha\ d_g \beta\,, \qquad (3)$$

where α and β depend on σ_p^2, with $0 < \alpha < 2$ ans $0 < \beta < 1$.

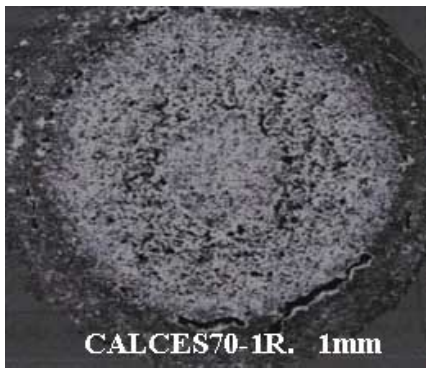


Figure7. Micrographs for superficial analysis to CALCES70-1R

In FIG. 8 show the influence of the time of conversion versus the diameter of the pellet, using log-log. The plot shows that the slope of the curve increases with pellet size. At very small sizes, the slope tends to zero, indicating an approach to the conditions of the chemical regime. When the pellet diameter decreases from 15mm to 5mm, the kinetics then pass form a diffusion-predominated intermediate regime(σ_p^2 >1) to a chemical regime(σ_p^2 < 1). This change in regime is accompanied by a significant reduction in the reaction time $t_{x = 0,9}$, falls from1000 to 400s. In order to accelerate the process industrial of $CaCO_3$, it is therefore highly desirable to use pellets less than 10mm in size. The optimum value is probably between 5 and 8mm. Below 5mm, there is no point in further decreasing, since the reaction is already in a chemical regime where pellet diameter has no influence.

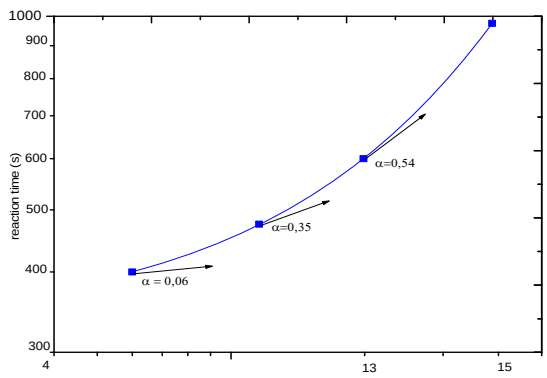


Figure 8. Influence of pellet diameter on the time necessary for 90% conversion

The CALC ES 70-1 after the experiments of adsorption denominated as CALC ES 701R-1R was characterized chemistry and physically, being used the techniques of X-ray diffraction patterns, thermogravimetric analysis showed in FIG. 9 e10, respectively.

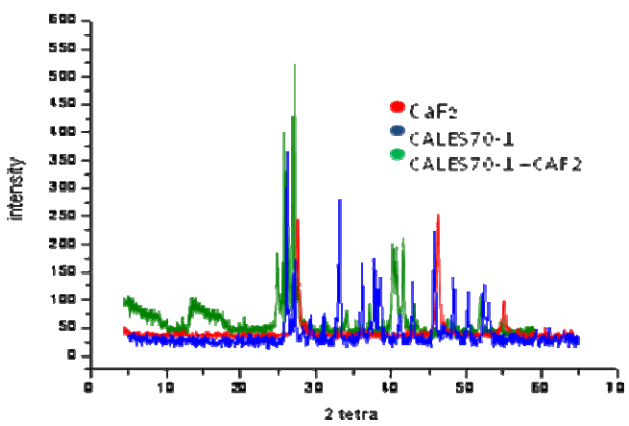


Figure 9. XRD patterns (a) CaF_2 ; (b) CaF_2 + $CaCO_3$ (CaF_2 + CALC ES 70-1) e $CaCO_3$ (CALCES 70-1R).

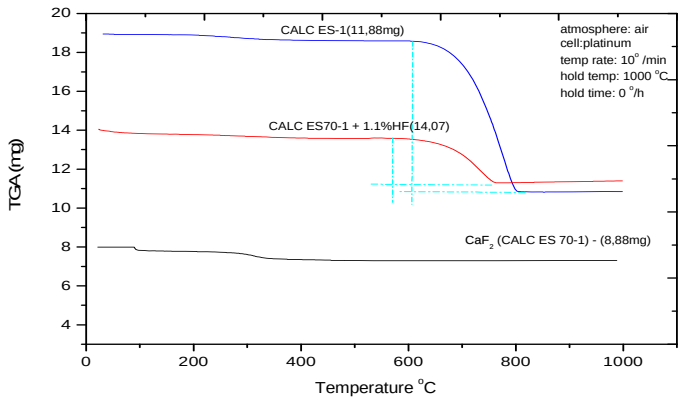


Figure10. TGA curves CALCES 70-1 and CALCES 70-1R

In the thermo gravimetric experiments variations were made a comparative study of CALC ES70-1 and CALC ES70-1R, in three different stages, in other words, CALC are 70-1 before the tests of adsorption (blue line), experiment of conversion of 60% of CALC ES70-1(red line) and test of conversion of 90% of CALC ES70-1(black line). After the conversion of 90% of CALC ES70-1 CALC ES70-1R'S the thermo gravimetric analysis came stable indicating a mass loss between 120 and 250°C, probably caused by the liberation of the water or residual free fluoride in the pellet (ball).

The superficial aspects of the sample CALC ES 70-1R exhibit different in relation to the sample CALC ES70-1. CALC ES70-1 shows granular and porous, as showed in FIG.3, while the sample CALC ES70-1R presents denser. The reaction product generated it consists of fluoride of calcium (CaF_2) and carbonate of calcium ($CaCO_3$), being a product solid, dry and stable.

The classification of the adsorbed was evaluated after the reaction according to NBR10.004[12], Brazilian Standard, resulting in a residue Class III, therefore being possible the disposition in landfill not controlled.

The utilization of reaction products as soil conditioners and de-acidification agents is thoroughly feasible. The only proviso here is where fluorine sensitive plants are cultivated. In horticulture, an improvement of the soil structure was observed after a 10-year application of the residues, and no damage to plants recorded. Utilization may be rendered more difficult because of the relatively small amounts of residues occurring. Intermediary storage is recommended in disused clay pits of those residues that can be re-utilized for agriculture or forestry [11].

Another possibility for utilization for the reaction product is to add it to the clay in production of coatings monoporous denominated tiles. The addition of small amounts in the ceramic mass is possible, once the employed minerals in formulations for monoporous are the carbonates, mainly the calcite. As the

necessary porosity to the material after it burns her (>10%) it can be obtained with additions of carbonates between 14 and 19% in the mass, that will correspond the porosity between 10 and 13%. Other important factor is the fact of the landing of it burns of ceramic coatings of fast one burn for monoporous to be in the interval of temperature from 1050 to 1100^0C. As the reaction product generated it consists mainly of fluoride of calcium (CaF_2) and carbonate of calcium ($CaCO_3$), we could reduce the production costs with the reutilization of the $CaCO_3$and CaF_2 in substitution to the chamotte.

3. REFERENCES

[1] Kollmeier, H. Emission control in brick and tile industry. *Ziegelindustrie International*, v.10, p. 516-530, 1986.

[2] Lorenzini, G. Fluoruri atmosferici: effetti fitossici e possibilitá di rilevamento biologico. *Laterizi, cotto e terracotte: impatto ambientale*, p. 65-72, 1991.

[3] Müller, W. Problems of clean air maintenance in the brick and tile industry of the new Federal German Regions – a stocktaking and survey of future prospects. *Ziegelindustrie International*, v. 7, p. 346-351,1991.

[4] Reis,M. J. L. Gerenciamento ambiental – um fator de sobrevivência para as empresas. In CONGRESSO DE GESTÃO EMPRESARIAL DO MEIO AMBIENTE, 14 -16 agosto, 1996, São Paulo.

[5] Anfarcer. Coordenação César Gomes Júnior. Desenvolvido pela Associação Nacional dos Fabricantes de Cerâmica para Revestimento. Apresenta texto sobre Brasil. Disponível em : <http://www.anfacer.org.br.> Acesso em: 27 nov. 2003.

[6] Barba, A.; Beltrán,V.; Feliu, C.; Garcia, J.; Ginés, F.; Sánchez, E.; Sanz, V. *Materias primas para la obtención de soportes de baldosas cerâmicas*, 1. ed. Castellón, Espanha: Instituto de Tecnologia Cerâmica: AICE., 1997.

[7] Blasco,A; Escardino, A.; Busani, G.; Monfort, E. Amorós, J. L.; Enrique, J.; Beltrán, V.; Negre, P. *Tratamiento de emisiones gaseosas efluentes líquidos y residuos sólidos de la industria cerámica*, Castellón, Espanha: Instituto de Tecnología Cerámica: AICE, 1992.

Gasch, G. M.; Gimeno, E. M.; Busani, G.; NavarrO, F. J. L. *Depuración de los gases de combustión en la Industria Cerámica*. Castellón, Espanha: Instituto de Tecnología Cerámica: AICE, 2001.

455 [8]Jonge, L. S. *Atmospheric pollution by the brick and tile industry*. *Ziegelindustrie*
456 *lnternational*, v. 39 (10), p. 531-540,1986.
457 [9] Boruff, C. S.; Buswell, A. M.; Upton, W.V. Adsorption of fluoride from salts by
458 aluminum floc. *Ind . Eng. Chem*., v. 29 , n. 10, p. 1154-1159, 1987.
459 [10] Vogel, H. R*eduction of pollution by changes to the kiIn and by flue gas*
460 *cleaning*. *Ziegelindustrie lnternational*, n. 41, p. 33-36. 1988.
461 [11] NBR 10.004–Associação Brasileira de Normas e Técnicas. Resíduos Sólidos,
462 2004.