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Evaluation of Pozzolanic Activity and Inhibition of the Alkali-Aggregate Reaction in Highly Reactive Pozzolans

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Abstract

This paper presents the results of an experimental study developed at the Federal University of Pará and at Furnas Centrais Elétricas S.A. The study aimed to investigate the reactivity of three highly reactive pozzolans: silica fume, rice husk-ash and metakaolinite, by determining the incorporation content of each for remotion of all the calcium hydroxide (CH) and for reduction the alkali-aggregate reaction. At the evaluation of the CH consumption, pastes with pozzolan and lime were cast in different proportions and observing compressive strength values in mini test specimens, correlating the former with the calcium hydroxide contents of those pastes. The expansive behavior originating from the alkali-aggregate reaction was assessed in the presence of reactive Pyrex-type glass, by means of mortar bars in the presence of the three studied pozzolans, employing the ASTM C-1260 accelerated method. In this test, the pozzolans were employed with contents of 4%, 8%, 12% and 16%, in addition to the reference sample. The results obtained indicated that the silica fume and the metakaolinite were the pozzolans with greater pozzolanic activity as well as the most effective in the reduction of expansions caused by the Pyrex glass reactivity. For total elimination of CH the optimum substitution contents were around 22%, while for the rice husk-ash 30% were required. In expansion reduction, contents of 8% of pozzolans were considered effective by mortar-accelerated test.

Keywords: alkali-aggregate reaction, calcium hydroxide, expansion, metakaolinite, pozzolan, reactivity, rice husk-ash, silica fume.

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1 INTRODUCTION

The use of pozzolans as mineral admixtures in mortar and concrete is a relatively common practice given the increase in mechanical strength and durability in aggressive environments, and the reduction in the rate of heat of hydration release, although the development of strength is slower. All these benefits are reached with the pozzolans and cementitious materials of more traditional use, such as natural pozzolans, calcinated clays, fly ash and ground blast-furnace slag.

There are, however, other pozzolans that feature a different behavior from those referred above, which are highly reactive pozzolans, whose reactivity with calcium hydroxide (CH) is much higher than that of the former, as they do not rely solely on the non-crystalline structure, but also on their high specific surface area. Because of their very fine particles or with greater specific surface area than those of portland cement, they make the transition zone between the aggregate and the cement paste denser in a much higher degree than the other pozzolans and they increase the number of nucleation points, thus favoring the precipitation of hydration products and reducing the size of the CH crystals [1,2]. Due to these effects, these pozzolans accelerate cement hydration, increasing strength in the initial stages, but affording a greater release of heat and, consequently, an elevation in the temperature of the mixture, which can lead to technical and hydraulic shrinkage problems.

The pozzolans considered as highly reactive are rice husk-ash (RHA) and metakaolinite (MTK), when produced in controlled conditions of calcination and grinding, and silica fume (SF). The latter is recognized as the pozzolan of the highest reactivity commercially available, and is widely employed in the production of high performance concrete. MTK has been rousing interest due to the improvements it effects on concrete and mortar properties, in addition to the availability of raw material and facility of controlling its production parameters. Some companies are marketing for MTK in the US, Europe and Brazil, which is produced from a kaolinite-rich clay. The reactivity in RHA, as in MTK, is related to the parameters of combustion, but in a higher degree than MTK, as it is not only the crystallinity that is dependent on the characteristics of the burning process, but also the microporosity of the particles, which is highly influenced by temperature and by the oxidation rate of cellulose and lignin, which may or may not preserve the cell structure of the rice husk. If the cell structure is preserved, RHA will have a very high specific surface area, of between 50 to 100 m^2/g, relieving it of the need to have very fine particles. According to Mehta [3], RHA is the pozzolan of highest reactivity among all, when produced within controlled conditions of combustion.

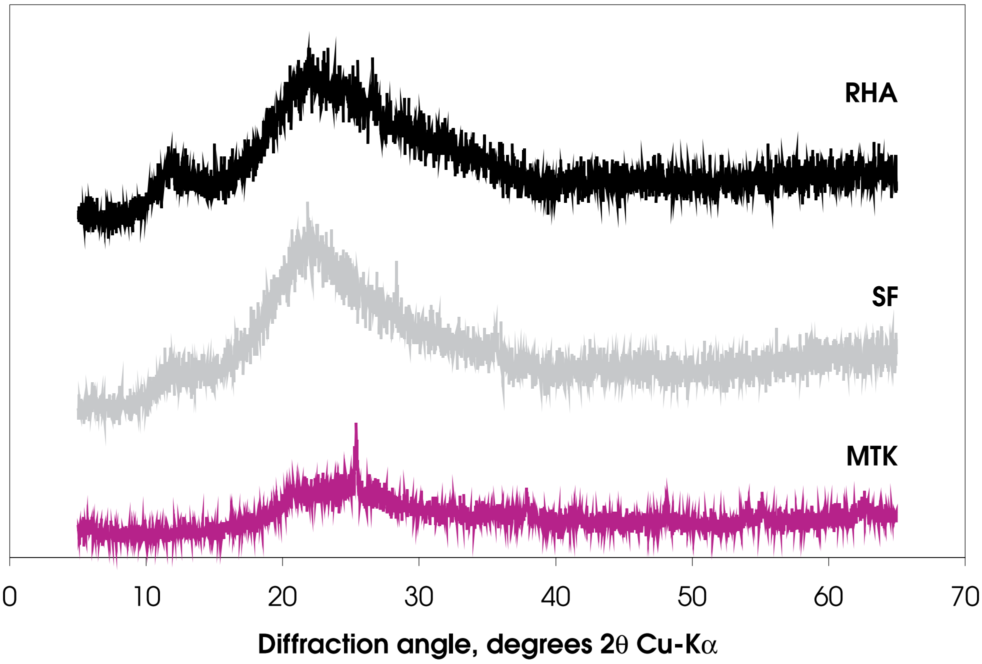
The maximum effect produced by the pozzolanic reaction is reached when the CH is totally consumed in the reaction. This leads to better results in mechanical strength and durability, especially in glass and natural fiber reinforced cement-based materials. The pozzolanic reaction should be expected to reduce the incidence of CH and avoid the alkali attack on the glass fiber and on the non-cellulose components of the natural fiber [4]

Table 1 – Characteristics of pozzolans and portland cement

Chemical composition (%)	MTK	SF	RHA	PC
SiO_2	50.38	96.00	86.00	19.85
Al_2O_3	43.29	0.06	0.16	4.22
Fe_2O_3	1.94	0.04	0.28	3.53
CaO	0.05	0.17	0.48	62.36
MgO	0.10	< 0.10	0.61	4.68
TiO_2	1.94	0.01	0.02	-
Na2O	0.03	0.51	0.16	0.21
K_2O	0.01	0.49	1.30	0.79
$Na_2Oeq.$*	0.04	0.83	1.01	0.72
SO_3	0.19	-	0.13	4.48
P_2O_5	-	-	0.47	-
C (total)	-	0.63	-	-
Ignition Loss	1.70	1.80	8.93	1.64
Mean particle size, µm	1.0 – 2.0	0.1 – 0.4	12.00	-
Specific gravity, kg/dm^3	2.57	2.22	2.08	3.13
Specific Surface, m^2/g	16.00	18.00	19.00	-

* $Na_2Oeq. = 0.658 \times K_2O + Na_2O$

Fig. 1 – X-ray diffraction analysis of the highly reactive pozzolans



The CH consumption is also important in the resistance against sulfates and in the alkali-aggregate reaction in concrete structures. In many situations it is therefore convenient to determine the percentage needed to consume all the CH, which depends more on the physical characteristics (grading and specific surface area) and mineralogical characteristics of the pozzolan than on its chemical composition [1], in addition, naturally, to other factors such as water/cement ratio, clinker constitution, the content of incorporated pozzolan, among others [5]. The further away from this ideal pozzolan percentage there will be lack or excess of CH. This study aimed to investigate the reactivity of three highly-reactive pozzolans by determining the incorporation content of each for remove all CH and eliminate the alkali-aggregate reaction.

2 EXPERIMENTAL PROGRAM

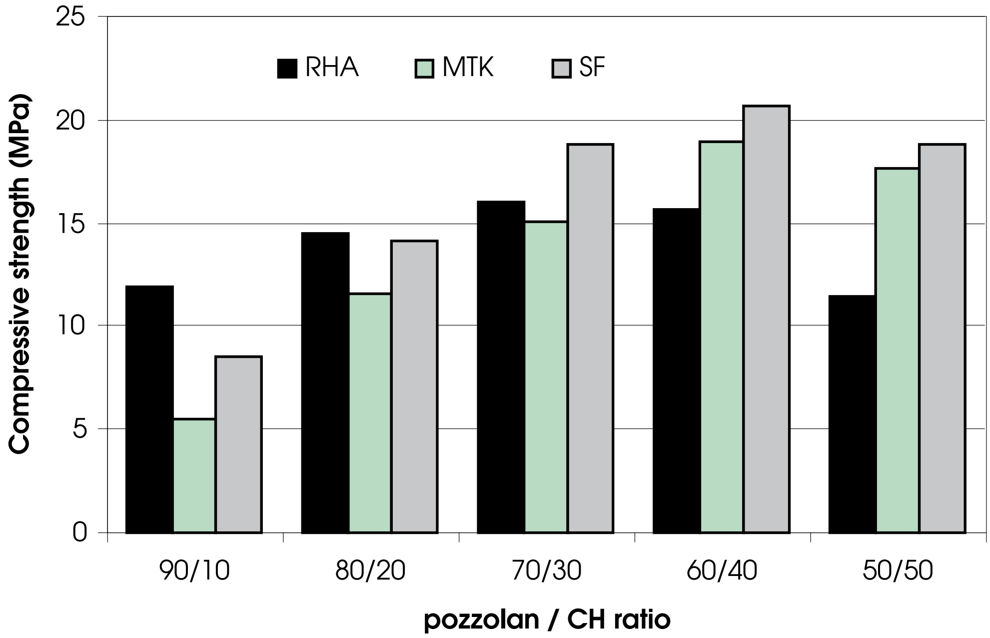
2.1 Materials

The pozzolans analyzed in the study were silica fume (SF), rice husk-ash (RHA) and metakaolinite (MTK). The SF was a by-product originating from the production of metal silicon alloys, commercialized in Brazil. The MTK came from the calcination and grinding resulting from the processing residue produced by a mining company, which explores kaolin in Amazonia, the Northern region of Brazil. This residue is extremely fine ($d_{50\%}$ = 0.5µm) and basically comprises poorly crystallized kaolinite. The RHA originated from the burning of rice husk produced in the process of electric power generation in thermoelectric plants in Southern Brazil. The CH was a product of high purity (97% of CH), with a specific gravity of 2.39 kg/dm³. The cement used in the test to determine the alkali-aggregate reaction was an ordinary portland cement, free of admixtures, designated PC I with total alkali content (Na_2O_{eq}) equal to 0.72%. The characteristics of the portland cement and of the studied pozzolans are shown in Table 1. Fig. 1 shows the X-ray diffractogram of the pozzolans.

2.2 Calcium hydroxide consumption

The methodology consisted in assessing the reactivity of the pozzolan by correlating the CH consumption results obtained in thermogravimetry with those of compressive strength at 28 days of the pastes produced with different pozzolan/CH proportions (in mass). The pozzolan/CH proportions employed in the study were 90:10, 80:20, 70:30, 60:40 and 50:50. The water/solids (pozzolan + CH) ratio was 0.60. A polyacrylate-based superplasticizer was used to provide an acceptable consistence to be cast. The SF and the RHA were the pozzolans that required higher admixture contents – around 2.5 % and 1.5% of the solid mass, while the MTK required only 0.80%.
The mixture of the pastes was performed mechanically for 5 minutes. The water employed was distilled and deionized. For each mixture, 10 test specimens were cast in stainless steel molds of 2cm in diameter and 4cm in height. After casting and 24 hours of air curing, the test specimens were stored in a glass container in vacuum conditions for 27 days. A CBR-type press, of 20 tons, with a two-ton load cell and a built-in digital analogical converter

Fig. 2 – Compressive strength results of pozzolans/CH pastes at 28 days



was utilized to test the rupture of specimens. The results were calculated for the average of the test specimens and values for relative deviation above 6% were excluded.

In determining the content of consumed CH, the powdered samples of the test specimens from the compressive test were used. The thermogravimetric test took into account mass losses related to free water (<80ºC), silicate and aluminate dehydration (80ºC – 400ºC), CH dehydration (400-550ºC) and the decarbonation of the $CaCO_3$. It was acknowledged that the presence of calcite in the pastes was originated from the partial carbonation of the free CH or the one not consumed. Powdered samples of about 5g were submitted to the test in an air atmosphere having a heating rate of 10ºC/min. To perform the thermogravimetry test, a simultaneous thermal analyzer STA 1500, from Stanton Redcrof, was employed.

2.3 Chapelle test

The pozzolanic activity of the three high-reactivity pozzolans was also determined by the modified Chapelle test [6], which consists of placing 1g of the pozzolan and 1g of calcium oxide (CaO) in water dispersion under stirring at a temperature of 90ºC for 16 hours. The test result is expressed by the amount of calcium oxide consumed by the pozzolan.

2.4 Alkali-aggregate reaction investigation

The alkali-aggregate investigation involved accelerated reactivity tests complying with ASTM C-1260/2001, featuring expansion analyses measured in mortar bars immersed in a solution of 1N sodium hydroxide (NaOH) at a temperature of 80ºC, for 30 days. Although this test method has some limitations due to very aggressive conditions, the purpose of this paper was to compare the behavior of two pozzolans, and not indicate the best content in suppressing AAR in concrete. The mortars were manufactured at a cement:aggregate ratio of 1:2.25 (in mass), using Pyrex glass instead as reactive aggregate in the form of artificial sand and the cement previously described. The water/cement ratio was set at 0.47, as prescribed in the aforementioned standard. In the presence of the admixtures, a polyacrylate-based superplasticizer was employed with a 1% content in relation to the cementitious cement mass.

The reduction in the expansions in the presence of the MTK, RHA and SF pozzolans was analyzed at 16 and 30 days, by casting the mortars with the admixtures employed in substitution for the cement mass, with 4%, 8%, 12% and 16% of content, in comparison to the reference sample, without admixture.

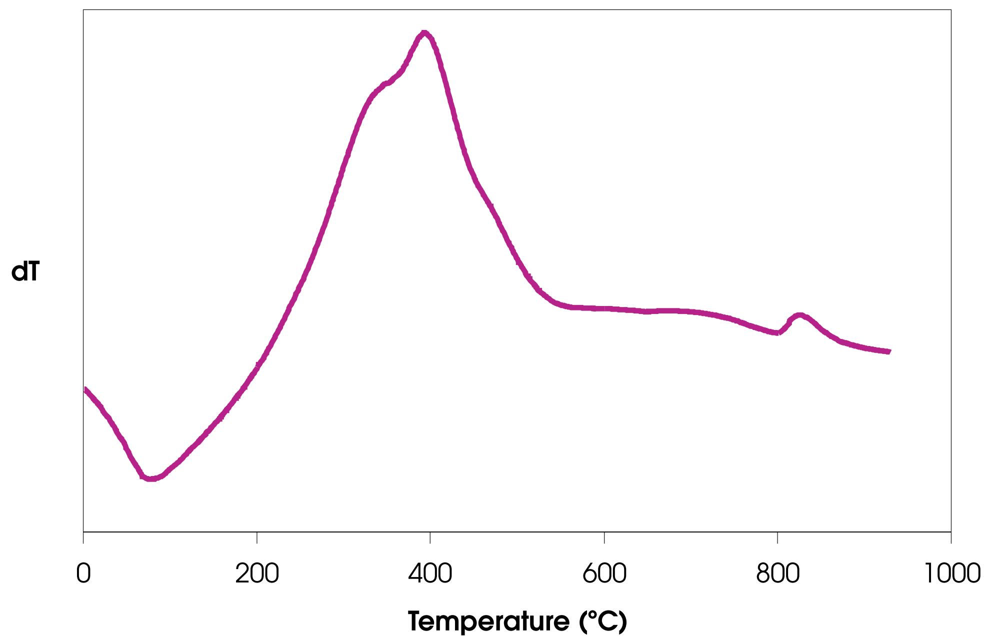
3 RESULTS AND ANALYSIS

3.1 Calcium hydroxide consumption / Chapelle test

Fig. 2 shows the graph of paste strength with different proportions of pozzolan/CH hydrated for 28 days. Table 2 displays the content of residual CH occurring in the pastes as determined by thermogravimetry. It was not possible to determine the CH in the pastes with RHA due to the high carbon content

Table 2 – Termogravimetric data of pozzolan/CH pastes at 28 days			
Pozzolan	**Pozzolan / CH ratio**	**Residual $Ca(OH)_2$ (%)**	**Reacted $Ca(OH)_2$ (%)**
SF	90:10	0	10
	80:20	0	20
	70:30	0	30
	60:40	0	40
	50:50	8	42
MTK	90:1	0	10
	80:20	0	20
	70:30	0	30
	60:40	0	40
	50:50	7	43

Fig. 3 – DTA analysis of RHA/CH paste (80:20)



in this pozzolan (significant loss of ignition = 9%), since the combustion reaction of the organic matter that remains in the RHA (lignin and cellulose) occurs in the same temperature band of the dehydroxilation of the CH, which prevented its determination in the paste in consequence of the overlapping of mass losses. In the DTA of the RHA/CH paste in the proportion 80:20, shown in Fig. 03, one can note the exothermal reaction at 400ºC resulting from the combustion of organic matter that is present in the RHA at 400ºC.

The performance observed for the three pozzolans was quite similar and shows that the compressive strength values of those mixtures is strongly influenced by the pozzolan/CH proportion, there being an excellent correlation between compressive strength and CH consumption. The highest strength value corresponded to the proportion in which the CH fully reacted with the pozzolan generating the highest quantities of hydrated products with binding properties. In pastes presenting with pozzolan/CH proportions above that of highest strength value (left in Fig. 2), there is a deficiency of CH (i.e. an excess of pozzolan), which causes part of the pozzolan to act as filler, while in pastes featuring proportions below that of highest strength value (right in Fig. 2), one can note an excess of CH. In both situations the amount of hydrated products with binding power is smaller as compared to the highest strength value, which directly reflects on the drop in compressive strength of the test specimens.

SF and MTK were the pozzolans that showed greater capacity of reacting with CH at 28 days, around 67% of their initial mass, while RHA was able to fix 43% of its

Table 3 – Chapelle test results

Pozzolan	Chapelle reactivity (g CH / g pozzolan)
SF	813.0
MTK	810.5
RHA	706.4

mass. The calculated content for RHA was based only on the compressive strength results of the test specimens for the pastes, as it was impossible to establish correlation with the thermogravimetry data. The maximum values of strength obtained with SF and MTK were reached with the pozzolan/CH proportion of 60:40, with SF providing a compressive strength slightly higher that of the paste with MTK. The highest strength value reached with RHA addition was 16 MPa for the paste with a 70:30 pozzolan/CH proportion, which is still lower than those obtained with SF and MTK admixtures, however, its specific surface was slightly greater than the latter's.

These results suggest that the burning conditions of the analyzed RHA were not ideal to form a product with a specific surface area between 50 and 100m^2/g, which affords a much higher reactivity to this pozzolan. This RHA, however, can still be considered of high reactivity, as can be confirmed by the results in the Chapelle test (Table 3), indicating its capacity to react with 706.4 mg of CaO for each gram of pozzolan. The test also indicated that SF and MTK produced similar pozzolanic activity values, around 810 mg CaO for each gram of pozzolan, showing a very good correlation with the mechanical strength and thermogravimetric tests.

Once the hydration reaction of a portland clinker produces approximately 20% of CH after 28 days, and that the cements incorporate, in addition to the pozzolan, 5% of gypsum, the optimum pozzolan content to be added (z) can be calculated by the following equation:

$$Z = 0.19 / (0.20 + x) \quad \textbf{(1)}$$

Where x is the amount of CH that the pozzolan can combine after 28 days of hydration. The deduction of equation 1 can be seen in PhD thesis of Zampieri [7]. By applying equation 1 one can obtain the admixture contents capable of consuming all the CH for each of the analyzed pozzolans (Table 4). The results showed that for the pro-

Table 4 – Determination of pozzolan content for consume all CH

Pozzolan	CH Equivalent that the pozzolan combines at 28 days (%)	Admixture content required to consume all the CH generated by the clinker (%)
SF	67	019/(0.87) = 22.0
MTK	67	019/(0.87) = 22.0
RHA	43	019/(0.63) = 30.0

Fig. 4 – Mortar expansions of reference and in the presence of pozzolans

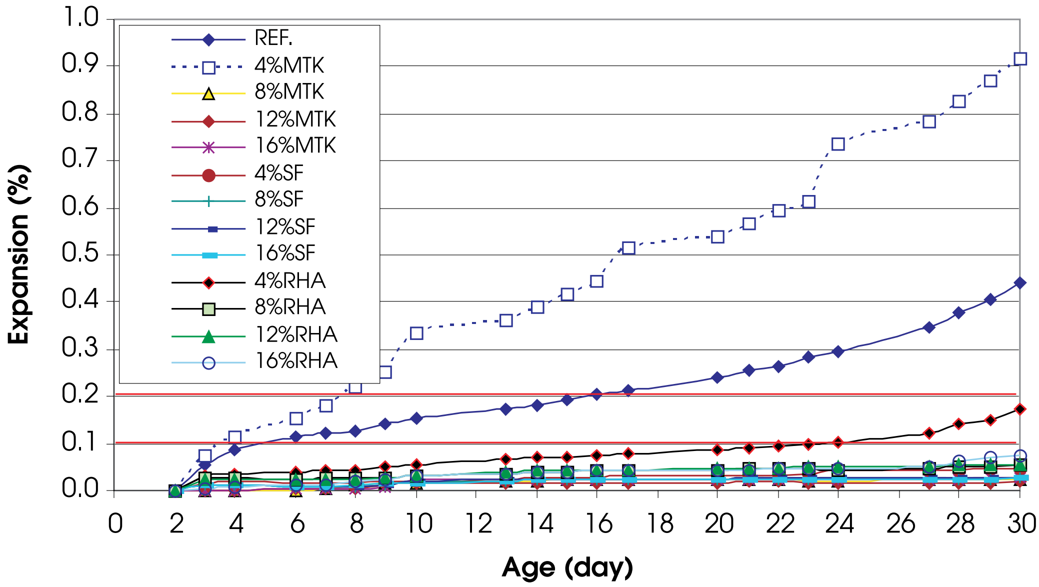
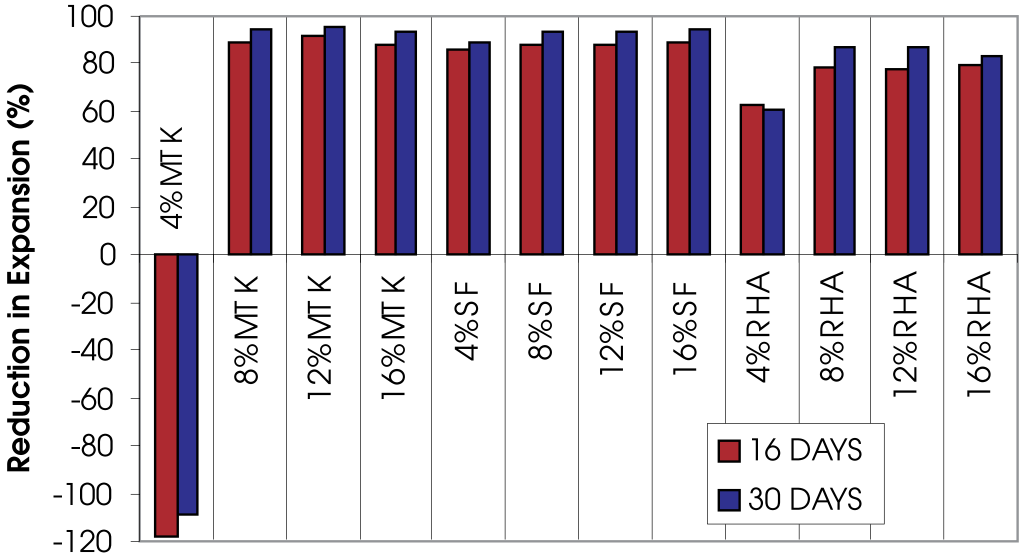


Fig. 5 – Reduction in Expansion (%)



duction of an ordinary Portland cement free of CH after 28 days, the incorporation of approximately 22% of SF or MTK, and 30% of RHA is required. The percentages obtained can yield slight variations, especially for lower water/cement ratios, due to the lower CH content generated in these pastes.

The high contents of mineral admixtures necessary to fix all CH can be only used in paste for the production of natural and glass fiber reinforced composites. In concrete mixtures these high contents of pozzolan are inappropriate for being used in practice taking into account the serious engineering consequences related to rheology and shrinkage, besides the high costs of some pozzolans as well as of superplasticizers and the risk of developing AAR.

Actually, the percentage of admixtures ranges from 8% to 12%, being the ones used in practice for concretes and mortars. Although these figures correspond to an excess of CH as compared to pozzolan, this is not implies on a drop of properties because the performance of these pozzolans depends not only on its reactivity properties but also on the filler effect.

3.2 Alkali-aggregate reaction investigation

Fig. 4 shows the expansions calculated from the dimensional variations measured in the mortar bars containing the analyzed admixtures.

When the determined expansions are compared to the limits of the 0.10% and 0.20% standard at 16 days, it is noted that all the admixtures and contents maintain values below this value, with the exception of 4% of metakaolinite, which shows an increment in expansions. At 30 days, the content of 4% of rice husk-ash also begins to go over the limit of 0.10%. Thus, all SF contents and those of 8%, 12% and 16% of MTK and RHA are effective in combating expansions at a level accepted by the standard.

The AAR expansion reduction potential of the three pozzolans, for the 4 contents analyzed (4%, 8%, 12% and 16%), was calculated in relation to the reference sample (in percentage - %), with a view to verifying the effective contents in combating the alkali-aggregate reaction (by reducing expansions). Fig. 5 shows the reduction of expansions in relation to the reference sample for the different pozzolan contents studied, at 16 and 30 days of test age.

It was verified that all the pozzolans and incorporation percentages analyzed, with the exception of 4% of MTK, were capable of significantly reducing expansions of mortars in the presence of pyrex, with MTK and SF proving the most effective and with similar behaviors at contents above 8%. Silica fume did not prove effective in reducing expansions at 4% content in the reactive quartzite either [8]. In view of the results obtained, it can also be noted that as the incorporation contents of the pozzolans were increased (above 8%), there is no expressive increase in effectiveness regarding expansion reduction.

4 CONCLUSIONS

a. The results for compressive strength showed a good correlation with CH consumption for all the pozzolans analyzed, proving that CH is the main reactive agent in the pozzolanic reaction.
b. Among the studied pozzolans, SF and MTK were the ones of higher reactivity, and were able to combine with approximately 67% of CH in relation to their masses. RHA yielded lower reactivity, combining with 43% of its mass. s
c. The pozzolan contents suitable to consume all the CH

in a portland cement paste would be 22% for SF and MTK and 30% for RHA. However, these percentages are inappropriate for being used in concrete and mortar due to the engineering consequences and the high costs of these pozzolans as well as of superplasticizers. In paste these high level of addition can be possible to avoid problems related to degradation of natural and glass fibers at alkaline pore solution.

d. In the accelerated tests for alkali-aggregate reactivity, it was noted that for all the contents of high reactivity pozzolans analyzed, with the exception of 4% MTK, there was an expressive reduction in expansions of mortars with Pyrex, by accelerated test method (ASTM C-1260) when compared to the pozzolan-free reference sample. The incorporation of 4% MTK was a pessimum content as it caused an increase in expansions, rather than a reduction. MTK proved very effective in reducing expansions from 8% incorporation upwards.
e. The optimum content for reducing expansions of mortars in the presence of Pyrex was 8% for all the pozzolans analyzed, by using ASTM C-1260 accelerated mortar bar test, considering that above this percentage there were not significant reductions in the expansions.
f. SF and MTK proved more effective than RHA in reducing the expansions caused by AAR, thus corroborating the observations made in the other tests performed in this study. Anyway, in the presence of other reactive aggregate this behavior can be changed. The efficiency of pozzolans will depend on the reactivity of aggregate employed and the type of concrete and cement used. In this case, it is suggested the use AAR concrete tests.
g. The SF and the MTK showed higher reactivity than RHA because the latter was not produced in a completely appropriate burning condition.
h. High contents of pozzolans to consume all CH is not interesting since its efficiency is not only due to reactivity but also to the filler effect producing a significant change in the produced products morphology as well as in the paste microstructure, besides serious engineering consequences related to rheology and shrinkage.

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