

EFFECT OF METAKAOLIN ON THE PERFORMANCE OF PVA AND CELLULOSE FIBERS REINFORCED CEMENT

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Abstract

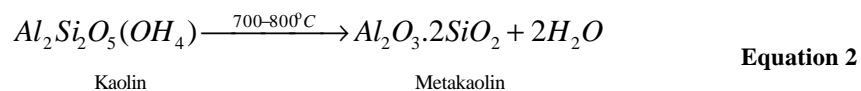
Silica fume is the most common pozzolan used in the formulation of cellulose and PVA fibers reinforced cement produced by Hatscheck method, but the use of metakaolin in cement based composites has been also considered. Comparative study of behavior of cellulose and PVA fibers reinforced cement made with different pozzolanic materials were realized. Up to 15% of the total cement was partially substituted by silica fume and metakaolin. The effect of cement substitution on hydrated phases, pore size distribution, mechanical properties, water diffusion and hygroscopic expansion were evaluated and both experimental details and preliminary results are presented.

1 Introduction

Silica fume is the most common pozzolan used in the formulation of cellulose and PVA fibers reinforced cement produced by Hatscheck method. Silica fume reduces the cement matrix alkalinity. The hydration of silica fume reaction consumes calcium hydroxide (CH) released from the hydration of C_3S and C_2S and diminish the CaO/SiO_2 ratio of the calcium silicate hydrate phase. As shown in Equation 1 (Rao, 2003), the pozzolanic reaction increases the content of C-S-H in the hydrated matrix. Additionally, a remarkable refinement of the pores is also observed. The overall alkalinity reduction and the reduction in permeability due to porosity changes help to protect cellulose fibers from alkali degradation. Moreover, silica fume is supposed to improve Hatscheck process, probably by enhancing the fresh composite rheology.



Metakaolin is a pozzolanic material too. It's obtained by calcination of kaolinitic clay at temperatures from 700°C to 800°C (Equation 2) (Zampieri, 1989). Kaolin's chemical composition is basically aluminous silicates hydrates associated with Mn, Fe, Ca, K, Na. It crystal has a lattice structure of tetrahedral and octahedral layers with interplanar distance of 7.2 Å (Santos, 1975).



The hydration reaction of metakaolin depends of Portland cement type, the AS_2/CH ratio, the quantity of free water and the temperature that the reaction will take place. At environmental temperature the hydrated products from metakaolin and lime compared with silica fume have been showed by Murat (1983) (Equation 3 to Equation 5).



Frías Rojas and Cabrera (2001) compared the hydration of 1:1 hydrated lime to meatakolin mixtures at 23°C and 60°C. They found C_2ASH_8 (stratlingite) and C_4AH_{13} appear, and finally the C_3ASH_6 (hydrogarnet), the later one only at high temperature, which partially contradicts Murat results. Nevertheless, it is possible to conclude that metakaolin hydration removes calcium hydroxide in a similar way of silica fume, but additionally to the C-S-H it produces phases that Taylor (1997) classifies as hydrogarnet or hydrogrossular phases.

Refinement of pore structure is also reported simultaneously to an increase on total porosity (Khatib and Wild, 1996 and Frías and Cabrera, 2000). Brooks and Magat Johari (2001) found that metakaolin reduces drying shrinkage as well as creep. This effect can be related to reduction of C-S-H content due to formation of hydrogarnet phases. Since wetting and drying movement are considered to play an important role on degradation of cellulose and PVA reinforced cement composite roof sheets, the shrinkage reduction has a potential to reduce degradation rate.

The use of metakaolin in composites has been intensively investigated. Marikunte *et all* (1998) found that metakaolin is more effective than silica fume in preventing the degradation process that causes de reduction of MOR and toughness on AR glass fiber reinforced cement. Purnell *et all* (1999) confirms the effectiveness of metakaolin in increasing GRC durability and demonstrates that pH of the pore water is reduced when 20% of the cement is substituted by metakaolin. Additionally to that, Purnell *et all* (2000) concluded that with 20% of metakaolin, the glass fibers are covered by a mineral phase other than calcium hydroxide. So metakaolin seems to be more effective in protecting alkali sensitive fibres from degradation. Banthia and Yan (1996) found metakaolin more effective in enhancing adhesion between steel fiber and cement paste than silica fume. Sales *et all* (1999) studied the use of metakaolin in the production of fiber-cement sheets with excellent mechanical results.

This paper presents the first results of the investigation, which is designed to compare the performance of cellulose and PVA fiber reinforced cement composites with silica fume and metakaolin partially replacing the Portland cement.

2 Experimental

Composites with cement replacement rate of 0, 5 and 15% (in mass) by both silica fume and metakaolin were produced. All other variables, like fibers and filler type and content were kept constant. The effect of replacement of cement by metakaolin and

silica fume in MOR, toughness, hygroscopic expansion, pore structure and cement mineral phases were analyzed.

2.1 Sample production and materials

Table 1 brings the mix proportions used for the experiments specimens' preparation. The mix standard (ST) has no pozzolan in its composition. The mixes SF5 and MK5 has 5% of the cement (in mass) substituted by silica fume and metakaolin respectively. The SF15 and MK15 mixes had 15% of pozzolanic material.

Table 1 – Mix proportions - % in weight.

MIX	PVA	Cellulose	Cement	Limestone filler	Silica Fume	Metakaolin
ST	2.00	3.00	85.00	10.00	0.00	0.00
SF5	2.00	3.00	80.75	10.00	4.25	0.00
SF15	2.00	3.00	72.25	10.00	12.75	0.00
MK5	2.00	3.00	80.75	10.00	0.00	4.25
MK15	2.00	3.00	72.25	10.00	0.00	12.75

The specimens were produced in laboratory by slurring the raw material in water solution (20% of solids) followed by a vacuum drainage of the excess of water and pressing at 3.2 MPa (see Savastano Jr. *et al.*, 2001). In order to improve dispersion, pozzolan was first mixed in water for one hour and half, then adding cellulose fibers and mixing for one hour, adding PVA fiber and mixing for half hour and adding filler limestone and cement and mixing for 25 minutes. It was observed that metakaolin dispersed easily than silica fume ones when the composites were prepared. An ongoing experiment will investigate the rheology of both mixtures for a definite conclusion. The paste was transferred to a casting box with 160 x 160mm and a vacuum was used to eliminate the excess of water and form the composite.

The regime of cure was two days in plastic bags and 28 days in water. After 7 days the samples were sawed to their final dimension (5 x 40 x 160mm).

Metakaolin was supplied by Metacaulim do Brasil. Cement, condensed Silica Fume and limestone filler were acquired in the Brazilian market. The chemical composition of the materials was measured by wavelength-dispersive x-ray fluorescence spectrometry (XRF) using the PANalytical Magix Pro. The results are showed in Table 2. Limestone filler used is rich in magnesium

Table 2 - Chemical composition in oxides.

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	SO ₃	LOI
Cement CPHI-F*	18.2	4.63	2.68	6.22	59.9	0.12	0.97	3.47	3.21
Limestone filler	6.48	1.67	1.10	18.8	31.6	<0.10	0.40	0.14	40.0
Silica fume	93.5	0.43	0.45	0.47	0.23	0.16	0.83	-	2.92
Metakaolin	52.8	36.3	4.21	0.81	<0.10	<0.10	1.41	-	3.53

*Ordinary Portland Cement with filler.

The results of TG analysis show that the limestone filler has a percentage of magnesium carbonate of 36.57% and calcium carbonate of 54.85%. Impurities are approximately 8.58% of limestone mass. Limestone filler content in cement was 4.02%.

Kaolin transformation to metakaolin was not completed during calcination, since TG revealed that a dehydration peak around 525°C with a weight loss of 2.84%. Also the Fe₂O₃ content is above 4% is high enough to affect the color of samples with 15% of replacement. XRD revealed also that the kaolin has crystalline phases with the presence of kaolin, quartz and hematite (Figure 1).

Silica fume SiO₂ content was not very high, 93,8%, moisture content was less than 1% and TG residual mass at 1000 °C was 97.94% of initial mass. Silica fume used was amorphous (Figure 2).

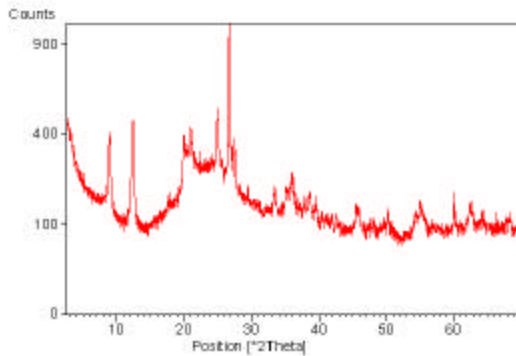


Figure 1–XRD of metakaolin.

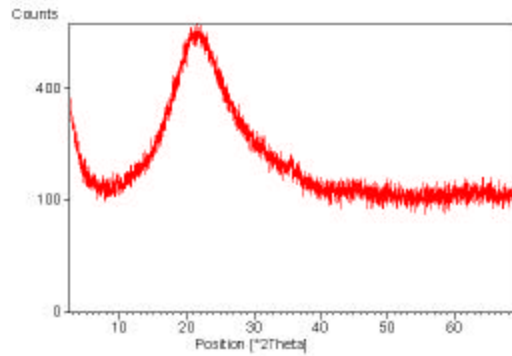


Figure 2–XRD of silica fume.

Table 3 presents specific surface area (BET, Micromeritics ASAP 2010), density (Helium picnometry, Quantachrome Multipycnometer) and pozzolanic activity measured by Chappelle Method (Raverdy *et al.*, 1980). Silica fume presents higher reactivity compared with metakaolin, but since the surface area of metakaolin is considerable lower, the specific pozzolanic activity has is equivalent. In a first test the measured pozzolanic activity of silica fume was bellow 500mg CaO/g. After the replacement of the Teflon pieces used to stir the solution and disaggregate the agglomerate particles and the hydrates by stainless steel bearing balls, a more accurate value for the silica fume was obtained, without altering metakaolin results. So a good dispersion of the condensed particles is critical aspect for maximizing the reaction of condensed silica fume.

Table 3 – Specific surface BET, density and pozzolanic activity of materials.

Material	SSA (m ² /g)*	Density **	Pozzolan activity (Chapelle)	
			Total (mg CaO/g)	Specific (mg CaO/m ²)
Cement CP II F	1.05	3.088	---	---
Metakaolin	16.30	2.629	622	38,2
Silica fume	22.20	2.247	798	35,9
Filler limestone	4.91	2.826	---	---

Unbleached kraft cellulose fiber has Kappa number of 45, and was mechanically refined to 65° Shopper Riegler was used. PVA fibers, produced in Japan, were 6mm long.

2.2 Test Methods

Mineralogy of the hydrates were measured by termogravimetry TG (Nezstch TG 209, 10°C/min, nitrogen atmosphere, using a larger crucible (sample weight ~1g).

Pore size distribution, density of the composites and total pore volume was measured by mercury intrusion porosimetry (Micromeritics AutoPore III) up to 476MPa.

Mechanical proprieties were evaluated by MOR, LOP (limit of proportionality), elastic modulus and fracture toughness in a four bending point method (Dias & JOHN, 2003). The equipment was an Instron 5569, with deflection measured in the center by LVDT.

2.2.1 Hygroscopic expansion

Higroscopic expansion was evaluated with experimental arrangement showed in the Figure 3. In this experiment, one oven dried (70°C) face sample is exposed to water supported in two points (span = 135mm). The vertical surfaces of the sample were previously covered by hydrophobic silicone rubber layer, forcing an unidirectional water intake. Sample deflection at mid-span is recorded over time with a resistive displacement sensor (GEFRAN mod. PZ12_25). Data acquisition was performed by a DAQ PAD MIO 16XE-50 device with DAQ PAD TB52 controlled by LabView software.

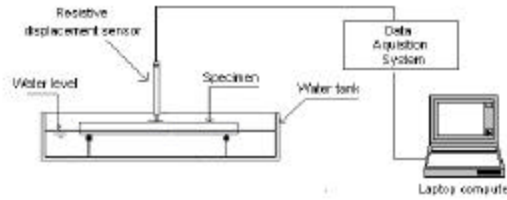


Figure 3 - Experimental arrangement for estimating hygroscopic expansion.

The deformation varies over time, with the progressive water diffusion. The hygroscopical expansion can be estimated by

$$a = \frac{16\delta_{\max}e}{3L^2} \quad \text{Equation 6}$$

- α = hygroscopic expansion (mm/mm);
- L = span (mm);
- δ_{\max} = maximum deflection during asymmetrical water intake (mm);
- e = thickness (mm).

Assuming that the maximum deflection corresponds approximately to 50% of the saturation limit, and other relevant simplifications (see Dan *et al.*, 1988; Sato, 1988) the water diffusivity (D , m²/s) can be estimated by:

$$D = \frac{0,04895 e^2}{t_{0,5}}$$

Equation 7

where $t_{0,5}$ is the time in seconds which corresponds to the maximum deflection.

3 Results and discussion

Results of TG are illustrated by Figure 4 to Figure 5 and summarized in Table 4, which includes the identification of the main peaks. The first peak occurs around 144°C and represents mainly the de-hydration of C-S-H and the presence of ettringite. The following peaks between 160°C to 310°C are related to hydrogarnet phases.

Both pozzolans reduced the amount of combined water, which is explained because the slower pozzolanic reaction. It is also possible to observe that carbonation did occur in some samples, especially MK5 and MK15.

They also did reduce the content of CH, as expected, but the silica fume was more effective at this degree of hydration. This fact can be explained by the relatively lower pozzolanic activity of metakaolin, and the difference will probably progressively disappear with the increase of hydration rate, because of high content of pozzolan, in the long term all available CH will be consumed.

Metakaolin containing samples presented a characteristic peak around 263-268°C. This is probably related to one of hydrogarnet phase, like C_2ASH_8 or, most probable to stratglingite (C_4AH_{13}) (Frias Rojas & Cabrera, 2001). This is consistent with the fact that metakaolin mixes presented the lowest content of water combined as C-S-H and ettringite phases.

Table 4 – Summary of TG results (values are % of total calcinations residue).

Phase	Temperature (°C)	ST	SF5	SF15	MK5	MK15
C-S-H – ettringite	142 - 147	9.8	7.7	9.5	6.7	6.3
Hydrogarnet 1 st peak	181 - 189	nd	nd	nd	3.5	4.2
Hydrogarnet 2 nd peak	263 - 268	5.4	4.9	4.4	4.4	5.4
Cellulose	255 - 257	1.7	1.6	1.4	1.8	1.8
PVA	395 - 413	1.5	1.3	1.3	1.6	1.6
CH	484 - 493	5.0	3.8	3.0	4.2	3.5
MgCO ₂	759 - 757	5.0	4.5	5.0	5.0	5.1
CaCO ₂	724 - 837	9.4	7.4	6.0	8.7	6.8
Combined water (%)	020 - 570	20.1	16.4	17.0	18.8	19.4
CO ₂ (%)	570 - 900	14.3	14.8	13.7	17.2	15.3

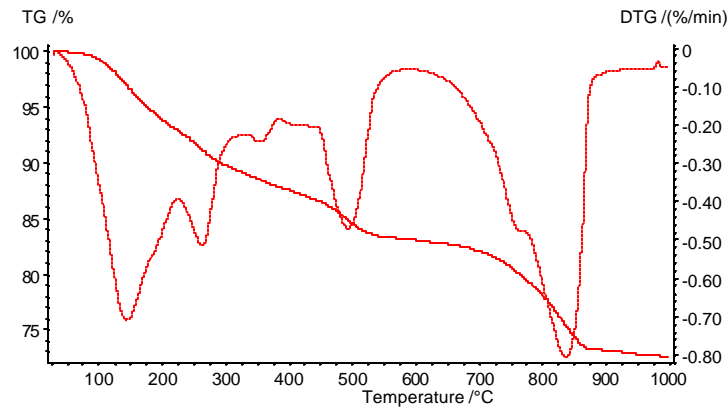


Figure 4-TG for standard mix.

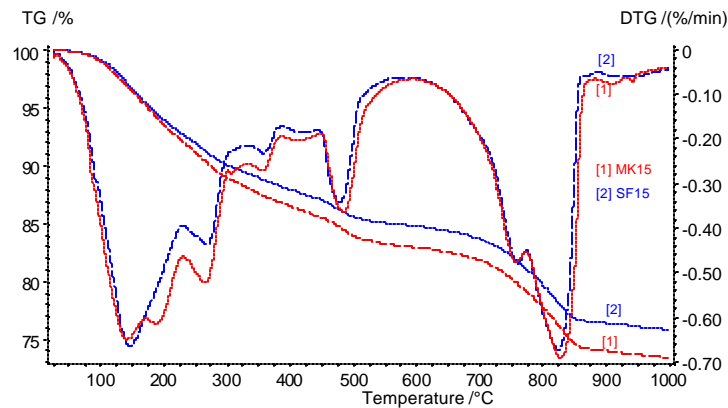


Figure 5-TG for MK15 and SF15 mix. The peak just bellow 200°C characteristic of metakaolin mixtures is easily observed in the MK.

Porosity for the mixes ST, SF15 and MK15 are in Table 5 and pore size distribution is presented at Figure 6. Both pozzolans did refine the pore structure, and presents higher content of pores bellow 20nm than the plain standard cement mixture, as previously reported elsewhere (Khatib & Wild, 1996; Frías & Cabrera, 2000). MK15 presented highest porosity due to high content of pores bellow 30nm. This is accordance with published results (Khatib & Wild, 1996 and Frías & Cabrera, 2000). SF15 presented the lowest total porosity.

Table 5 – Physical properties of composites -data from Mercury intrusion porosimetry.

MIX	Bulk density (g/cm ³)	Apparent skeletal density (g/cm ³)	Porosity (%)
ST	1.740	2.073	16.1
SF15	1.666	1.954	14.7
MK15	1.579	1.981	20.3

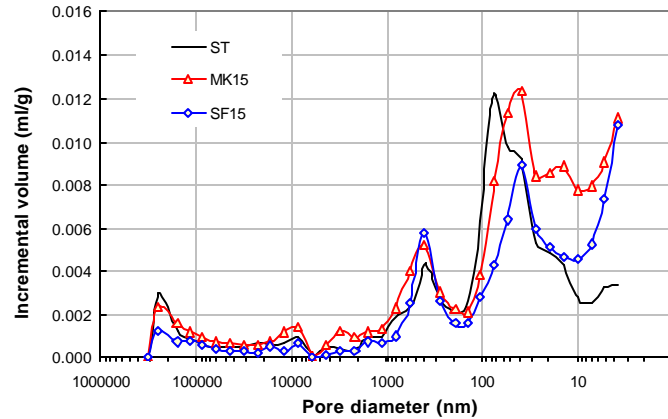


Figure 6 – Pore size distribution of the composites

The pozzolans didn't affect significantly the mechanical properties of the composite, as can be seen in Table 6 and Figure 7 and Figure 8. This observation includes MK mixtures, which presented significantly higher total porosity and SF mixtures, which presented the lowest pore volume content. The formation of more resistant phases, the role of the PVA fibers on the post-cracking behavior of the matrix (especially in the MOR results) and the influence of the larger porosity associated with the cellulose fibers (around 300nm see Figure 6) are possible explanations.

Table 6 – Mechanical properties of saturated composites samples after 28 days of wet curing. Average (and standard deviation) of at least 10 samples.

MIX	MOR (MPa)	Young modulus (GPa)	LOP (MPa)	Toughness (kJ/m ²)*
ST	9.53 ±1.30	13.26±1.57	6.88±1.15	1.80±0.96
SF5	10.79±1.67	16.74±2.50	8.23±1.28	1.49±0.41
SF15	10.36±0.95	15.97±2.04	7.46±0.76	1.81±0.93
MK5	10.66±1.60	14.34±4.05	7.97±1.51	1.89±0.71
MK15	10.62±1.50	14.21±3.36	8.06±1.36	1.73±0.70

* Fracture toughness to 50% of maximum load in the post-cracking zone.

Both pozzolans reduced significantly the bulk gravity of the composite, with those containing metakaolin with the lowest bulk gravity. This tendency, which is confirmed by water absorption measurements, means that a standard fiber-cement sheet can be produced using smaller amount of raw materials if metakaolin is used as pozzolan.

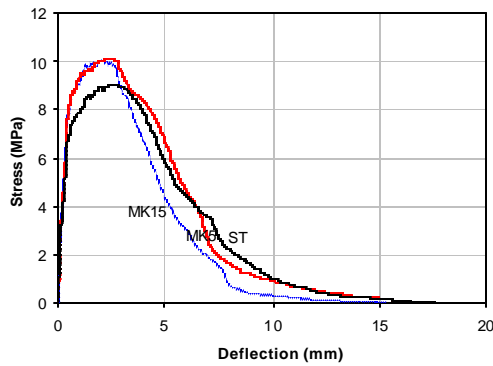


Figure 7 - Average stress curve for ST, MK5 and MK15.

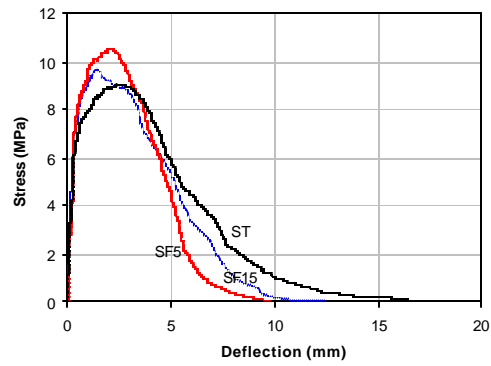


Figure 8 - Average stress curve for ST, SF5 and SF15.

Table 7 presents the preliminary results of hygroscopic expansion and water diffusion measurement. Hygroscopic expansion was higher for mixes with pozzolans than for the standard mix, but this difference is not considered to be significant. By the other side, pozzolan mixtures presented significant lower water diffusion.

Table 7 – Preliminary results of hygroscopic expansion coefficient and water diffusion

Specimen	Hygroscopic expansion (mm/mm).		Water Diffusion (m ² /s)	
	results	average	results	average
ST1	7.35E-04	6.88E-04	1,581E-09	1,888E-09
ST2	6.41E-04		2,194E-09	
SF15_1	8.10E-04	8.99E-04	1,563E-10	1,782E-10
SF15_2	9.89E-04		2,001E-10	
MK15_1	8.38E-04	8.25E-04	6,120E-10	3,933E-10
MK15_2	8.12E-04		2,497E-10	

4 Final remarks

The short term performance of cellulose and PVA fibre reinforced cement with silica fume and metakaolin as substitutions of cement was investigated. From the preliminary results some remarks are presented.

The bibliographical review suggests metakaolin is more effective protecting alkali-sensitive fibers than silica fume.

Both pozzolans are effective in removing CH from the matrix, but the removal was not concluded after 28 days of wet curing. Metakaolin MK mixes presented different mineral composition than SF and ST ones, with the formation of hydrogarnets phases and a comparatively lower content of C-S-H. Metakaolin samples presented high pore volume content than other mixes. Silica fume resulted in the lowest total pore volume among the three mixes. Nevertheless this variation did not affect the mechanical performance. Hygroscopic movement was not significantly affected by the substitution of the cement by pozzolans. By the other side, water diffusion was remarkably reduced by both pozzolans.

Metakaolin samples presented the lowest bulk specific gravity, followed by SF mixes, which means that the use of this pozzolans helps to reduce the raw materials consumption.

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6 References

- Banthia, N.; Yan C. Bond-Slip Characteristics of Steel Fibers in High Reactivity Metakaolin (HRM) Modified Cement-Based Matrices. In: **Cement and Concrete Research**, Vol. 26, No. 5, pp. 657-662, 1996
- Brooks, J. J.; Megat Johari, M. A. Effect of metakaolin on creep and shrinkage of concrete. In: **Cement and Concrete Composites**, Volume 23, Issue 6, December 2001, Pages 495-502.
- Dan, W., Quénard, D., Sallée, H., Cope, R. Comportement hydrique d'un composite ciment-polymère-verre (CCPV) et influence de l'humidité sur ses propriétés mécaniques. **Cahiers du CSTB**. Livrasion 295, Cahier 2304, Décembre, 1988.
- Dias, C.M.R., John, V.M. Modelagem da variação dimensional de placas de cimento-celulose-PVA submetidas à molhagem. In: **V Simpósio EPUSP sobre Estruturas de Concreto**, São Paulo, 2003.
- Frías Rojas, M.; Cabrera, J. The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin-lime-water systems. In: **Cement and Concrete Research**, Volume 32, Issue 1, January 2002, Pages 133-138.
- Frías, M.; Cabrera, J. Pore size distribution and degree of hydration of metakaolin-cement pastes, **Cement and Concrete Research**, Volume 30, Issue 4, April 2000, Pages 561-569.
- Khatib, J. M.; Wild, S. Pore size distribution of metakaolin paste. In: **Cement and Concrete Research**, Volume 26, Issue 10, October 1996, Pages 1545-1553.

Marikunte, S.; Aldea, C.; Shah, S.P. Durability of Glass fiber reinforced cement composites: effect of silica fume and metakaolin. In: **Advanced Cement Based Materials**. V.5, p.100-108, 1997.

Murat, M. Hydration reaction and hardening of calcined clays and related minerals. I – Preliminary investigation on metakaolinite. In: **Cement and Concrete Research** 13. p259-266. 1983.

Purnell, P. Short, N.R.; Page, C.L.; Majumdar A.J. Microstructural observations in new matrix glass fibre reinforced cement. In: **Cement and Concrete Research** 30 (2000) 1747-1753.

Purnell, P., Short, N.R.; Page, C.L.; Majumdar A.J., Walton, PL. Accelerated ageing characteristics of glass-fibre reinforced cement made with new cementitious matrices. In: **Composites: Part A** 30 (1999) 1073–1080.

Rao, G.A. Investigations on the performance of silica fume – incorporated cement pastes and mortars. In: **Cement and Concrete Research** 33. p1765-1770. 2003.

Raverdy, M.; Brivot, F.; Paillère, A.M.; Dron, R. Appreciation de l'activité pouzzolanique dos constituents secondaires. In: **7th International Congress on the Chemistry of Cement**, Paris 1980, Vol.3, pp. 36-41.

Sales, G.W. et al. Strength improvement in Portland cement-based boards. In: **Cement and Concrete Research** 29 (1999) 1693–1695.

Sato, N.M.N. Análise da porosidade e de propriedades de transporte de massa em concreto [PHD Thesis]. São Paulo, 1998.

Savastano Jr., H., Warden, P.G., Coutts, R.S.P. Ground iron blast furnace slag as a matrix for cellulose-cement materials. In: **Cement & Concrete Composites** 23, 389-397, 2001.

Taylor, H.F.W. Cement Chemistry. 2nd edition. Tomas Telford, 1997.