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Efficiency Evaluation of Metakaolins for Use in Concrete

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Abstract. *The use of metakaolins has been shown to be effective in modifying the properties of cementitious materials related to durability, highlighting the very positive impact in terms of increasing the electrical resistivity of concrete and reducing ionic transport in this porous medium. In this sense, the present work aims to evaluate the efficiency of different metakaolins in terms of pozzolanic activity, linking the efficiency to various characteristics of the metakaolin. Five samples of different Brazilian commercial metakaolins were then characterized, using the following methods: BET specific surface area, X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, thermal analysis (TA/DTA), thermogravimetric analysis (TG/DTG) and determination of pozzolanic activity by the modified Chapèlle method. As the main results, it was found that the BET specific surface area and the Al_2O_3 content, obtained by XRF, better explain the pozzolanic activity of metakaolins (Pearson correlation coefficients equal to 0.89 and 0.94, respectively). The amorphous content (quantified by Rietveld in the XRD) showed only a reasonable correlation with the pozzolanic activity determined by the modified Chapèlle method. In general, the chemical-mineralogical characteristics that indicate purity and amorphism of metakaolin, expressed by the Al_2O_3 content, Al_2O_3/SiO_2 ratio, $SiO_2+Al_2O_3$ sum, and amorphous content, represent important performance parameters of metakaolins. The specific surface area compensates for lower purity or chemical reactivity and significantly influences pozzolanic activity.*

Keywords: *Metakaolin, Pozzolanic Activity, Modified Chapèlle Method, BET Specific Surface Area, Rietveld – XRD.*

1 Introduction

The cement and construction industry is responsible for a considerable part of CO_2 global emissions. Data from the *World Business Council for Sustainable Development* (WBCSD) reveal, for example, that cement is the source of approximately 5% of the world's CO_2 emissions, something, therefore, quite significant. The pressure for more sustainable manufacturing processes (less polluting and more efficient) has encouraged research on the replacement of part of the clinker by supplementary cementitious materials (SCMs). In general, these researches aim to reduce costs and environmental impact, as well as improve the performance and durability of mortars and concretes (Cardoso et al. 2022).

One of the most used SCMs is metakaolin, obtained from the calcination of kaolinitic clays ($Al_2O_3.2SiO_2.2H_2O$). The dehydroxylation process through thermal activation (endothermic process) amorphizes the crystalline structure of kaolinite, originating the reactive material, of pozzolanic nature. The high pozzolanicity of this mineral addition, which provides chemical reactivity with calcium hydroxide, generates additional hydrated calcium silicate (C-S-H) to the cementitious matrix (Sperinck et al. 2011, Inocente et al. 2021).

In general, metakaolin-modified cementitious systems are characterized by having a less

porous internal structure and with greater refinement of pores, which gives the material higher mechanical resistance and better performance against the attack of chlorides, for example (Sun et al. 2019, Cascudo et al. 2021, Cardoso et al. 2022). However, some recent studies have concluded that different metakaolins can influence in different ways both the pozzolanic reactivity (Ababneh et al. 2022) and the performance of concretes (Cascudo et al. 2021), which reinforces the importance of a consistent characterization of the material, with emphasis on the evaluation of the efficiency of different metakaolins, thus promoting the rational use of this material in cementitious systems.

In this context, this work aims to evaluate the efficiency of different metakaolins in terms of pozzolanic activity and relate it to various characteristics of the material (chemical, physical and mineralogical), with a view to thoroughly discussing the reactivity of the material based on general parameters of its characterization.

2 Experimental

2.1 Materials

Five samples of commercially available metakaolins were used in the present work (Figure 1), named from M0 to M4 (in increasing order of specific surface area).

Figure 1. Metakaolins studied.

2.2 Methods

The metakaolin samples were subjected to chemical, physical and mineralogical characterizations by means of the following methods:

- Specific gravity: determined by helium pycnometer; the equipment used was AccuPyc II 1340 Micromeritics.
- BET specific surface area: through nitrogen gas adsorption analysis (ASTM C 1069: 2009); the equipment used was Quantachrome Autosorb IQ, model 0002-3.
- X-ray diffraction (XRD) for identification of crystalline phases: patterns were recorded on a D5000 - Siemens X-ray diffractometer with a Cu Kα anode operating at 40 kV and 30 mA. The diffraction patterns were collected over an angular range of 3° to 70° with a step size of 0.05° without sample rotation. The sample was prepared by ball milling and sieving in a 75 μm mesh sieve and pressing.
- Rietveld quantitative X-ray diffraction (XRD) - quantitative analysis of crystalline and amorphous phases: it was used a Bruker D8 Discover diffractometer, with a Cu Kα anode operating at 40 kV and 40 mA. The diffraction patterns were collected with a step size of 0.01° with 15 rpm sample rotation. Sample preparation was initially performed by drying at 105°C for 12 hours, pulverizing using a planetary ball mill (agate), and subsequently pressing. The quantification of phases by the Rietveld method used 10% Al_2O_3 as a spike to determine the

amorphous fraction, based on the adjustment of the calculated composition to the experimental diffractogram using the Diffrac.Topas® 4.2 software.

- X-ray fluorescence (XRF): the chemical composition was determined using the WDS Bruker S8 Tiger, with Rh tube. The sample was prepared with calcination at 1000°C for 5 hours and then melted.
- Fourier Transform Infrared Spectroscopy (FTIR): the spectra of the samples were acquired by the Attenuated Total Reflection technique (ATR) in the infrared absorption spectrometer Bruker Vertex 70, with the accessory Platinum ATR Unit A 225. The samples were placed on a diamond cell (2 x 2 mm), operating in single reflection mode with an interaction angle of 45°. This spectral analysis was performed with 64 scans over the range 350-4100 cm^{-1} at a resolution of 4 cm^{-1}. Through the use of data analysis software, the signs of carbon dioxide and water vapor present in the atmosphere were subtracted.
- Residual Potential of Dehydroxylation (RPD): the relationship between the mass loss experienced in the thermogravimetric test (TG/DTG) and the theoretical mass loss from the transformation of kaolinite to metakaolinite (13,76%, according to Shvarzman et al. 2003). The equipment used was Shimadzu DTG-60H. The measurements were made in a flow of Argon (200 mL/min), within a temperature range of 25-1200°C, in 70 μL alumina crucibles.
- Efficiency of metakaolins: determination of pozzolanic activity by the modified Chapèlle method, according to ABNT NBR 15895: 2010 Brazilian test method.

3 Results and Discussion

The results are summarized in Table 1. The characterization and the correlation analysis of characteristics are presented in subsequent topics.

Table 1. Metakaolins characterization.

	M0	M1	M2	M3	M4
Specific gravity (g/cm³)	2.60	2.58	2.58	2.60	2.60
BET specific surface area (m²/g)	19.8	22.1	24.7	28.7	31.0
SiO_2 (%) - XRF	56.5	52.7	51.3	47.6	51.4
Al_2O_3 (%) - XRF	32.2	37.1	37.8	39.5	42.5
Amorphous (%) – XRD-Rietveld	61	70	66	59	76
Pozzolanic activity – Chapèlle (mg $Ca(OH)_2$ / g metakaolin)	877	1037	999	1075	1296

3.1 XRD and XRF Analyzes

The diffractograms of the studied metakaolins show similarity with the indication of an amorphous halo centered between 23° and 26°. Figure 2 presents, by way of example, the diffractogram obtained for metakaolin M1 and Table 2 presents the major and minor phases (traces) found in the different samples of metakaolin, as well as the main chemical elements of the chemical formulas of the minerals (except oxygen and hydrogen).

The mineralogical analysis indicates significant amounts of quartz, kaolinite, and illite in almost all metakaolins. Efficient calcination could eliminate all kaolinite; on the other hand,

quartz persists after the high calcination temperatures at which metakaolins are produced. Metakaolin M4 did not present kaolinite, thus demonstrating more efficient calcination, and did not present quartz, which means greater purity of the raw material.

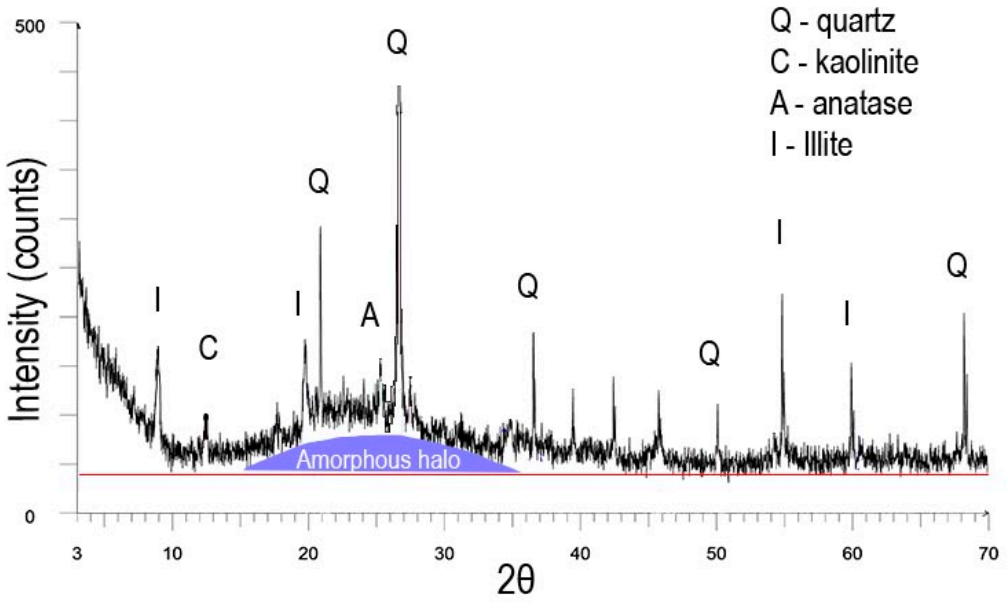

Figure 2. M1 – XRD pattern.

Table 2. Phases detected by XRD - metakaolins.

		Chemical elements	M0	M1	M2	M3	M4
Major phases	Quartz	Si	✓	✓	✓	✓	X
	Illite	K, Al, Mg, Fe, Si	✓	✓	✓	✓	✓
	Kaolinite	Si, Al	✓	✓	✓	✓	X
Minor phases	Anatase	Ti	✓	✓	✓	✓	✓
	Goethite	Fe	X	X	X	✓	X
	Sericite	K, Al, Si	✓	X	X	X	✓
	Spinel	Mg, Al	X	X	X	✓	X
	Rutile	Ti	✓	✓	✓	X	X
	Almandine	Al, Fe, Si	✓	X	X	X	X
	Maghemite	Fe	X	✓	✓	X	X
	Anorthite	Ca, Al, Si	X	✓	✓	X	X

Legend: ✓ - Detected; X – Not detected

Table 3 presents the chemical composition of metakaolins. It is noted that the chemically purer metakaolins had fewer minority phases in the constitution (compared to the results of the XRD analysis – Table 2). The sum of SiO_2 and Al_2O_3 indicates greater chemical purity of metakaolin M4, corroborating the results of the XRD analysis and quantification of amorphous (Table 1). Furthermore, the Al_2O_3/SiO_2 ratio demonstrates a greater balance in the chemical composition of M4 and M3 – theoretical values for pure kaolinites of 0.85 (Grim 1962). This

balance ratio is relatively higher in M1 and M2 and is not shown in metakaolin M0. The imbalance of the Al_2O_3/SiO_2 ratio indicates the presence of non-amorphous SiO_2 in other crystalline phases such as quartz, for example.

Table 3. Chemical composition by XRF - metakaolins.

	M0	M1	M2	M3	M4
SiO_2	56.5	52.7	51.3	47.6	51.4
Al_2O_3	32.2	37.1	37.8	39.5	42.5
Fe_2O_3	2.2	2.3	2.2	5.3	2.0
MgO	0.7	1.0	1.0	0.3	0.3
CaO	0.2	0.1	0.1	0.1	0.2
TiO_2	1.5	1.5	1.5	1.1	1.1
Na_2O	0.0	0.1	0.2	0.1	0.0
K_2O	2.2	2.1	2.2	0.6	1.0
LOI	4.3	2.7	3.2	4.7	1.3
$SiO_2 + Al_2O_3$ (%)	88.6	89.8	89.1	87.1	94.0
Al/Si ratio	0.57	0.70	0.74	0.83	0.83

3.2 FTIR and RPD Analyzes

Figure 3 presents the metakaolin spectra, indicating significant differences in the region between 3620 and 3690 cm^{-1}, corresponding to hydroxyl groups inner layers typical of kaolinites. M0 and M3, in qualitative analysis, show larger peaks and, therefore, more traces of the well-ordered structure of kaolinites. M1 and M2 present peaks of lesser intensity and M4 did not produce evident peaks, which suggests that the dehydroxylation to which it was submitted (M4) was the most efficient among all the metakaolins.

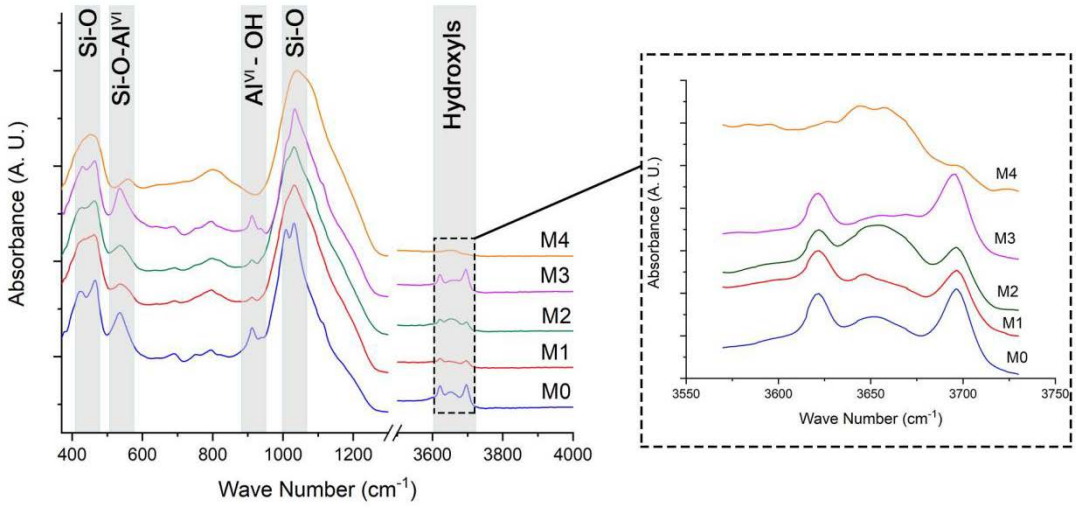

Figure 3. FTIR results.

The bands close to 1100 cm^{-1} correspond to regions of Si-O-Si vibration in the stretching plane. Close to this region, at 910 cm^{-1}, the presence of an OH group linked to iron or aluminum is indicated with more evidence for M0 and M3. In this region are concentrated the indications of Al_2OH coming from the inner layers of kaolinites.

The presence of Si-O-Al^{VI} bonds (octahedral position) is evidenced in the 560 cm^{-1} wave vibration region. The vibration of Si-O (tetrahedral SiO_4) is presented close to 470 cm^{-1}.

In the main regions of vibration of the bonds in the spectra, M0 and M3 are highlighted as the metakaolins that contain the greatest evidence of the presence of the raw material kaolinite (result previously indicated in the amorphization content – Table 1). The RPD results reinforce the result of less efficient dehydroxylation in these mineral additions (Table 5) and help in the quantitative interpretation of the FTIR spectra. The most prominent peaks related to hydroxyl groups (~3620 to 3690 cm^{-1} - characteristic of well-ordered kaolinite) are present in metakaolins M0 and M3; in the sequence, the peaks of M1 and M2 are highlighted. M4 does not have marked peaks in this region but has an RPD identical to M2.

Table 5. Results of the RPD analysis - Residual Potential of Dehydroxylation.

	M0	**M1**	**M2**	**M3**	**M4**
Mass loss between 250 and 700°C (%) [kaolin dehydroxylation]	3.4	2.1	1.6	3.0	1.6
RPD (%)	25	15	12	22	12

3.3 Metakaolin Efficiency – Correlations

The results presented in the previous topics help in the qualification of metakaolins, since they contribute with information about the chemical composition, mineralogical constitution, degree of purity, and formed reactive phases. The occurrence of chemical and mineralogical impurities, and the evaluation of the degree of dehydroxylation that originated the material's amorphization and reactivity, provide important information regarding the potential performance of these mineral additions as pozzolans in cementitious systems.

The performance of metakaolin as a pozzolanic addition and its efficiency in physical-chemical terms in concrete (with a view to durability) are linked to the intensity of its pozzolanic activity (in addition to its performance as a microfiller). The modified Chapèlle test quantifies the pozzolanic action by the consumption of calcium hydroxide during the test.

In order to understand the relationship between the results of pozzolanic activity (Table 1) and the physical-chemical and mineralogical characteristics, the correlations between the main characteristics of metakaolins are discussed below.

Figure 4 exemplifies the correlation between BET specific surface area and pozzolanic activity. The presented correlation demonstrates that the specific surface area alone is not able to explain the pozzolanic activity, but it is a favorable factor for higher levels of pozzolanic activity, as highlighted by Mitrović and Zdujić (2014), and Siline and Mehsas (2022).

Figure 5 summarizes the other Pearson correlation coefficients (R) and indicates whether the correlation is linear positive or negative (directly or inversely proportional).

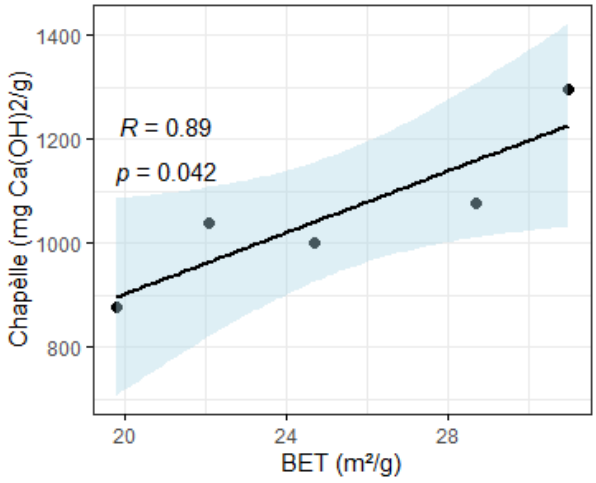

Figure 4. Correlation between Chapèlle and BET tests.

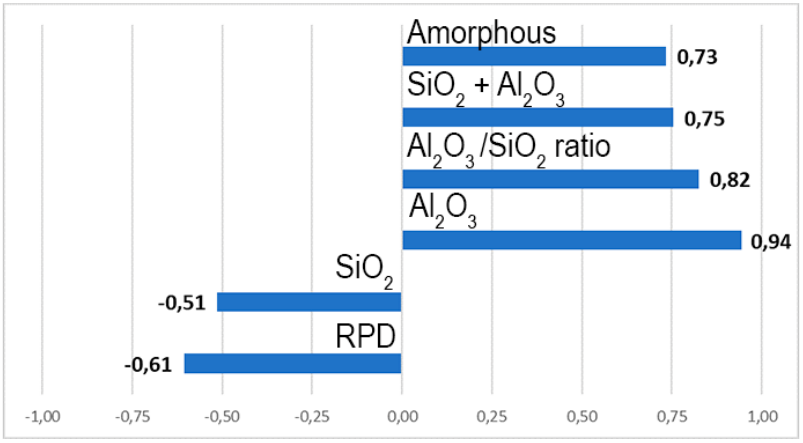

Figure 5. Pearson correlation coefficients (R) – Metakaolin characteristics versus Chapèlle.

The chemical composition influences the reactivity of the pozzolanic mineral additions, which is mainly shown by the R coefficient of Al_2O_3 (%). However, the R coefficient shows a negative correlation between SiO_2 (%) and pozzolanic activity. The chemical composition data does not consider the crystallinity/amorphism, that is, the amount of quartz or amorphous silica in the sample. Therefore, a more coherent analysis should be guided by the joint analysis of the Al_2O_3/SiO_2 ratio, which manages to capture the balance between silica and alumina in metakaolins, explaining that an excess of SiO_2 may be related to the non-reactive crystalline phase.

The sum of SiO_2 and Al_2O_3 (parameter $SiO_2+Al_2O_3$) indicates the degree of purity of the samples since these are the major chemical compounds of kaolinite. At the same time, this indicator partially takes into account the amorphous content, since its determination accounts for amorphous and crystalline phases involving silica and alumina. As it captures the degree of purity and, in part, the amorphous, this parameter proved to be interesting to express the reactivity of metakaolins (given its relationship with Chapèlle).

The Residual Potential of Dehydroxylation (RPD) has a negative R correlation coefficient.

This happens because the presence of kaolinite that has not yet been dehydroxylated (not amorphized) implies lower reactivity of metakaolins.

4 Conclusions

As the main results, it was found that the BET specific surface area and the Al_2O_3 content, obtained by XRF, better explain the pozzolanic activity of metakaolins (Pearson correlation coefficients equal to 0.89 and 0.94, respectively). In a systemic analysis, it is concluded that the chemical-mineralogical characteristics that indicate purity and amorphism of metakaolin, expressed by the Al_2O_3 content, Al_2O_3/SiO_2 ratio, $SiO_2+Al_2O_3$ sum, and amorphous content, represent important performance parameters of metakaolins. At the same time, the increase in the specific surface area (obtained by the milling process) acts to compensate for the lower chemical reactivity of metakaolin, exerting a significant influence on the pozzolanic activity.

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