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# Influence of the levels of replacement of portland cement by metakaolin and silica extracted from rice husk ash in the physical and mechanical characteristics of cement pastes

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## ABSTRACT

The present research aimed to study the replacement of ordinary Portland cement (OPC) by metakaolin (MKL) and silica extracted from rice husk ashes (SRHA) in binary mixtures. To investigate the pozzolanic reactivity, thermal and microstructural analyses were performed in binary mixtures. To understand the physical effect of these blends, the packaging density was calculated according to the model of compressible packaging (MCP) and the compatibility/saturation levels of superplasticizers was studied with cementitious materials. Considering the substitution levels adopted, the results indicated that the paste with 40% of MKL provided a total consumption of calcium hydroxide to 28 days; however, the packaging density of the particles was reduced, while the compressive strength was maintained. The addition of 16% of SRHA in binary mixtures showed partial consumption of calcium hydroxide; nevertheless, this effect, together with the physical effect, led to an increase in the compressive strength for the same age.

## 1. Introduction

In the past few years, many investigators have proposed solutions to mitigate the negative environmental impacts of the Portland cement industry, where consumption of this material is estimated to be among the highest in the world [1–3]. A range of technical options can be adopted with a view to reduce the environmental damage; one of the prominent options is the partial replacement of cement by pozzolanic materials, which typically are (a) materials that require lesser thermal and electrical energy during manufacture as compared to cement, or (b) waste. The most commonly investigated low-energy-consuming materials are calcined clay; blast furnace slag; fly ash; silica fume; rice husk ash; sugarcane bagasse ash; rock-cutting waste; ceramic blocks ground; ceramic wastes; and, most recently, silica from rice husk ashes (SRHA) [4–11]. The use of these alternative materials in cementitious matrix allows for the reduction of the consumption of cement and consequently the cost of the final product; in addition, it also alleviates the environmental problems related to the final disposal of waste as well as provides maintains or improves the mechanical properties of modified cementitious products.

Studies on the addition of metakaolin (MKL) from calcined clay [5,8,12,13], rice husk ash (RHA) [10,14,15], and silica from rice husk ashes (SRHA) [11] show that the use of these materials produces reactions in cementitious systems, which are usually associated with physical and chemical effects that improves the mechanical properties of the composite. The physical effect is related to the particle packaging and depends on the size, shape, texture of the grain, replacement of the cement content, and initial porosity of the mixture [14,16,17]. This effect leads to filling of the empty spaces of the matrix, making it more compact and, therefore, more strength. On the other hand, there are the pozzolanic effects, which are related to the ability of the cement to react chemically with calcium hydroxide ($Ca(OH)_2$ or CH) in the presence of water, forming compounds that have cementitious properties. The main reactive phases of pozzolana are silica ($SiO_2$) and alumina ($Al_2O_3$) amorphous, which form the hydration products calcium silicate hydrated ($CaO-SiO_2-H_2O$ or C−S−H, designated by the chemical notation of cement), calcium aluminate hydrate ($CaO-Al_2O_3-H_2O$ or C−A−H), and calcium aluminum silicate hydrate ($CaO-Al_2O_3-SiO_2-H_2O$ or C−A−S−H) [15,18]. Thus, there is an increase in the compressive strength of cement-based materials by transformation of CH in most resistant compounds and by refinement of its pores, where such effects are observed after some days until several months,

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depending on the amount and the solubility of silica/amorphous alumina into material [19].

In this context, the present work was aimed at studying the partial replacement of cement by two pozzolana: metakaolin (MKL), obtained from the calcination of kaolinite clay, and silica extracted from rice husk ashes (SRHA).

MKL is one of the most important materials with high pozzolanic reaction [20] since it is a siliceous material that is finely ground in the presence of water and reacts chemically with calcium hydroxide to form cementitious compounds [21]. Clay deposits contain a mixture of different clay minerals (kaolinite, illite, montmorillonite, and others); those containing kaolinite and some with montmorillonites have pozzolanic reactivity, while the rest can be considered of low reactivity [22]. The main source of MKL is kaolin, with kaolinite as the main constituent element, which is a hydrated aluminum silicate with composition $2H_2O{\cdot}Al_2O_2{\cdot}2SiO_2$. It is structurally composed of alumina octahedral sheets and silica tetrahedral sheets stacked alternately with the theoretical composition of 46.54% $SiO_2$, 39.5% $Al_2O_3$ and 13.96% $H_2O$ [20,21]. The kaolin under normal environmental conditions is stable; however, when heated to 650 °C–900 °C temperature (calcination), it losses 14% of its mass and there is a breakdown of structure such that the alumina and silica layers become wrinkled and disorganized, resulting in the formation of MKL, an amorphous material with pozzolanic reactivity [20,21]. Although one of the main sources of MKL kaolin, it can also be obtained by the calcination of lateritic soils [21]. Therefore, the properties of calcined clays depend on the nature and abundance of clay minerals in the raw material, the conditions of calcination, and the fineness of the finished product [21]. In this way, the Amazon region distinguishes itself by virtue of its thick layer of clay soils, including deposits with the potential for the production of MKL.

Although MKL is known as an environment-friendly option for pozzolanic materials, SRHA provides the additional environmental and economic advantages of low temperatures for extraction, and the associated low energy consumption for production.

In this sense, research has shown that with the application of the appropriate extraction process, RHA (containing silicon dioxide ($SiO_2$) between 80% and 90%) yields significant amount of amorphous silica (above 90%), which is slightly higher than that found in residual ashes [11,23,24]. This is because of the chemical reactions triggered by the application of the hydrothermal extraction method [11,23,25], which results in the production of greater quantities of amorphous silica as compared to other methods. The hydrothermal method involves the extraction of silica in the form of sodium silicate, which is homogenized with an acid and converted to silica in the gel form [11,23,25]. In this study, we used dried and ground silica gel, which is technically called xerogel [11]. Lima et al. [11] obtained silica gel at high purity levels and amorphous structure and applied it in cementitious pastes. They analyzed the products for 28 days and showed that the use of silica gel resulted in the consumption to almost 60% of CH and a significant increase in the compressive strength of pastes with partial replacement of 5% for ordinary Portland cement (OPC).

In addition, research in the field of microstructure engineering has shown that composites consisting of fine particles ($d \leq 100\,\mu m$) and a low water/binder ratio feature dense matrices obtained from granular materials, which allows for packaging optimization [16,19] and adequate workability is by means of particle dispersion promoted by the addition of chemical additives to the mixture [16,19]. Thus, obtaining cementitious mixtures with adequate workability (fresh state) and high mechanical strength and durability (hardened state) is possible with the utilization of superplasticizers additives (dispersants) and mineral additions [19]. In this study, we sought to investigate the potential of pozzolana as a replacement to Portland cement; the use of appropriate dispersant and better dosage of saturation may provide several cementitious arrangements, which include considerable water reduction, resulting in mixtures with higher packaging density. Thus, two binary mixtures containing MKL and SRHA as partial cement replacements in addition to the reference paste (without replacement) were manufactured. The chosen replacement levels were 20%, 30%, 40%, and 50% for MKL and 10%, 13% and 16% for SRHA. Scanning electron microscopy (SEM) and thermal analysis (TG/DTG) were used to investigate the hydration reactions and the pozzolanic activity of the materials. The study of compatibility of cement was conducted with five types of dispersants and the ones with the lowest additive consumption were identified. The individual packaging density of raw materials and of the binary mixtures was determined according to the model of compressible packaging developed by De Larrard [26].

## 2. Materials and methods

### 2.1. Materials

Alternative raw materials used in this work were clay and RHA in the production of MKL and amorphous silica ($SiO_2$), respectively. MKL was collected at the deposit located in the municipality of Itacoatiara, Amazon State, Brazil (3° 1 ′ 47 “S; 58° 32 ′ 37″W). This choice was made on the basis of a previous study [27] showed that the clay from this deposit was suitable for obtaining MKL when calcined for 2 h at 700 °C. The burning conditions adopted for the calcined clays as well as their physical and chemical characteristics directly influence pozzolanic activity [21], with temperature ranges that allow dehydroxylation of kaolinite and transformation to MKL between 550 °C and 900°C[22]. RHA was supplied by a processing industry located in Jaguará do Sul, Santa Catarina, Brazil. The waste was reduced by using a rotary ball mill for 60 min, in order to improve the process of extraction of silica. The materials used in the extraction of silica from RHA were water and chemical reagents: hydrochloric acid (HCl) to 37% and sodium hydroxide (NaOH). For the production of cementitious pastes, OPC was used without mineral addition, similar to type I (ASTM) [28], in addition to MKL, silica from the ashes; water; and a polycarboxylic ether-based superplasticizer additive, Glenium® 51 (aqueous solution with 31.13% solids). Before the testing with Glenium® 51, a study was conducted with two types of dispersants, namely, Muraplast FK 32 and Tec Flow 9030 to evaluate their compatibility with cement and the best dosage of saturation.

### 2.2. Production and characterization of metakaolin

The diagram in Fig. 1 shows the production procedure of MKL, where after the collection, the clay was subjected to natural drying (minimum 7 days); then, the sample was homogenized and the reduction in turf was performed in extruder with posterior refinement using a porcelain capsule and pistil. Mechanical sieving was performed (# 200 mesh), the dry material in oven at 100 °C for 24 h (aiming at reducing the moisture gained in the process before calcination). After calcination, the material was placed for 2 h in a muffle oven Q318M Quimis® maintained at 700 °C (temperature of calcination), followed by 12 h cooling.

The X-ray diffraction (XRD) of the samples of raw and calcined clay at 700 °C were obtained using X'PERT PRO MPD diffractometer (PW 3040/60), with Cu—K-Alpha tube (1.5406 Å), between 5° and 60° (2θ) at goniometer speed of 0.02°/step and counting time of 50 s. The minerals were identified by comparing the diffractograms maintained in the database of International Center Diffraction Data-Powder Diffraction Data (ICDD-PDF).

The characterization of MKL was performed as followed. Particle size distribution was obtained through the Mastersizer 2000 laser analyzer (Malvern Instruments), with deionized water as a dispersant; composition was expressed in oxides by X-ray fluorescence spectroscopy (EDX-720 Shimadzu). Specific mass was determined using the gas pycnometer (AccuPyc 1340 Micromeritics). Thermal analysis (TG/DTG) was conducted using SDT Q600 TA Instruments (whose fire loss was obtained by mass loss curve (TG) at 950 °C), while SEM was