Evaluation of the potential incorporation of titanium dioxide nanoparticles into porous geopolymeric preliminary matrices for CO_2 capture

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Abstract

The development of carbon dioxide (CO_2) capture technologies has been intensifying due to the need to change the scenario of excessive greenhouse gas emissions caused by human activities. Inside the construction industry, binder materials have been modified to achieve this goal. Among the materials being studied and evaluated for their contribution to this issue are microporous aluminosilicate-based materials. This study aims to evaluate the effect of adding titanium dioxide nanoparticles on the potential CO_2 adsorption process of geopolymeric matrices. Mixtures were prepared using commercial metakaolin and granulated blast furnace slag as precursor materials, activated by an alkaline activating solution. Hydrogen peroxide, mineral oil, and nano-TiO_2 were used as additives. The results showed that the added nanoparticles did not promote any effect on accelerating CO_2 adsorption through carbonate formation. However, they contributed to a reduction in compressive strength due to the formation of pores on a different scale from those produced by hydrogen peroxide.

Keywords: Geopolymer; Porosity; Nano-TiO_2; CO_2 capture.

1 Introduction

Brazil has committed to reducing national CO_2 emissions by 50% by the year 2030 [1]. One of the key strategies to achieve this reduction, which is also a target of several other countries, is the capture and storage of CO_2, an interesting tool for mitigating environmental impacts in the long term [2].

Geopolymers have emerged in the construction industry as an alternative binder to conventional Portland cement, offering materials that emit fewer greenhouse gases during production and incorporate industrial waste as raw materials [3]. Although the cement industry has adopted sustainable practices to reduce carbon emissions in recent years, it still releases large amounts of CO_2 into the atmosphere and consumes significant energy during production [4]. In this context, alkali-activated materials offer the potential to replace Portland cement due to their comparable mechanical properties, representing a more sustainable alternative for the construction sector [5].

CO_2 capture based on physical or chemical adsorption processes has been the subject of several studies in the field of cementitious materials. In these systems, capture occurs through cement carbonation reactions, which involve a dissolution/precipitation process that generates carbonate-based products and silica gel [6]. However, these reactions can also promote a detrimental effect on cementitious matrices. The formation of carbonates leads to system acidification (evidenced by a reduction in pH), creating an environment conducive to the formation of corrosive oxides in the reinforcing steel. Additionally, when formed in high proportions, carbonates can inhibit the formation of new calcium silicate hydrate (C-S-H) and, through interaction with iron oxides, indirectly promote the formation of microcracks [7,8].

Consequently, the use of low-CaO geopolymers as cementitious materials serves as an alternative to mitigate the formation of these detrimental carbonates. Unlike the $CaCO_3$ formed in Portland cement matrices, geopolymer carbonation typically results in Na_2CO_3. This compound is highly soluble, and its impact on the passivation of reinforcement may be less severe than in cementitious matrices due to the resilience of the system's high alkalinity, provided that $Ca(OH)_2$ is available and there is little leaching of Na^+ species [9]. The application of geopolymers under these conditions also involves a transformation of reaction products, leading to the formation of crystalline structures with controlled porosity and high surface area, which facilitates adsorption. For this reason,

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they are often referred to as zeolite precursors [10,11], if certain hydrothermal conditions are altered. Although their efficiency for adsorption process can be reduced when compared to pure zeolites.

In this context, the incorporation of titanium dioxide nanoparticles (nano-TiO_2) into geopolymers has become a major research focus. This approach has proven effective in enhancing the adsorption capacity for organic and inorganic pollutants in conventional matrices, as demonstrated in studies reported in the literature [12,13]. Several materials have been studied and evaluated for their contribution to this field, particularly ceramic-based materials featuring a microporous network [14]. Would it be possible to observe its effect at lower CO_2 concentrations in post-combustion situations?

This research investigates the potential for CO_2 capture capacity at low concentration, through mineralization, of porous geopolymeric matrices with different porous structures, and comparing if the nano-TiO_2 addition on matrices promote acceleration of its mineralization through the formation of carbonate phases, utilizing a predetermined percentage that does not compromise the system's fluidity or mechanical strength. These systems were evaluated using one or two precursors, an activating solution based on sodium silicate and sodium hydroxide, and foaming agents that induce the formation of stable pores.

2 Materials and methods

Metakaolin (MK) and Ground Granulated Blast Furnace Slag (GBFS) were used as precursors. Both exhibit high reactivity for geopolymerization; their chemical compositions are summarized in Table 1.

An alkaline activator solution (AS) was prepared using sodium hydroxide and sodium silicate in a 0.074:1 ratio. According to results obtained in preliminary tests, the foaming agent used to produce stable pores was hydrogen peroxide (H_2O_2), in combination with mineral oil. The use of mineral oil justified by its potential to refine the size distribution of the pores produced by H_2O_2. The effect of H_2O_2 in systems containing only MK resulted in porous with high diameter, against to systems with GBFS, just H_2O_2 did not promote significative macropores [15].

Six different formulations were developed and divided into two main groups: one group based exclusively on metakaolin and the others groups containing blast furnace slag as a partial substitute for metakaolin, were detailed in Table 2. For the titanium dioxide-enhanced groups, nano-TiO_2 particles were added at a dosage of 4% by mass of the precursor, based on recommendations for cementitious materials [12,16]. According to the published literature, additional dosages of nano-TiO_2 beyond 4% can cause unsuitable dispersion and reduce the porosity.

For the manufacturing of the pastes, the foaming agents were added to the activator solution (with or without nano-TiO_2) and dispersed using a portable mini-mixer. After this step, the solution was mixed with the dry precursors.

In fresh-state was evaluated the spread using the mini-slump test. In this procedure, the paste in was emptied into a truncated cone mold (upper diameter -19 mm, lower diameter - 38 mm, height -57 mm) positioned on a flat surface, and after filled the cone was removed and made two measurement about the diameter spread for each sample.

The specimens were then cast into cylinders (average dimensions: 24 mm for diameter × 27 mm height) and discs (20 ± 2 mm thickness). The specimens were kept in the molds for up to 14 days, after which they were demolded and placed in an environment similar to a wood-fired setting (used as fuel in a kiln for firing ceramic pieces). Exposure occurred for 4 hours per day over 5 non-consecutive days.

This type of exposure was chosen due to the increased CO_2 levels in the environment and as an exposure environment where the CO_2 capture process could potentially occur,

Table 1. Chemical composition of precursors

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Others
MK (wt%)	59.10	36.38	2.13	0.84	1.50	0.09	0.04
GBFS (wt%)	39.23	6.70	0.48	41.56	6.30	3.03	2.71

Table 2. Proportions between components

Group	MK (g)	GBFS (g)	AS (g)	H_2O_2 (ml)	Oil (ml)	Nano-TiO_2 (g)
MK	160	-	200	-	-	-
MK-H_2O_2	160	-		2	1	-
MK-H_2O_2+TiO_2	160	-		2	1	6.4
MK+GBFS	128	32		-	-	-
MK+GBFS-H_2O_2	128	32		2	-	-
MK+GBFS-H_2O_2+TiO_2	128	32		2	-	6.4

with concentrations estimated using a CO_2 meter reaching 1550 ppm-1800ppm. Under normal conditions, the recorded level was 400-550 ppm.

Following this exposure (38 days after fabrication), compressive strength tests were performed (using an Instron 3400 at a loading rate of 0.25 mm/min), along with mineralogical composition analysis via X-ray diffraction (XRD) (The AXRD Benchtop). Four specimens from each group were tested for compressive strength. Following the tests, the crushed material from these specimens was ground into a fine powder for XRD analysis.

3 Results and discussion

The first test performed in the fresh state was the workability evaluation via mini-slump test. The measured diameters are listed in Table 3.

Based on the test results, there is a tendency for nano-TiO_2 to reduce the material's fluidity exclusively in a system containing only MK. A system containing GBFS, however, appears to be less susceptible to changes due to the presence of nano-TiO_2.

The appearance of the specimens was recorded after demolding and before exposure, as shown in Figure 1. Pore formation in the systems containing H_2O_2 is evident, as well as the effect of adding nano-TiO_2, which causes a distinct variation in the matrix's color.

Additionally, the surface morphology of the discs subjected to exposure was analyzed using a digital optical microscope, as shown in Figure 2. Initial observations indicate soot deposition on the surfaces directly exposed to the firing process (Figures 2a,c,e,g,i, and k). Conversely, whitish stains are noticeable on the opposite surfaces of certain groups (Figures 2b, d, f, j, and l). Pore sizes were also affected by the presence of nano-TiO_2, and their homogeneity varied across the surfaces.

When compared with other systems designed to capture pollutant compounds, the pore sizes are larger than those reported by other authors [17,18]. However, under these conditions, the pronounced effect of the incorporated additives can be evaluated: H_2O_2 produces spherical pores ranging from 0.4 to 1.1 mm in the MK-based groups, while in the MK+GBFS-based groups their pore size did not exceed 0.8 mm. These pores are not uniformly distributed throughout the specimen, showing a buoyancy-driven migration from the base to the top of the sample (Figure 1). These porous are smaller at the base and range from medium to large from the center to the top, likely due to coalescence. Pore rupture at this stage may result in irregular edges, as seen in Figure 2d.

This migration phenomenon is normal due to the paste density and the pressure differential that, according to Zhang et al. [19], exists along a specimen, which is usually relatively slender and therefore records differential moments throughout its structure. In the discs, however, there is an abrupt transition between the distribution of small and large pores, mainly due to the thickness of the discs. These pores, defined as entrapped air, are unstable elements that tend to reach equilibrium (surface tension). If not restricted by the stiffening of the material, this instability leads to collapse at the surface [20].

Finally, the addition of nano-TiO_2 caused pore significative deformation in the MK-based groups, while

Table 3. Mini-slump test result

Group	Average diameter (mm)
MK	119.0 (± 0.3)
MK-H_2O_2	110.1 (± 2.0)
MK-H_2O_2+TiO_2	86.4 (± 1.0)
MK+GBFS	115.4 (± 1.0)
MK+GBFS-H_2O_2	116.0 (± 2.2)
MK+GBFS-H_2O_2+TiO_2	114.0 (± 2.3)

Figure 1. Specimens after demolding. (a) MK-based group; (b) MK+GBFS-based group.

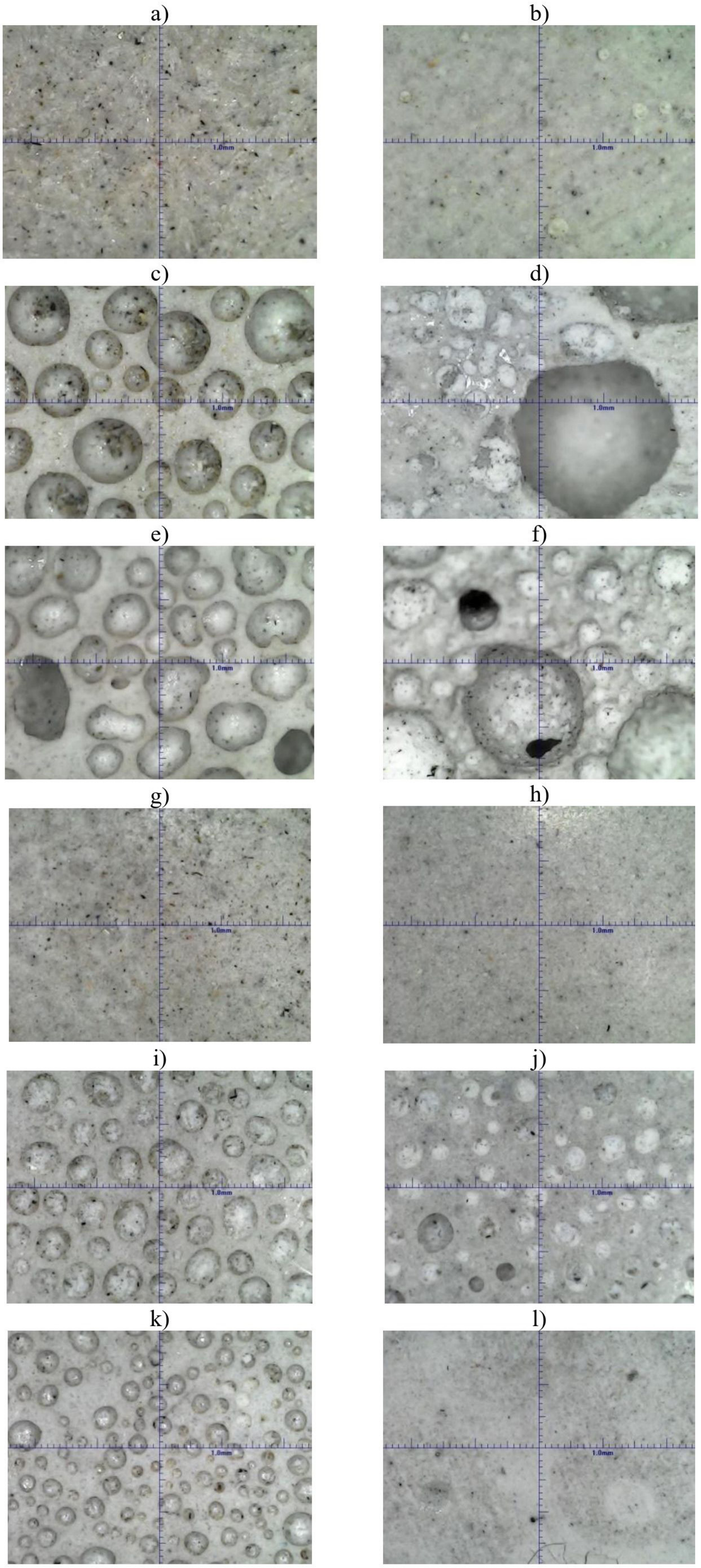

Figure 2. Disks Surface of the samples after exposure on both sides: (a) and (b) MK; (c) and (d) MK-H_2O_2, (e) and (f) MK-H_2O_2+TiO_2; (g) and (h) MK+GBFS; (i) and (j) MK+GBFS-H_2O_2 and, (k) and (l) MK+GBFS-H_2O_2+TiO_2.

in the MK+GBFS-based groups, it resulted in the formation of smaller pores, up to 0.6 mm. Leading even to register one of the faces of the discs without significant presence of pores (Figure 2). Fajardo et al. [21] explained that the interaction between H_2O_2 and the nanoparticle surface leads to the creation of multiple nucleation sites for air bubbles, as a consequence of hydrolysis on the surface of nano-TiO_2 that forms Ti-OOH or Ti-O-Ti, titanium peroxo complexes, which alter the kinetics of air bubble generation and, consequently, the number and size of the pores. The presence of mineral oil could block this effect on MK systems. There is not precedent for this phenomenon discussed by [21] in presence of oil.

Compressive strength tests were performed for all groups 38 days after molding. The results are shown in Figure 3. In MK-only mixtures, the additions caused a progressive decrease in strength. The use of hydrogen peroxide proved effective in forming pores, which leads to a reduction in paste density and, consequently, in strength [22]. In the MK-H_2O_2+TiO_2 mixture, compared to the MK-H_2O_2 mixture, there was an approximate 94% decrease in strength due to the addition of nano-TiO_2 particles, which is consistent with the visual appearance of the specimens shown in Figure 1, indicating a greater presence of pores. This reduction may be justified by the formation of a larger volume of pores due to the interaction between nano-TiO_2 and H_2O_2. It is possible that pores of smaller diameters were formed and interconnected within the matrix [23].

The mixtures containing a MK+GBFS-base showed better mechanical performance under the effect of the additions. When analyzing samples from the MK+GBFS-H_2O_2 group after fracture, it was observed that the pore formation occurred only in the outer surface layer as closed pores (lacking internal continuity), which did not compromise mechanical strength.

XRD analysis results are presented in Figure 4. In the MK-based groups, characteristic formations of geopolymerization reactions are observed, with an amorphous halo between approximately 20° and 35° [22]. This feature was also observed in the other groups, along with the presence of calcite, characteristic of GBFS [24], and anatase, one of the mineral forms of titanium dioxide.

The absence of significant carbonate formation indicates that, for this exposure time, no CO_2 mineralization process occurred, even with the incorporation of TiO_2 nanoparticles. In cementitious composites, besides the material characteristics, exposure conditions are an influential factor in the carbonation process [25]. To obtain more meaningful results, it is necessary to evaluate the behavior of the materials under longer exposure times and, if possible, under controlled conditions like humidity and temperature.

4 Conclusions

The results demonstrate that the incorporation of titanium dioxide (TiO_2) nanoparticles into these geopolymer matrices did not promote the acceleration of carbonate phases formation. Furthermore, the addition of these nanoparticles led to a decrease in compressive strength in the metakaolin-only system, as it promoted higher porosity within the matrix — a phenomenon attributed to the combined effect between TiO_2 and hydrogen peroxide. Future studies

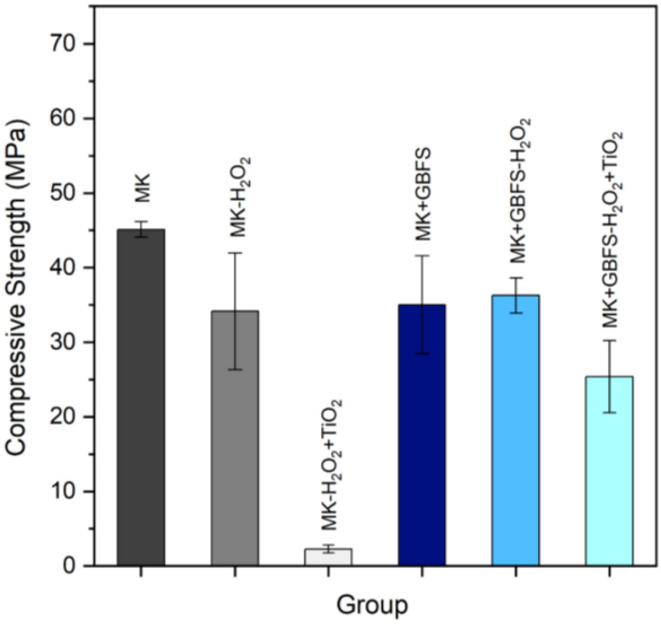

Figure 3. Compressive strength results.

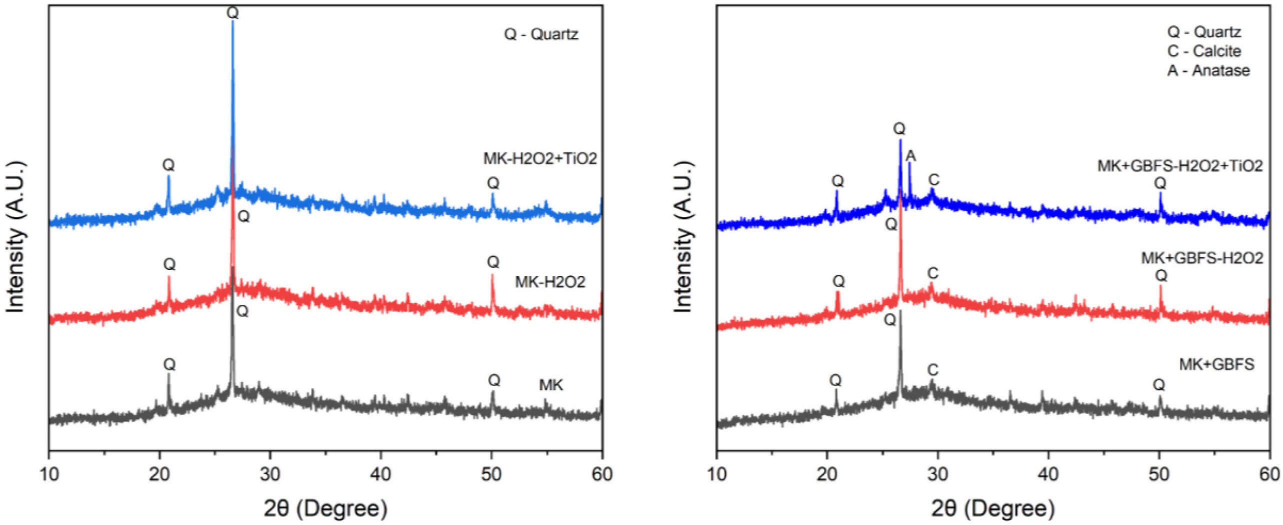

Figure 4. X-ray diffraction patterns of the manufactured matrices. MK-based group (right), MK+GBFS-based group (left).

should evaluate the effects of these additions under varying exposure durations and environmental conditions to provide a more comprehensive assessment, as well additional experiments to ensure the presence of carbonate phases with greater precision. Additionally, further research should focus on optimizing pore size distribution to facilitate sustained interaction between CO_2 and the internal components of the geopolymeric matrices.

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