Influence of Titanium Dioxide Photocatalytic Residue Incorporation on Fresh State Properties of Cement-Based Materials

Emilly Pereira Sá Teles[1*], Marianna Luna Sousa Rivetti[2], Paulo Roberto Lopes Lima[3], Pedro Manoel Moreira Novaes Santos[4]
[1] *State University of Feira de Santana, Department of Technology, Feira de Santana, Bahia, Brazil*
[2] *SENAI CIMATEC University Center, Salvador, Bahia, Brazil*
[3] *State University of Feira de Santana, Department of Technology, Feira de Santana, Bahia, Brazil*
[4] *Grupo Civil, Simões Filho, Bahia, Brazil*
**State University of Feira de Santana, Department of Technology, Feira de Santana - BA, 44036-900, Brazil; emilly_sateles@outlook.com*

Abstract: Nowadays, due to high levels of emission of polluting gases such as carbon dioxide (CO_2), it is very common in the construction industry to search for sustainable alternatives that contribute to the reduction of environmental impacts. Therefore, the incorporation of photocatalytic residues, such as titanium dioxide (TiO_2), has shown to be a valuable ally in this approach, since it is known for its photocatalytic properties, which contribute to the degradation of atmospheric pollutants and to the improvement of concrete durability. This study aims to analyze the behavior of the insertion of different contents of photocatalytic residue in cement pastes and evaluation of its impact on fresh state properties, especially investigating an optimal dosage that balances workability and environmental sustainability. This work represents only a first step, though an essential one, toward more comprehensive studies that consider the photocatalytic properties of TiO_2 and its potential to contribute to environmentally responsible solutions in civil construction. In this regard, different contents of titanium dioxide were incorporated in cementitious matrices (10%, 15%, and 20%) with a constant water-to-cement ratio of 0.5 to analyze the influence of the residue on fresh state properties of cement-based materials. The experimental methodology involved the preparation of cement paste samples using Portland Cement V-ARI RS, with standardized mixing procedures, aiming to ensure homogeneous TiO_2 dispersion and optimize the results of the experiments. In addition, the proposal also aims to understand the performance and evolution of the paste strength over time, as well as to evaluate the effects of TiO_2 incorporation focusing on paste workability. The analyses were conducted through mini-slump and setting time tests. The study reinforces the potential of TiO_2 potential as a sustainable additive, especially when properly dosed and incorporated.

Keywords: Titanium dioxide. Photocatalytic properties. Cement paste. Fresh-state properties.

Abbreviations:
CO_2, Carbon dioxide.
TiO_2, Titanium dioxide.

1. Introduction

The current problematic of environmental impacts caused by human activities is historical. Since the Industrial Revolution, with the advancement of industrial and technological practices, there has been an aggravation of problems related to the environment, whether due to the generation of solid waste or the emission of polluting gases [1].

Furthermore, in addition to the emission of carbon dioxide resulting from human activities, the release of other atmospheric pollutants, such as nitrogen oxides (NOx), is also emphasized, being considered hundreds of times more harmful than CO_2, for example. In this context, the heterogeneous photocatalytic activity of titanium dioxide is capable of acting in the degradation of these pollutants and other organic compounds, causing a decrease in the concentration of these gases in the environment. In this sense, the ability to "break down" organic molecules adsorbed on its surface gives this residue the property of self-cleaning [2].

Thus, there is an urgent need for combinations in cement-based-materials that can contribute to sustainability. A good example of this is the incorporation of titanium dioxide residues in cement pastes, mainly because of their effective catalytic properties in photocatalytic degradation processes. Its application, through heterogeneous photocatalysis, in which TiO_2 acts as a solid semiconductor, either in powder or film form, proves efficient in the decomposition of organic compounds. Moreover, studies indicate that photocatalysis is not especially effective in breaking down large amounts of dirt or organic matter, such as on already deteriorated surfaces. However, it is capable of preventing the accumulation of these substances when applied to new coatings, promoting the decomposition of organic particles or polluting gases upon contact with the surface [3-4].

Furthermore, according to studies, the incorporation of photocatalytic residues can help increase concrete strength. However, when used at high contents, mechanical strength may be compromised due to the agglomeration of photocatalytic particles, leading to non-uniform distribution in the cementitious matrix [5-6].

Additionally, the method of incorporating photocatalytic residues into cement-based-materials can affect both mechanical strength and fresh-state properties, especially when improperly incorporated. Thus, the correct handling and incorporation of the residue are crucial to obtain good responses, concerning strength and workability, providing long term structural performance in residences or buildings [7].

Given the critical importance of proper incorporation methods and the need to understand their impact on material performance, this work will focus on studying analytical experiments to evaluate the incorporation process impacts on fresh state properties, aiming to prove how characterization methods can provide valuable knowledge about how photocatalytic residues interact with the cement matrix and how photocatalytic residues affect fresh concrete behavior.

The evaluation of properties in the fresh state is essential to consolidate the use of this cement paste, in order to guarantee that the cement-based material meets required performance standards in civil construction [7].

Thereby, the cement paste characterization will be done in the fresh state, by analyzing the behavior of the materials with or without the residue incorporated in both stages, evaluating the impacts that the incorporation of the residue may cause in the pastes, specifically to understand its effect on their workability [8-9].

Hence, the work aims to evaluate the properties of the mixtures in the fresh state, analyzing consistency through mini-slump and setting time.

2. Experimental Methodology

The experimental procedure was developed in the following stages: materials characterization, formulation of mixtures and analysis of concrete in its fresh state. For this, mixtures produced with Portland Cement V-ARI RS were developed. An industrial residue from pigment production, rich in titanium dioxide, in powder form with irregular granulometry (Figure 1), was incorporated, used without grinding to simulate real industrial environmental conditions.

The materials used in the mixtures included: Portland Cement V-ARI RS, potable water and the photocatalytic residue. No chemical additives were added, aiming to analyze the isolated effect of the residue on the concrete behavior in the fresh state.

For each mixture, the components were weighed on precision scales, and the mixing procedure followed standard procedures. Initially, the cement was mixed with the residue, followed by gradual addition of water. The mixing was performed in a standardized mixer in order to guarantee the homogeneity of the material.

All tests were performed at ambient laboratory temperature, and each measurement was carried out precisely, following the standard procedures specified in the respective norms.

Figure 1. Photocatalytic titanium dioxide residue used in the mixtures.

Residue contents of 10%, 15%, and 20% were incorporated into the pastes, maintaining a constant water-to-cement ratio of 0.5, to evaluate their influence on cement paste consistency.

The mix proportions were designated as CREF, C10, C15, and C20, respectively for 0%, 10%, 15%, and 20% of incorporated residue present in the mixture, as presented in Table 7. This nomenclature will be adopted in all subsequent figures and tables to refer to each cement paste proportion.

Table 1. Mix proportions and nomenclature used in the study.

Nomenclature	Mix proportions
CREF	Reference paste (without titanium dioxide residue)
C10	Paste with 10% incorporated titanium dioxide residue
C5	Paste with 15% incorporated titanium dioxide residue
C20	Paste with 20% incorporated titanium dioxide residue

Thus, setting time tests were conducted on both residue-incorporated and non-incorporated pastes to evaluate the impact of residue incorporation on the hardening of the pastes.

Moreover, mini-slump tests were performed to analyze the influence of the residue on the fluidity and workability of the mixtures [13].

2.1. Setting time test

The setting time test was executed for the reference cement (without the residue) CP V ARI RS, according to NBR 16607:2018, using the normal consistency that was previously determined by testing, according to the norm NBR 16606:2018. This test was also performed for cement pastes with different incorporated residue contents, following NBR 16607:2018 as well, aiming to analyze the impact of residue incorporation on the pastes [10-11].

2.2. Mini-slump test

The mini-slump test was made, in accordance with NBR 16889:2020, using a mini cone. The tests were applied to both the reference cement paste and the pastes with different incorporated titanium dioxide contents, aiming to evaluate the residue's influence on the fluidity and workability of the pastes [12].

Mini-slump spread diameters were obtained and compared between the reference paste and the pastes with different incorporated titanium dioxide residue contents. The spread diameter measurements were analyzed using ImageJ software.

3. Test results and discussions

3.1. Setting time test

The setting time test was performed on the pastes in their fresh state. The graphs present the results of the test for the reference paste and for the pastes with different contents of incorporated residue**.**

Figure 2. Total setting time from initial water contact with cement and residue to final setting stage.

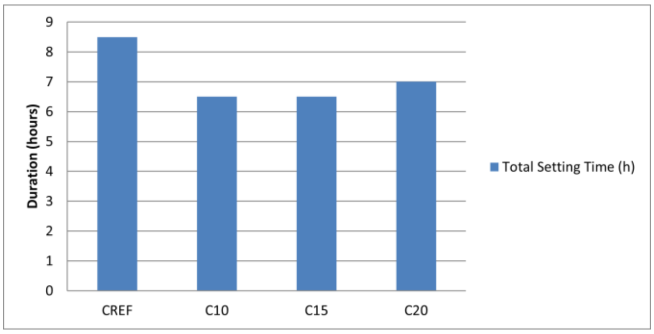
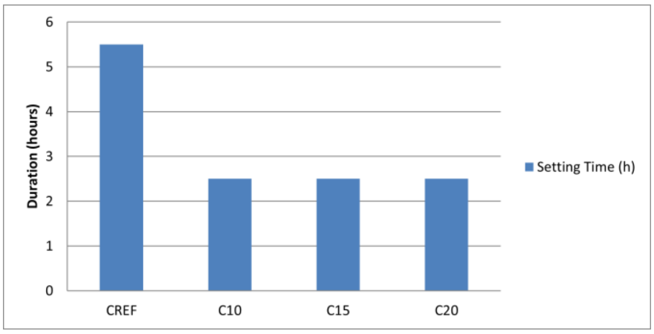


Figure 3. Duration of the setting time of the cement paste, determined between the initial and final setting stages.



Regarding the setting time, a considerable reduction in setting time was observed in the mixtures with addition of titanium dioxide residue, mainly at higher contents. As shown in Figure 2 and Figure 3, which demonstrated that increasing residue content decreased the setting time in the mixtures, both considering the time from initial to final setting stages and from initial water contact with cement and residue to final setting stage, with the most significant reductions observed in pastes containing 10% and 15% incorporated residue content.

3.2. Mini-slump test

The mini-slump test was performed in the fresh state, following the NBR 16889:2020 standard, for a cone of reduced volume. The figures 4,5,6 and 7 present the results of the mini-slump test for the reference paste and for the pastes with different residue contents [12].

Figure 4. Mini-slump for reference paste (without residue).

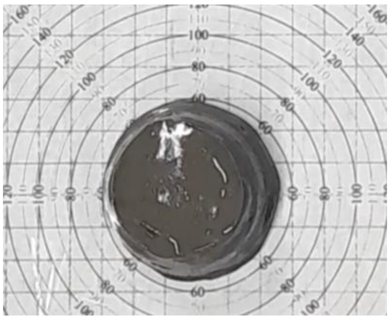


Figure 5. Mini-slump for paste with 10% incorporated residue.

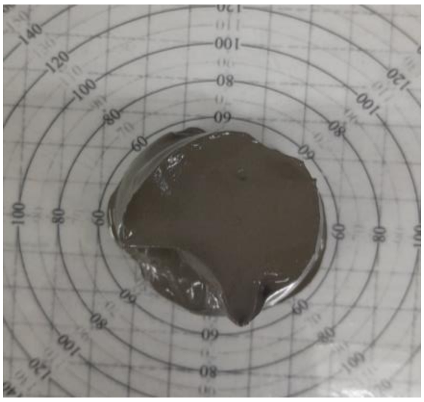


Figure 6. Mini-slump for paste with 15% incorporated residue.

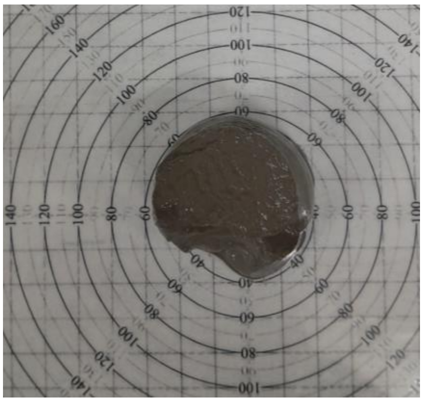
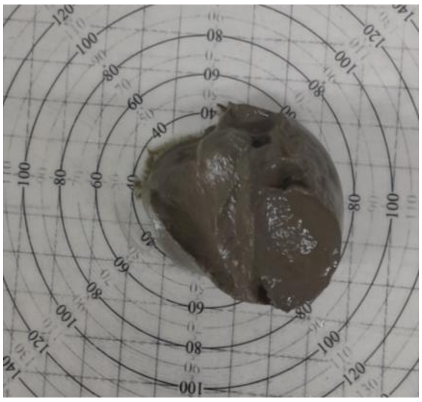


Figure 7. Mini-slump for paste with 20% incorporated residue.



Throughout the figures, as the incorporation of residue in the pastes increases, it makes the paste mixtures drier, thus they lose consistency. This way, it can be seen that titanium dioxide directly affects the workability of the mixtures, as its content in them increases. This can be verified with the decrease in the spread diameter of the pastes, as the photocatalytic residue content is increased. The spread diameter values obtained were approximately 56 mm for the reference paste, 53 mm for the paste with 10% incorporated residue, 49 mm for the paste with

15% incorporated residue, and 47 mm for the paste with 20% incorporated residue.

It is important to emphasize that, even during the preparation of the samples for the test, the alteration in the consistency of each paste was already perceptible, becoming more evident as the content of titanium dioxide residue in the mixture was elevated. Therefore, the utilization of the residue may require adjustments in the mix proportion in order to assist the workability. Thus, the use of additives may be required to maintain adequate consistency when incorporating higher residue contents in the mixtures.

4. Conclusions

The results obtained in this study show that incorporating titanium dioxide (TiO_2) into cement-based materials affects pastes behavior in their fresh-state. In this context, mini-slump tests indicated a significant reduction in fluidity as the TiO_2 content increased, revealing a negative impact on workability. On the other hand, setting time tests showed a considerable decrease in this parameter, possibly due to increased water demand and interference of the residue in the hydration process.

Therefore, it can be concluded that the incorporation of TiO2 residue affects the consistency and hydration product formation in cement pastes, as observed through the results of setting time and mini-slump tests.

However, further studies are still needed to better understand the interaction between titanium dioxide residue and the cement matrix in cement-based materials.

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