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ORIGINAL ARTICLE

Fresh and hardened properties of cementitious composites with the addition of nanofibrillated cellulose

Propriedades no estado fresco e endurecido de compósitos cimentícios com a adição de celulose nanofibrilada

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Abstract: Evaluating the effects of nanomaterials in cementitious systems is paramount to projecting high-performance construction materials. However, the synthesis of some nanomaterials on a large scale and their toxicity may limit their application. In this context, nanofibrillated cellulose (NFC), a biodegradable and natural material stand out. Thus, this paper aims to study the influence of NFC on the fresh, hardened properties (compressive and flexural strengths) and mineralogy of cementitious systems. The results indicated that incorporating up 0.075 wt.% to CNF reduced the spread of cement pastes by up to 14.0%. A CNF content of 0.025 wt.% increased the 28-d compressive and flexural strengths by 22.0% and 25.0%, respectively, compared to the control sample. The X-ray diffraction (XRD) results indicate that higher NFC contents (>0.025 wt.%) resulted in lower intensity portlandite peaks after 7 days, which may show a lower hydration degree, especially concerning the plain cement paste. These results suggest that the NFC can affect the hydration of cementitious matrices at early ages; however, it did not significantly affect the hydration degree after 28 days of hydration.

Keywords: cellulose, nanofibers, compressive strength, flexural strength, mineralogy.

Resumo: Avaliar os efeitos dos nanomateriais em sistemas cimentícios é fundamental para projetar materiais de construção de alto desempenho. No entanto, alguns nanomateriais tem a sua aplicação limitada à toxicidade e síntese em larga escala. Nesse contexto, destaca-se a celulose nanofibrilada (NFC), um material biodegradável e natural. Assim, este trabalho tem como objetivo estudar a influência do NFC nas propriedades no estado fresco, endurecido (resistências à compressão e à flexão) e mineralogia de sistemas cimentícios. Os resultados indicaram que a incorporação de até 0,075% em massa da CNF reduziu o espalhamento das pastas de cimento em até 14,0%. Um teor de CNF de 0,025% em massa aumentou as resistências à compressão e a flexão de 28 dias em 22,0% e 25,0%, respectivamente, em comparação com as amostras de controle. Os resultados da difração de raios-X (DRX) indicaram que maiores teores de CNF (>2,5%) resultaram em picos de portlandita de menor intensidade após 7 dias, o que pode indicar um menor grau de hidratação, principalmente em relação à pasta de cimento de referência. Esses resultados sugerem que a NFC pode afetar a hidratação de matrizes cimentícias em idades precoces; entretanto, não afetou significativamente o grau de hidratação após 28 dias de hidratação.

Palavras-chave: celulose, nano fibras, resistência à compressão, resistência à flexão, mineralogia.

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1 INTRODUCTION

Recently, the feasibility of producing cementitious nanocomposites has been widely investigated. Cement-based nanocomposites with the incorporation of nano silica [1]–[3], carbon nanotubes [4]–[7], graphene [8]–[10], and nano titanium [11]–[13] stand out in the scientific field. Incorporating nanomaterials aims to produce composites with properties that focus on applicability (e.g., self-sensing application) or enhance mechanical properties. However, the application of these nanomaterials is conditioned to some limitations associated with the synthesis in large quantities to consolidate their incorporation in mortars and concretes. Therefore, most studies of nanomaterials are carried out in cementitious pastes [14].

In addition, another widely discussed aspect concerns the toxicity of some nanomaterials, such as carbon nanotubes (CNT). Thakur et al. [15] extensively reviewed studies that assessed the toxicity of carbon nanotubes, identifying that their toxicity is related to the presence of impurities, length, size, and type (single or multi-walled CNT). Similarly, Mohanta et al. [16] reported that the cellular toxicity of CNT is associated with generating free radicals that cause oxidative stress. Moreover, the nanomaterial can cause inflammatory responses and the formation of reactive oxygen species, leading to several adverse effects on cells. Lam et al. [17] also mention that CNT can produce epithelioid granulomas, fibrosis, and biochemical/toxicological changes in the lungs.

Therefore, nanomaterials of natural origin can present significant advantages concerning the previously mentioned nanomaterials. Studies on cellulose have been of great importance since it is the most abundant polymer in the world. It has an estimated production of 1,014 tons per year and can be found in different forms, such as green plants, fungi, and protozoa [18]. Cellulose-based materials are used in paper production, in the timber industry, as a possible emulsifier and dispersing agent [19]. Although it is a natural product, it can potentially replace synthetic polymers. Moreover, they can also be used to produce nanomaterials, such as nanofibrillated (NFC) and nanocrystalline celluloses (NCC) [20], [21]. Additionally, compared to other nanomaterials like CNT, the NFC are inert, biodegradable, and from a biological origin and, thus, present small potential risks concerning toxicity [22]. Thus, since cellulose nanoparticles are environmentally friendly, their reduce the environmental footprint of cementitious composites compared to industrial nanofillers (e.g., carbon nanotubes, graphene) [23].

Nanofibrillated cellulose (NFC) is produced from the mechanical disintegration of cellulosic fibers, thus disrupting the cell wall and exposing fibrils and microfibrils [21]. NFC has currently been studied to manufacture films, packaging, and biomedical products [24]. Its use is also reported for producing membranes for lithium batteries due to the NFC's excellent electrolyte wettability [25], [26]. NFC is characterized by amorphous and crystalline domains of cellulose, high aspect ratio (i.e., length-to-width ratio), and large specific surface area (SSA), which can favour their agglomeration and thus their dispersion in cementitious matrices [27]. This can limit the NFC reinforcement ability of mechanical properties if not properly dispersed.

Cellulose nanoparticles significantly modify cementitious composites' rheological and mechanical properties, even with low contents (~0.1%) [28]. This is due to the high mechanical properties, elasticity moduli ranging from 65 GPa to 150 GPa, and high aspect ratio of NFC, which can improve cementitious materials' mechanical properties [22].

The addition of cellulose nanomaterials has been investigated to improve the mechanical properties of cementitious composites [29]–[32]. This application usually employed cellulose nanoparticles in powder or aqueous suspensions. Liang et al. [33] assessed the effect of different NFC aqueous suspension contents (up to 0.15% by binder weight) on cementitious composites' hydration and mechanical properties. The NFC incorporation extended the induction period by 11.84 hours compared to control samples, which can be attributed to the adsorption of NFC on the cement particles' surface. Nevertheless, after 28 days of hydration, the NFC increased the hydration degree of the composites (identified by thermogravimetric analysis) and increased the 28-d compressive and the initial cracking stress by 46.1% and 91.2%, respectively.

Similarly, Onuaguluchi et al. [34] also observed that the cellulose nanofiber (in a suspension form) reduced the early-age hydration of cement composites. Nevertheless, the nanomaterial incorporation increased the cumulative heat and hydration degree after 28 days. Moreover, increments in flexural strength up to 106% were reported by a cellulose nanofiber of 0.1 wt.%. Souza et al. [35] reported that an NFC content of 1.0% significantly increased the flexural strength (5x) of cement pastes compared to the control sample. Therefore, NFC dispersions in pulp form still need to be further investigated. Thus, given the context above and the theme's relevance, the present work aims to evaluate the fresh and hardened properties and the mineralogy of cement pastes containing NFC contents of 0.0%, 0.025%, 0.05%, and 0.075% NFC.

2 MATERIALS AND METHODS

2.1 Materials

Ordinary Portland cement (OPC), denominated as high initial strength cement (CP-V), was employed for cementitious composites production. Its chemical composition, presented in Table 1, was supplied by the manufacturer Votorantin Cimentos (Curitiba, Brazil).

Table 1. Chemical composition and physical properties of Portland cement.

Property	MK
Chemical composition (wt.%)	
SiO_2	19.3
Al_2O_3	4.47
Fe_2O_3	2.97
SO_3	2.85
CaO	62.1
Loss on ignition	3.51
Free Lime	1.28
Insoluble Residue	0.67
Equivalent Alkali	0.66
Physical property	
#200 (%)	0.05
#325 (%)	0.28
Density (g/cm^3)	3.09
Blaine Fineness (cm^2/g)	4.49

The NFC was produced from the bleached kraft pulp of Eucalyptus sp., disintegrated in a blender with 450W of power for 30 seconds. It was later processed in the Super Masscollider Masuko Sangyo Microprocessor. The parameters for obtaining the NFC were: 1500 rpm of rotation, 10 passes through the mill and a concentration of 1.0% (i.e., 1.0% of NFC and 99.0% of water). The term nanofibrillated cellulose pulp refers to the gel where the NFC's are suspended in water, as shown in Figure 1. The image evidences the viscous appearance of the NFC pulp. NFC properties are shown in Table 2.

Figure 1. Nanofibrillated cellulose (NFC) pulp.

The characterization results of the nanofibrillated cellulose pulp using the X-ray diffraction test are shown in Figure 2. The test was conducted on a diffractometer using CuKα1 radiation ($\lambda = 1.54056$ Å), in the range of 1 to 70 °, with a step size of 0.015 ° and a 100s count time every 1.05°. The XRD pattern of nanocellulose of Eucalyptus sp. is characteristic of type I cellulose, where the amorphous halo and the crystalline peak are located between $18° \leq 2\theta \leq 19°$ and $22° \leq 2\theta \leq 23°$ [36].

Figure 2. XRD pattern of NFC pulp

2.2 Mix proportions

The composition of NFC cementitious composites produced is presented in Table 2. Three different contents of NFC pulp of 2.5, 5.0, and 7.5 wt.% were assessed and incorporated as an addition based on cement weight. These contents resulted in NFC percentages of 0.025, 0.05, and 0.075 wt.%, considering that the pulp concentration is 1.0% (99.0% of water and 1.0% of NFC). All the cement pastes evaluated were produced with the same water-to-cement ratio of 0.449. Nevertheless, as the pulp is mainly composed of water, this value was deducted from the mixing water to produce compositions with the same w/c ratio. Moreover, no superplasticizer admixture was used to avoid interaction with the NFC and, therefore, be able to evaluate the effect of the nano addition individually.

Table 2. Composition of NFC cementitious composites.

Cement Paste	Cement (g)	Pulp (g)	NFC (g)	Water (g)
0.0%	100.0	0.00	0.000	44.95
0.025%	100.0	2.50	0.025	42.47
0.05%	100.0	5.00	0.050	40.00
0.075%	100.0	7.50	0.075	37.52

The mixing procedure for cementitious pastes was based on the Brazilian standard NBR 16541 [37]. The mixing time adopted was 2 minutes. The process was followed by: (i) manual mixing of NFC pulp with water; (ii) mixing the cement with the water solution and NFC pulp in a mixer with a capacity of 5 liters and with a vertical axis at a slow speed for 1 minute; (iii) 30 seconds for removing material adhered to the walls of the mixer, and (iv) 30 seconds of mixing at slow speed.

2.3 Test methods

The consistency index of cementitious composites was determined in the fresh state, following the procedure established in NBR 13276 [38]. In the hardened state, compressive and flexural strengths were evaluated at 7 and 28 days of hydration following NBR 13279 [39]. The influence of NFC addition on the mineralogy of cementitious composites was assessed by X-ray diffraction (XRD) after 7 and 28 days of hydration. Some cementitious composite fragments were selected and immersed in isopropanol for 24 h and then dried in an oven at 40° C for another 24 h to stop cement hydration reactions. The use of isopropanol for this purpose was widely employed in previous studies [40]–[42]. After the procedure above, the diffraction data of all samples were collected in a diffractometer, operating in transmission mode, using CuKα1 radiation ($\lambda = 1.54056$ Å), in the range of 10 to 70 °, with a step size of 0.015 ° and a 100s count time every 1.05°. The phase identification was conducted in Match! Software, using the Crystallography Open Database (COD).

3 RESULTS AND DISCUSSIONS

3.1 Consistency Index

Figure 3 shows the consistency index of NFC cementitious composites and the polynomial that describes the behaviour of the data ($R^2 = 0.927$). Overall, the increase in NFC content progressively reduced cement pastes' consistency index, with a reduction of up to 16.0%, compared to the control sample. The results indicate that the NFC reduced the flowability of cement-based materials. This behaviour can be associated with (i) the high viscosity of NFC pulp (see Figure 1), (ii) the higher SSA of NFC (~ 80 m^2/g) compared to OPC, (iii) the agglomeration of NFC, mainly at higher contents, which can entrap the mixing water and, thus, reduce the water available for particle lubrification, and (iv) the hydrophilicity of NFC that can adsorb water on their surface, also reducing effective w/c ratio of cement pastes. Similar results were reported regarding carbon nanotubes' effect on the fresh-state properties of cement-based materials [43].

Figure 3. Consistency index of NFC cementitious composites

Nevertheless, it should be noted that for NFC contents higher than 0.05 wt.%, there is a tendency for the consistency index to stabilize. Thus, even with higher NFC contents (0.075 wt.%), which would be expected to cause an even more significant reduction in the consistency index, this value was still maintained. This may be related to the dispersant effect of cellulose previously reported in the literature. For instance, Montes et al. [44] observed that at lower contents of cellulose nanocrystals (< 0.2%), the material could have a dispersing effect, similar to a reducing admixture, with reductions of up to 45% of the yield stress of cement pastes (determined by rotational rheometry test).

Nassiri et al. [45] verified that cellulose nanocrystals (CNC) maintained the workability of cement pastes for contents up to 0.035 wt.%. Furthermore, contents between 0.045 and 0.6 wt.% progressively reduced the mini-slump spread values compared to the plain cementitious composite. In contrast, regardless of the NFC content evaluation (0.02 – 0.2 wt.%), it reduced the spread of cement pastes, with reductions directly proportional to the incorporated content of NFC. The increased consistency with incorporating NFC is attributed to the entangled nanofiber network. At the same time, the dispersing effect of CNC is assigned to the shorter and higher mobility of this type of nanomaterial [45].

It should be noted that nanocellulose-modified cementitious composites can present an internal self-curing associated with good water retention of nanocellulose [23], which also justify the behaviour observed in Figure 3.

3.2 Compressive Strength

Compressive strength results of NFC cementitious composites after 7 and 28 days of hydration are presented in Figure 4. Figure 5 shows the analysis of variance (ANOVA) and Tukey's hypothesis test, performed to verify the difference between the experimental samples. In Figure 5, the red lines indicate that the null hypothesis is observed, i.e., the statistical universes are different (with statistically significant differences). The black lines represent no statistical difference between the means, and the variables are statistically equal. The confidence value for these tests was equal to 95%.

Figure 4. Compressive strength of NFC cementitious composites after (a) 7 days and (b) 28 days of hydration

Figure 5. ANOVA and Tukey test of compressive strength results (a) 7 days; (b) 28 days

According to Figure 4 and Figure 5, NFC cellulose did not contribute to the gain in compressive strength at early ages (7 days), considering the ANOVA and Tukey test results. However, at 28 days, there was an increase in the compressive strength of ~ 22.0% in the sample with 0.025% NFC compared to the reference sample and the other NFC contents (0.05 and 0.075%). This result demonstrates that there is optimal content concerning NFC incorporation. Thus, contents greater than this optimal content (0.025 wt.%) do not result in progressive gains in compressive strength. This may be associated with the agglomeration tendency of nanomaterials. This trend was previously reported in studies regarding nanocellulose incorporation in cement-based materials [34], [45].

According to Wang et al. [23], several studies indicated that nanocellulose enhances cement-based materials' compressive strength, with increases controlled by the type of nanocellulose and its content. Hisseine et al. [46] assessed the effect of cellulose filaments (CF) at dosages of 0.0%, 0.05%, 0.10%, 0.20% and 0.30 wt.% on the compressive strength of cementitious systems. After 7 days of hydration, CF contents of 0.05% and 0.10% increased compressive strength by 25% and 15%, respectively. At 28 days, these increments were 26% (0.05%) and 17% (0.10%). The authors identified that these enhancements in mechanical performance are attributed to an increase in cement hydration degree of 15% at 28 days. The hydrophilicity and hygroscopicity of CF can explain the phenomenon, as it enables internal self-curing that releases water for the continued reactions of anhydrous cement particles [46]. The previously mentioned phenomenon also helps to explain why the NFC increments are more significant at 28 days of hydration compared to the compressive strength results at 7 days.

3.3 Flexural Strength

The mean values and standard deviation of the flexural strength results at 7 and 28 days are shown in Figure 6. Figure 7 contains the ANOVA and Tukey's hypothesis test of flexural strength results. As mentioned in section 3.2., the black lines represent statistically equal values (with no statistically significant differences), considering a significance level of 5%. The red lines indicate flexural strength values with statistically significant differences. Overall, incorporating NFC did not affect flexural strength, except for the 0.025 wt.% content, which resulted in an increase in the mechanical property of approximately 25% compared to the control sample (0.0% NFC) at 7 and 28 days of hydration.

Figure 6. Flexural strength of NFC cementitious composites after 7 and 28 days of hydration

Figure 7. ANOVA and Tukey test of flexural strength results: (a) 7 days; (b) 28 days.

Adding NFC promoted a slightly higher flexural strength than the previously discussed compressive strength. This behavior is expected due to the shape of the nanoparticles. Due to the large aspect ratio, the NFC acts like a fiber, bridging the crack of cement-based materials. A Similar contribution of carbon nanotubes in cement-based materials was also observed [14]. In this context, under compression, the CNT acts as a filler. Nevertheless, under tension acts as a bridging avoiding the crack propagation and, thus, delaying the material failure [47].

In this context, Souza et al. [35] observed an optimal NFC content of 1.0 wt.%, which resulted in flexural strength and elastic modulus of up to 3x and 5x, respectively. Moreover, authors reported that using a superplasticizer enhanced the dispersion of NFC, resulting in increases of 5x and 8x, respectively, on the flexural strength and elastic modulus.

Furthermore, it is verified that the optimal content of NFC concerning flexural and compressive strength are equal (0.025 wt.%). From a practical and economical point of view, this is interesting, resulting in NFC cementitious composites with a lower cost.

3.4 Nanocomposites Mineralogy

Figure 8 presents the X-ray diffraction (XRD) results of cementitious composites with different NFC contents after 7 and 28 days of hydration. The identified crystalline phases are ettringite (COD 96-901-1577), portlandite (COD 96-900-0114), and alite (COD 96-901-6126). The NFC incorporation did not generate the formation of new crystalline phases, as expected, due to the low addition content. Between 7 and 28 days of hydration, there is a decrease in the intensity of the alite peaks (e.g., 29.3° 2θ) and a concomitant increase in the intensity of the portlandite peaks (e.g., 17.9° and 34.1° 2θ). This indicates an advance in the degree of hydration of cement pastes. The XRD results of cementitious pastes can be misinterpreted due to the impact of preferred orientation in sample preparation, particularly on the portlandite peak around 17.9° 2θ [48].

Figure 8. XRD results of NFC cementitious composites at (a) 7 days and (b) 28 days of hydration. Note: E - Ettringite, P - Portlandite, A - Alite

At 7 days of hydration, it can be observed that 0.05 and 0.075 wt.% cementitious composites exhibited slightly lower portlandite peaks and higher alite intensity peaks, which can indicate a lower hydration degree compared to 0.025% and 0.0% NFC cement pastes. This is consistent with the 7-d compressive strength results since even for higher NFC contents, there is no enhancement in mechanical performance. This effect is possibly associated with NFC hydrophilicity and hygroscopicity, resulting in mixing water absorption and, thus, a delay in the initial cement hydration reactions, as discussed in section 3.2. At 28 days, the portlandite and alite peaks have similar intensity, as seen in Figure 8b. Thus, despite the influence of higher NFC contents on the degree of hydration of cement pastes at 7 days, at 28 days there is no significant influence on the mineralogy of the composites.

It should be noted that the effective NFC content of up to 0.075 wt.% evaluated in this study is lower than the percentages (up to 0.15 wt.%) assessed by Liang et al. [33]. Thus, the authors identified an increase in the hydration degree of cementitious composites for higher NFC contents, different from that observed in this study. Therefore, possibly the NFC contents evaluated were not enough to affect the degree of hydration of cement pastes at 28 days.

Previous studies regarding the effect of other types of nanomaterials on the microstructure of cement-based materials reported similar results. For instance, Andrade et al. [49] observed that CNT contents up to 0.1% by cement weight did not significantly affect the intensity of the peaks of the crystalline phases at 28 days of hydration. Similarly, Silvestro et al. [43] observed that although 0.1 wt.% of carboxyl-functionalized CNT hindered the early-age hydration of cement paste (evaluated by 48-h in-situ XRD assessment), it did not affect the hydration degree of cement pastes at 28-days, which was identified by XRD and verified by quantitative analysis by thermogravimetry.

3.5 Prediction of Mechanical Properties

In the preliminary stages of a project, it is necessary to estimate the mechanical properties of the constituent materials. Numerical simulation needs input like compressive strength and flexional strength at various ages. Therefore, in this section, two empirical equations developed to predict the uniaxial compressive strength (fc) and flexural modulus of rupture (MRF) will be presented as a function of the NFC content for cement pastes with a fixed water-to-cement ratio of 0.4495. Thus, Figure 9 presents the cubic equations used to obtain fc and MRF estimates, as presented by Equations 1 and 2. The fit was conducted on OriginLab software. The proposed empirical equation adequately describes the compressive strength data. The adjustment reinforces the existence of an optimal NFC content near 0.025%, corroborating the compressive results discussed in section 3.2. In contrast, the equation that estimates the MRF did not show a good fit ($R^2 = 0.30$) to the data, which makes its application difficult.

$$f_c = 39.622 + 272 \cdot NFC + 5.653\, NFC^2 - 129.792 NFC^3 \tag{1}$$

$$MRF = 7.693 + 220.7 \cdot NFC - 67.1\, NFC^2 + 51.143 NFC^3 \tag{2}$$

Figure 9. Equations to predict the 28-d compressive and flexural strengths of NFC cementitious composites

Equations that describe the compressive strength of cementitious matrices over time are of particular interest because they make it possible to estimate this property, especially when dealing with cementitious composites with the incorporation of nanomaterials because it still does not have a well-established behaviour in the literature. Hence, an analytical equation is calibrated regarding the ABNT NBR 6118 [50] (or CEB), which determines the evolution of fc concerning time, as presented in Figure 10. An NFC content of 2.5% exhibited a higher compressive strength evolution over time compared to the plain cement pastes and the other NFC contents. Moreover, the contribution of NFC is more expressive for more advanced ages (e.g., 28 days), while for initial ages, they are not so impactful in such a property. These results are interesting since many studies mention that nanomaterials have more significant contributions at early ages, such as a nucleation effect associated with a high specific surface. However, NFC has hydrophilic characteristics, which may result in a self-healing effect and contribute more significantly to the mechanical properties of cementitious matrices at more advanced ages.

Figure 10. Equations to predict the 28-d compressive and flexural strengths of NFC cementitious composites.

Figure 11 shows a summary radar graphic of the investigated parameters. In this way, the range of flowability, compressive strength and flexural strength are plotted. A significant region was observed at an NFC concentration of 0.025%, indicating good flowability and the best mechanical properties in the cases investigated. Therefore, the 0.025% mixture is more balanced for industrial applications in these investigated cases. This procedure can be used whenever this material has been previously studied for accurate scale applications.

Figure 11. Determination of studied properties and the equilibrated mixtures

4 CONCLUSIONS

This study assessed the effect of different nanofibrillated cellulose contents (0.0%, 0.025%, 0.05%, and 0.075%) on the consistency index, compressive and flexural strengths, and mineralogy of cement pastes. The following conclusion can be drawn:

- The increase in NFC content progressively reduced cement pastes' consistency index, with a reduction of up to 16.0% concerning the plain cement paste. This is associated with the viscosity of NFC pulp and higher SSA and hydrophilicity of the nanomaterial.
- The optimal content of NFC of 0.025 wt.% was identified for the mechanical performance of nanocomposites. Compared to the control sample, it increased 22.0% and 25.0% on the 28-d compressive and flexural strengths of cement pastes.
- The XRD results indicated that NFC contents greater than 0.025% resulted in a lower degree of hydration of the pastes at 7 days, which can be identified by less intense portlandite and more intense alite peaks. However, at 28 days, no differences were observed in the crystalline phases of the composites with NFC, indicating a similar degree of hydration concerning the plain cement paste.

Nanofibrillated cellulose (NFC), a biodegradable and natural material, proved to be a promising material for reinforcing the mechanical properties of cementitious materials. An addition content of only 0.025% promoted increases in compressive and flexural strengths of up to 25.0% of cement pastes. For future work, it is suggested to evaluate different dispersion methods and their impact on mechanical properties.

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