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The influence of mixing on the rheology of fresh cement paste

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Abstract

The influence of mixing shear rate on the rheological properties of cement paste was investigated. Cement pastes were mixed, sheared at a constant rate in a rheometer, and then subjected to increasing and decreasing shear rates, producing a hysteresis loop when plotted against shear stress. The extent of structural breakdown within the paste was evaluated as a function of mixer type and speed, based on hysteresis loop area. Plastic viscosity was measured using the linear portion of the hysteresis loop down curve. Well-mixed pastes exhibited a decreased propensity for further structural breakdown and a low plastic viscosity. Paste removed from a no-fines concrete had rheological properties similar to paste mixed at moderate speeds in a high shear blender

Keywords: Rheology; Workability; Cement paste; Mixing

1. Introduction

The shear rate during mixing is one of the most important variables affecting the rheological properties of fresh Portland cement pastes [1]. It has been suggested that high shear mixing breaks down cement powder agglomerates, many of which are formed prior to the addition of water to the paste. Tattersall and Banfill further developed this idea in terms of "irreversible structural breakdown" [2]. They proposed that agglomerated groups of cement particles share a single hydrate membrane. Thus, under shear the agglomerates are broken and a new membrane rapidly forms around the dispersed cement particles, partially inhibiting further agglomeration. Existence of a membrane is supported by environmental scanning electron microscopy [3,4]. Detailed rheological studies have shown the flow-inhibiting properties of these agglomerated structures [4].

Increasing the shear rate of mixing has been shown to reduce the plastic viscosity of cement slurries used for oil field applications [5] and to decrease the area between the up and down curves of controlled-rate hysteresis loops [1,6]. Studies performed on pastes at constant shear rates indicate the agglomerated network structure can be broken as shear rate is increased. However, at very high shear rates hydration products are released into the aqueous phase resulting in decreased flow properties [1].

In concrete the extent to which cement paste is mixed through the ball-milling action of aggregates is of great engineering importance. Powers suggested that "the rolling mass of aggregate in the concrete mixer homogenizes the paste as effectively as the most vigorous laboratory stirrer" [7]. This idea agrees with recent experiments in which cement paste is extracted from normally proportioned concretes by sieving out the aggregates [8]. However, low shear rate mixing of sieved cement powder produces pastes rheologically similar to pastes mixed under high shear, which suggests that sieving may confound any attempt to compare flow properties of a high shear-mixed paste to paste extracted from concrete [4]. Consequently, due to the difficulty of extracting paste from concrete with the original microstructure intact, the great majority of studies on the influence of mixing shear rate on rheology have focused only on cement paste.

In this paper the results of viscometric testing on fresh Portland cement pastes subjected to different mixing shear rates is reported. Pastes were mixed, then placed into a cone on plate rheometer. An initial shear rate was applied to the sample for a specified time (preshear). Next, controlled shear rates were applied, first increasing, then decreasing, to obtain hysteresis loops. The results were analyzed to evaluate the shear-induced structural breakdown in each paste. The area enclosed by the up and down curves of the hysteresis loop was used to quantify the degree of structure in the paste as a function of mixing shear rate. The plastic viscosity of each paste was also evaluated using the linear portion of the down curve of the hysteresis loop (Fig. 1).

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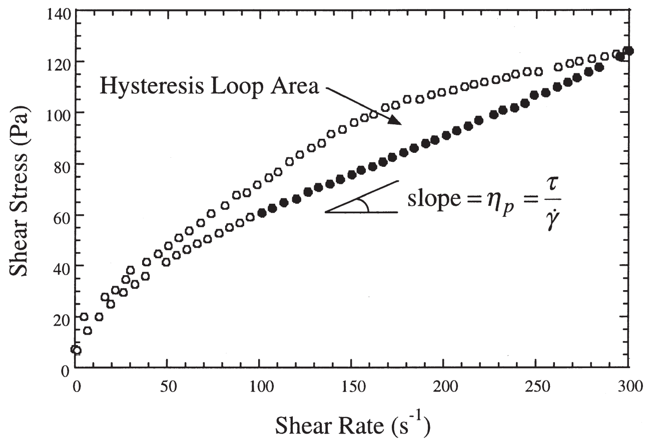

Fig. 1. Typical hysteresis loop for hand-mixed paste presheared at 100 s^{-1}. Bingham plastic viscosity calculated using the slope of the hysteresis down curve from 300 to 100 s^{-1} (filled black circles).

2. Experimental procedure

A typical Type I Portland cement was used for the experiments. The composition is listed in Table 1. Deionized water was used for all the mixes at a constant water/cement (w/c) ratio of 0.40. Six methods were used to mix the cement pastes. In all cases, cement powder was added to the preweighed quantity of mix water and mixing was conducted at room ambient temperature.

2.1. Hand mixes

Hand-mixed pastes were prepared by adding the weighed quantity of cement powder (~30 g) to the mix water in a small cup. Approximately half of the powder was added to the water and the mixture was briefly stirred to break up large heterogeneities. The remaining cement powder was added and stirred in a manner as gentle as possible to produce consistent pastes. The total mixing time was about 15 s. The goal of this technique was to produce a paste with the least possible initial mixing.

Table 1
Composition of cement powder

Compostion (%)
SiO_2, 20.79
Al_2O_3, 5.31
Fe_2O_3, 2.25
CaO, 63.54
MgO, 3.72
SO_3, 2.84
C_3S, 53.70
C_2S, 19.08
C_3A, 10.27
C_4AF, 6.85
Equivalent alkalis, 0.51
Blaine fineness (m^2/kg), 368
Loss on ignition, 1.09
Insoluble residue, 0.10

2.2. Paddle mixes

A 1/6 horsepower Hobart planetary mixer (Model N-50, Hobart Manufacturing Company, Troy, OH, USA) was used to mix cement paste in a procedure very similar to ASTM C-305 [9]. The cement powder was added to the mix water within 1 min. The mixer was set at the 140-rpm setting (speed #1) for 30 s and then paused for 1 min. A rubber paddle was used to scrape the sides of the mixing bowl during the 1-min pause. Next, the mixer was set at the 285-rpm setting (speed #2) for 2.5 min, after which the sides were again scraped. The mixer was then set at 285-rpm for another 2.5 min for a total of 5 min of mixing at setting #2. The mix time was extended beyond the usual ASTM C-305 standard requirements to minimize any effects due to incomplete mixing with respect to the capability of the machine.

2.3. High shear mixes

Cement pastes were mixed using a Ross high shear mixer (Model ME-100LC, Charles Ross and Sons Company, Hauggauge, NY, USA). In this mixer, two uniaxial impellers drive the paste through narrow apertures located in a small ring around the base of the support column (Fig. 2). Flow is characterized as a smooth convection, as opposed to the turbulent and frothy mixing action typical of Waring high shear blenders. The speed of the mixer is electronically controlled at a specified rpm.

For the high shear mixes, the mix water was placed in a 1500-mL beaker. The support column of the mixer was then lowered until there was a 3-cm gap between the column and the bottom of the beaker. The mixer was then turned on at an initial speed of 500 rpm and cement powder was added over a 1-min time period. The paste was then mixed at the desired speed (e.g., 500, 1500, or 2500 rpm) for 5 min, continuously turning the beaker and scraping the sides as necessary to break up large clumps. The temperature of paste mixed at 2500 rpm increased less than 2°C during mixing.

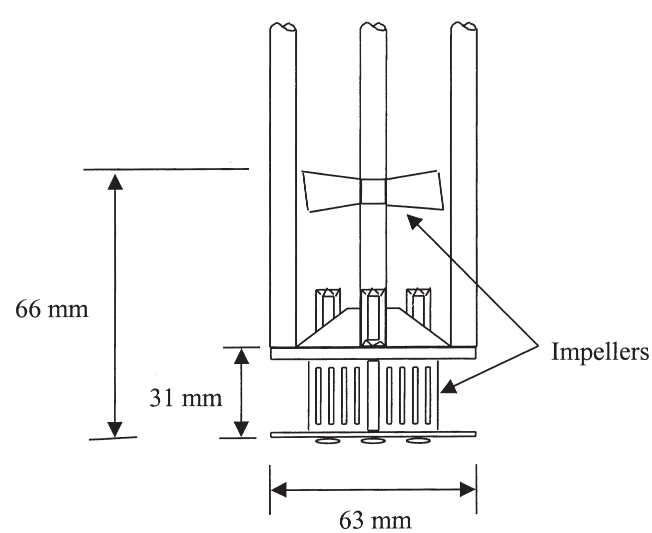

Fig. 2. Ross 1 Horsepower High Shear Mixer (Model ME-100LC).

2.4. Concrete mixes

Concrete with a water:cement:river gravel ratio of 0.40:1:1 was used. The aggregates were sized below 9.5 mm and were carefully sieved to remove all fines below 4.75 mm (ASTM sieve #4). The gravel was washed to remove dust, oven dried at 200°C for 24 h to remove all moisture, and then soaked in the mixing water 2 days prior to mixing to ensure homogenous absorption. Additional water equal to 1.33% of the aggregate weight was added to compensate for adsorption following ASTM C 127 [10]. The aggregate and water were weighed immediately before mixing and a small amount of water was added as required to compensate for evaporation. These steps ensured that the concrete was free of fine aggregates and that the paste in the fresh concrete would have a w/c ratio of 0.40.

The concrete was mixed using a tilting-drum concrete mixer (3 cubic feet capacity; 20 rpm constant speed). The interior surfaces of the mixer were wetted with a small quantity of deionized water. The excess water was discharged after allowing several minutes for adsorption on the walls of the mixer. The aggregate and mix water were added to the mixer followed by the addition of the cement powder. After 2.5 min of mixing, the mixer was stopped and the sides were scrapped free of clumps. The mixer was then restarted and allowed to turn for an additional 2.5 min.

Small portions of aggregate-free cement paste were extracted from the no-fines concrete. Careful attention was paid to avoid removing any aggregates in the process. The cement extracted from the concrete was evaluated in the same manner as the paste mixed in the other mixers.

2.5. Rheometer

A Rotovisco CV20-N rheometer (Haake, Inc., Karlsruhe, Germany) was used to measure the shear stress response to applied strain rate. Data acquisition and control were performed with a PC-coupled to a RC20 Rheocontroller and RV20 Rotovisco, (Haake, Inc., Karlsruhe, Germany) unit. A cone-on-plate sensor system (PK45) was used, with a cone angle of 4°. The tip of the cone sensor was truncated by 0.7 mm to prevent binding of cement particles between the tip and plate. A solvent trap was placed over the cup to prevent moisture loss during the experiments.

The cone-on-plate geometry was chosen for three reasons. First, a constant rate of shear is produced throughout the specimen. Additionally, only a small sample volume is required. Finally, paste can be loaded into the rheometer with a minimum of additional shearing.

2.6. Rheometer experimental program

After placing the pastes into the rheometer, the specimens were left to equilibrate for 30 s and were then sheared at a constant rate for 1 min (referred to as "preshear"). The applied rate of preshear to each paste ranged from 0 to 300 s^{-1}. Following the preshear, the sensor was lifted and the sample was gently stirred to mitigate the formation of preferential shear planes due to particle orientation. This stirring has been found to prevent anomalous low shear stress results during subsequent testing [11]. The sample was then subjected to a controlled rate hysteresis loop where the shear rate was increased from 0 to 300 s^{-1} over 1 min and then immediately decelerated back to 0 s^{-1} over an additional 1 min. The viscometric testing program is illustrated in Fig. 3.

The area enclosed by the up and down curves of the hysteresis loops were used to evaluate the structure remaining in the cement paste as a function of preshear for each mixing technique. The plastic viscosity, η_p, was also determined from the Bingham equation using the slope of the linear region of the down curve of the hysteresis loop (Fig. 1) [2].

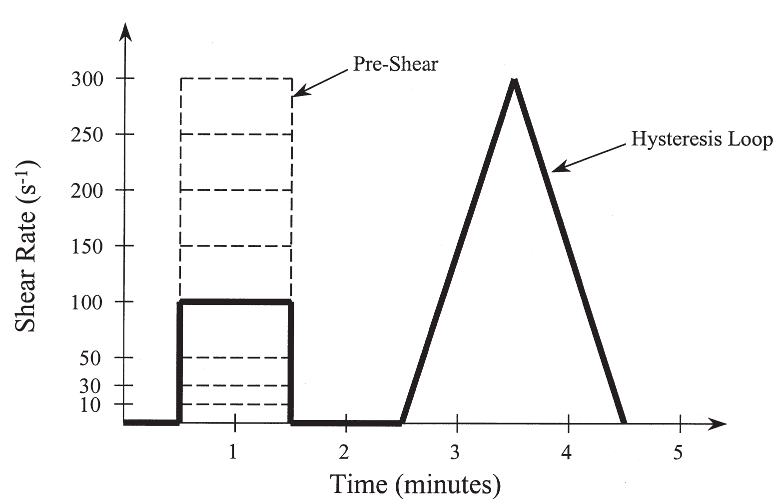

Fig. 3. Viscometer test program. A preshear was applied ranging from 0 to 300 s^{-1} (dashed lines) followed by the application of a hysteresis loop. The bold line is an example of a 100 s^{-1} preshear/hysteresis program.

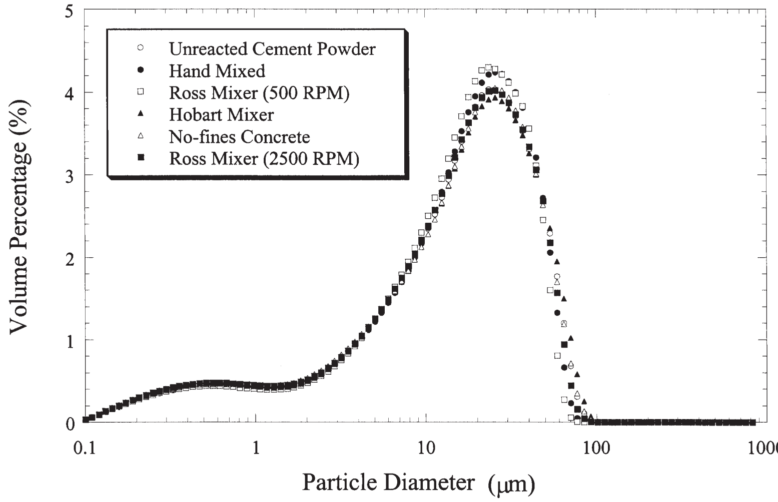

Fig. 4. Particle size distribution for different mixing techniques.

2.7. Particle size analysis

The particle size distribution (PSD) of the cement paste was measured to determine any systematic changes occurring as a result of mixing. Particle size analysis was also used to determine if any dust particles from the concrete aggregates entered the paste. Finally, the PSD data was used to check the concrete sampling techniques to verify that the method used to extract paste from concrete did not result in the preferential removal of certain particle sizes.

A Coulter LS130 (Coulter Corporation, Hialeah, FL, USA) instrument was used to determine the PSD. The cement paste particles were suspended in deionized water and pumped through a sample cell where they interrupted a collimated laser beam, causing Fraunhofer diffraction. Measurements were performed in sets of three consecutive 1-min runs per sample. Using this technique, particle sizes from 0.1 to 900 μm can be measured. Less than a gram of cement paste was added to 180 mL of water. The particle size of unreacted, dry cement powder was also measured using isopropyl alcohol (IPA) as the suspending medium.

3. Results and discussion

The results of the particle size analysis are shown in Fig. 4. Regardless of the mixing technique, all of the pastes have a similar PSD. Moreover, the PSD of the cement pastes were extremely close to that of the unreacted, dry cement powder. The low solids concentration and mechanical pumping required to perform the particle size measurements were most likely sufficient to completely disperse the pastes, independent of the mixing procedure. The measurements confirm that the PSD of the paste extracted from the fresh concrete conformed to that of the other samples. If small particles of paste tended to preferentially congregate near the aggregate surfaces, the effect was not significant enough to affect the particle size distribution of the extracted paste. In addition, the similarity in the PSD data between the high shear and gently hand-mixed pastes suggests that there was little comminution of the cement particles or hydrate due to overmixing.

Hysteresis loop area as a function of preshear for different mixing techniques is shown in Fig. 5. The hysteresis areas were smaller for the high shear-mixed pastes (Ross 1500 and 2500 rpm), indicating that the structure was comparatively broken down more during mixing. For a given mixing technique, as a higher preshear rate was applied, the area enclosed by the hysteresis loop decreased. Thus, the preshear acted as a highly controlled mixer, breaking down agglomerates at a known shear rate and making the paste more flowable. Initially well-mixed pastes were less sensitive to the rate of preshear. In these pastes, the agglomerated structure was already largely broken down.

The curves for the high shear mixer became nearly flat at preshear rates over 100 s^{-1}. More gently mixed paste required a higher shear rate to break down all of the structure left after mixing. For example, the hysteresis loop area for the hand-mixed paste did not approach zero until the preshear rate exceeded 200 s^{-1}.

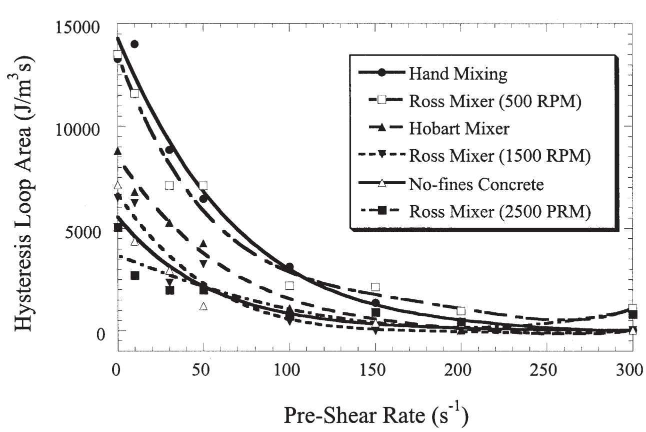

Fig. 5. Hysteresis loop area as a function of preshear for various mixing techniques.

Table 2
Hysteresis loop area and plastic viscosity at a preshear rate of 0 s^{-1} and corresponding estimated effective shear rates for different mixing techniques

Mixing technique	Hysteresis loop area (J/m^3s)	Estimated effective shear rate (s^{-1})	Plastic viscosity (Pa-s)	Estimated effective shear rate (s^{-1})
Hand mixing	13,300	–	0.44	–
Ross mixer (500 rpm)	13,500	12	0.42	25
Hobart paddle mixer	8,800	30	0.36	150
Ross mixer (1500 rpm)	6,500	50	0.33	200
No-fines concrete	7,100	45	0.31	230
Ross mixer (2500 rpm)	4,000	88	0.23	390

The hysteresis loop areas shown in Fig. 5 indicate that the paste extracted from the no-fines concrete was mixed at relatively high shear. Its structure appeared to be intermediate between pastes mixed in the Ross mixer at 1500 and 2500 rpm. However, these results suggest that paste from the no-fines concrete was not as highly sheared as Powers suggested [7].

The areas of the hysteresis loops were used as a basis for estimating the effective shear rate for each mixing technique. As an example, Hobart-mixed paste with a preshear of 0 s^{-1} has a hysteresis area of 8800 J/m^3s. Assuming hand-mixed paste has the maximum structure possible, a paste mixed by hand would have to be presheared at 30 s^{-1} to have a structure similar to Hobart-mixed paste. An estimate of effective shear rates appears in Table 2 for each of the mixing techniques.

The slope of the down portion of the hysteresis curve between 100 and 300 s^{-1} was used to determine plastic viscosity. The viscosity data for the various mixing techniques is shown in Fig. 6. More intensive shearing techniques produced pastes with lower plastic viscosities. Regardless of the method used to mix the pastes, lower viscosities were observed at higher preshear rates. More viscous pastes were increasingly sensitive to this additional shearing, as indicated by the increased magnitude of the negative slopes of the fitted lines in Fig. 6. The best-fit line for the highly sheared paste (Ross 2500 rpm) had the smallest slope and was the least sensitive to preshear. The viscosity of the paste extracted from concrete appeared to be very similar to the paste mixed at 1500 rpm in the Ross mixer.

The fan-shaped arrangement of the lines fit to the viscosity vs. preshear data in Fig. 6 suggest that the structure of the pastes should approach a limiting minimum viscosity at sufficient levels of preshear (see insert in Fig. 6). This hypothesis suggests that mixing mechanically disperses the pastes and that a very high shear rate would be sufficient to completely disperse the pastes. The results are in agreement with the coagulation rate theory model developed by Hattori et al. [12,13]. Due to the limitations of the rheometer, none of the preshear rates were high enough to observe the proposed convergence of the plastic viscosity curves. It is yet to be determined experimentally if high shear mixing alone could result in a fully dispersed cement paste suspension. Furthermore, the extent of this effect at lower solids concentrations has not been explored.

The data from Fig. 6 was used to generate an estimate of the effective shear rate for each mixing method. As an example, the fitted line for the Hobart paddle mixer intercepts the viscosity axis at 0.36 Pa-s. This value corresponds to the viscosity without any applied preshear (i.e., paste in the original as-mixed state with a preshear rate of 0 s^{-1}). A preshear rate of 150 s^{-1} is required to break down the struc-

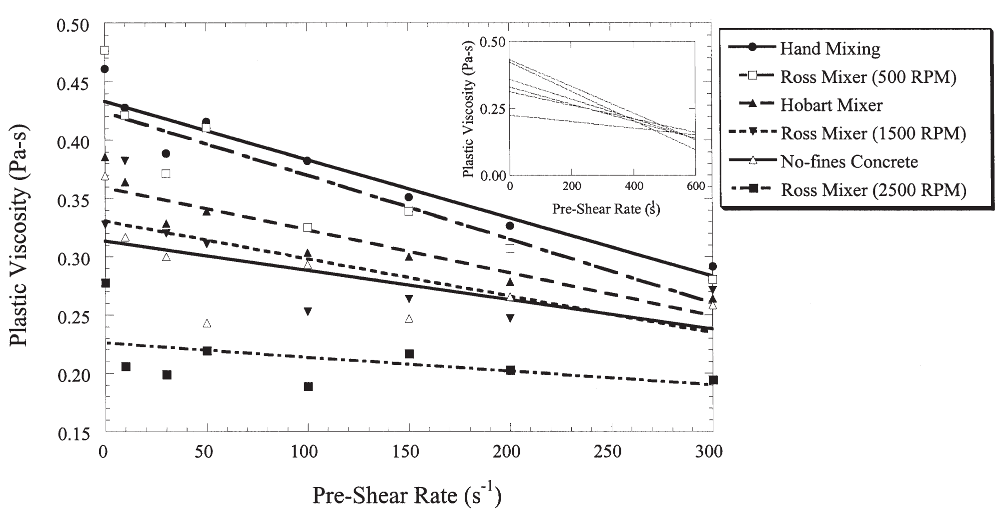

Fig. 6. Plastic viscosity as a function of preshear rate for various mixing techniques. Insert shows extrapolated plastic viscosity best-fit lines converging at a shear rate of approximately 490 s^{-1}.

ture of hand-mixed paste to achieve the viscosity of paste mixed in the Hobart mixer. Using the same approach, the effective shear rate for each of the mixing techniques is presented in Table 2. The paste extracted from the no-fines concrete had a plastic viscosity similar to a hand-mixed paste subjected to a preshear rate of 230 s^{-1}.

Mixing cement paste involves breaking up particle agglomerates. In a well-mixed paste, the number of agglomerates in the suspension is small and the particles are dispersed. In such pastes, there are few hydrate membrane linkages susceptible to disruption by the application of additional shear [1]. Our results agree with this explanation. Both the hysteresis loop area and plastic viscosity of the Ross 2500 rpm paste were less dependent on the applied preshear rate than hand-mixed pastes. The large decrease in hysteresis loop area and plastic viscosity for hand-mixed paste subjected to additional shear also conforms to this theory. These results suggest that high shear-mixed pastes contain fewer agglomerates, a view confirmed by visual inspection [14].

4. Conclusions

A new technique was developed and used to investigate the effects of mixing on cement paste rheology. This was accomplished by measuring the structural breakdown in fresh cement pastes through evaluation of hysteresis loop area and plastic viscosity. The susceptibility of a fresh paste to further breakdown upon controlled mixing in a rheometer was used as a method to compare the efficacy of various mixing techniques. High shear mixing resulted in improved flow properties. The rheology of the paste portion of a drum mixed no-fines concrete was found to be intermediate between moderate sheared (Ross 1500 rpm) and high sheared (Ross 2500 rpm) paste. Although the milling action of the aggregates produced a well-mixed paste, it was not sufficient to fully break down the agglomerated structure of the cement particles.

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