Effect of polyacrylic acid molar mass as a surface modifier on rheological properties of calcium carbonate suspensions

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Abstract: Suspensions of calcium carbonate are of a major concern in various fields, such as coating, painting and ceramics and their rheological properties are very important. The effect of polyacrylic acid (PAA) of different molecular mass as a surface modifier on the surface and rheological properties of the aqueous suspension of calcium carbonate was investigated. The effect of the volume fraction of particles and polymer concentration on the viscosity at lower shear rate was discussed. The flow behavior of the concentrated suspension in the presence of PAA can be explained by the difference of the repulsive force among particles, induced by the adsorbed polymer. The results showed that the dispersibility is more pronounced by the steric hindrance behavior rather than the electrostatic behavior.

Keywords: calcium carbonate, surface modification, poly-acrylic acid, rheology, adsorption

1. Introduction

Calcium carbonate mineral (CaCO$_3$) is a naural sedimentary rock as calcite and aragonite. Calcite mineral is composed of calcium atoms coordinated by six oxygen atoms, while aragonite mineral is coordinated by nine oxygen atoms (Ropp, 2013). Calcium carbonate is used, as a filler material, in a variety of industries including paper, plastics, paint, and pharmaceuticals. Some of the important characteristics that determine its grade and price are its particle size, brightness, strength, hardness, etc. The establishment of the criteria to control rheological properties and the physical stability of its suspension so as to attain a solid volume with adequate fluidity, while maintaining sufficient stability against aggregation and sedimentation of the particles should be taken into consideration (Tobori and Amari, 2003).

During the past years, many investigations have been carried out to know the limitations parameters, which can reduce successful processing (Childs et al., 1999; Liu-Lan et al., 2003; Kim and Creasy, 2004; Koo et al., 2006; Schmidt et al., 2007; Schmidt et al., 2014; Kumar, 2014). The most important parameters are attributed to the variable thermal properties and particle size of the polymer/ composite powder (Goodridge et al., 2012). The blending of the polymer matrix with an environmentally friendly filler material, such as calcium carbonate reduced the manufacturing and material costs, as well as improving energy efficiency (Guo et al., 2014). The dispersing agents, based on polyelectrolyte, provide electrostatic and steric repulsive forces among the particles by the adsorption onto particles surfaces and influence their stability, dynamic properties and the flocculated structure of the suspensions (Zupancic et al., 1997; Inagaki et al., 1999; Ilyin et al., 2016). The effect of adsorbed polymer on the rheological behavior of the higher solid content suspension is not yet well understood (Zaman et al., 2002).

The rheology and fluid characterization is complex. Depending on the viscosity as a function of shear rate and stress, the fluids are classified into Newtonian or non-Newtonian. Newtonian fluids shows a linear increase in stress with increasing shear rates. Most fluids are non-Newtonian, which means that

their viscosity is dependent on shear rate (Shear Thinning). The proper characterization of viscosity must be carried out at a shear rate that is relevant to the specific process (Singh et al., 2016).

Calcium carbonate is often treated with stearic acid to decrease its polarity. It has a strong influence on its thermoplastic structure and distribution. The treated $CaCO_3$ had a significantly higher heat of fusion, moisture resistance and higher tensile strength. It enhances the interfacial interaction between matrix and filler (Cao et al., 2016). The carboxylic acid groups of a modifier can react with a hydroxyl groups on the calcite surface during the condensation reaction, thus, free amino groups on the bound molecule at the surface of the mineral filler material are formed (Goodman, 2005). The hydrogen bonding to an external material can take place, which improves the adhesion between the filler and the polymer matrix. The best-suited surface modifier as well as modification amount can be transferred onwards to a successional investigation in an actual additive manufacturing process (Goodman, 2005).

The aggregation of $CaCO_3$ particles in poly-caprolactone was investigated based on morphology and viscoelastic analysis. The tensile property of the composite as a result of the particle aggregation showed that the particle aggregation gives a negative effect to mechanical performance (Kim et al., 2020). Calcium carbonate–polyamide composites have been prepared through surface modification using 6-amino hexanoic acid, caprolactam and glutamic acid. The modifier agent has an influence on the mechanical properties with respect to the ductility, toughness and stiffness. The modified calcium carbonate as a functional filler showed the impact of particle size and filler quantity on thermal conductivity and crystallization within the polymer matrix. A combination provides a development pathway in additive manufacturing and can be transferred in a subsequent investigation in the selective laser sintering process (Ippolito et al., 2020).

This work aims to investigate the effect of polyelectrolyte, as polyacrylic acid (PAA) with diffirent molecular mass, on the rheological properties of aqueous suspensions of calcium carbonate particles. Suspensions with different volume percent were tested at different shear rate.

2.   Materials and methods

2.1.   Materials

A sample of natural pure calcium carbonate mineral (99.9%) was kindly delivered from Egyptian-Jordanian for Mining Industries Co. The sample was dry ground in a porcelain mill. The size fraction of less than 500 mesh (30 μm) was used in adsorption and rheological studies. Poly(acrylic acid sodium salt) [PAA] with average molecular mass of 2100, 5100 and 8000, Sigma-Aldrich Co, were used as dispersants. Analytical grade NaOH and HCl were used for pH regulation.

2.2.   Methods

2.2.1.   Zeta potential measurements

A Laser Zeta-meter "Malvern Instruments" model "Zeta-Sizer 2000" was used for zeta potential measurements. A sample of 0.01 g was placed in 50 ml double distilled water with definite electrolyte concentration (ionic strength) of NaCl. The pH was adjusted to the required value. The suspension was, then, shaken for 1 hour and transferred into a standard cuvette for zeta potential measurement.

2.2.2. Adsorption measurements

Adsorption experiments were carried out by adding 0.5 g sample to 50 ml of double distilled water at the definite concentration of polymer. After conditioning for desired time, the pulp was centrifuged at 15,000 rpm for 15 min to separate the supernatant. The total organic carbon (TOC) content (residual polymer concentration) in the supernatant was determined using a "Phoenix 8000" Total Carbon Analyzer.

2.2.3. Viscosity measurements

Successful characterization of viscosity and the shear rate are important for a specific application. Many viscometers on the market measure index viscosity but often lack proper characterization of shear rate

and absolute or true viscosity. Absolute viscosity is one of the most important parameters in the development and modeling of applications that involve fluid flow.

A digital rotational viscometer was used according to the Searle principle (Anton Paar, Model DV-3P). Principle of measuring by this viscometer is based on dependency of sample resistance against the probe rotation. The combination of spindles and speed allows an optimal measuring. Its feature can measure viscosity, temperature, shear rate, stress and torque percent. It provides superior range of viscosity/shear rate measurements.

A cup is matched with a so-called spindle that is placed in the sample. The speed on the viscometer is preset and the spindle starts to rotate. The sample in the cup follows this movement and in further consequence the torque (force) required for turning the spindle against the fluid's viscous forces is measured. The sample was first subjected to a torque and then it was allowed to stand for 5 min. The equilibrium shear rate was determined as a function of the torque. Temperature of the pulp was maintained constant in all experiments at 25°C. The Viscometer is L Model with Spindles from L1 to L4. The used spindle is L2 in which Minimum and maximum Viscosity are calculated values for L standard speeds (10 to 200 rpm). With respect to L2 spindle, the minimum viscosity is ranging from 50 to 100000 mPa. S. The cup was a 100 mL glass beaker with a diameter of 10 cm. The formula used is: (Vozarova et al., 2015):

$$\underbrace{\tau}_{\text{Shear Stress}} = \underbrace{\eta}_{\text{Viscosity}} \times \underbrace{\dot{\gamma}}_{\text{Shear Rate}}$$

The shape of the Spindle Used

Scheme 1. Formula by Vozarova et al. (2015), and shape of the spindle used

3. Results and discussion

3.1. Effect of conditioning time on adsorption of PAA

Fig.1. shows the effect of conditioning time on the adsorption of poyacrylic acid of different molecular mass at solid content of 1% and polymer concentration of 1000 mg/l. The adsorption rate was very high within 30 min and then a plateau was occurred after 60 min. This is may be due to gradually decreasing of the e adsorption site and the transpotation of polymer molecules from the bulk liquid phase. So the adsorption is increased with time until saturation (Abdel-Khalek et al., 2020; Selim et al., 2020).
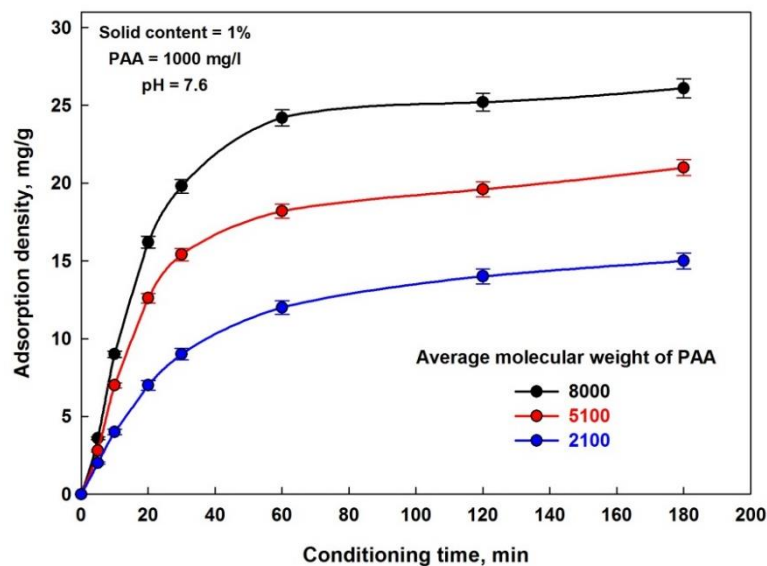

Fig. 1. Effect of conditioning time on adsorption of different polyacrylic acid

3.2. Effect of PAA concentration

Fig. 2 shows the effect of poyacrylic acid concentration on its adsorption density. The adsorption isotherm of PAA onto calcium carbonate, was carried out at constant temperature (25°C), and natural pH 7.6. The adsorbed amount of PAA is increased with increasing the polymer concentration. At low concentrations of PAA, the isotherm is typical high affinity, (Langmuir-type) isotherm, but after monolayer formation, there is further adsorption of PAA. Only a little higher than monolayer concentration, the adsorption layer is probably recognized to allow a denser packing of PAA molecules at the surface, and with higher concentrations of PAA, multilayer adsorption is expected (Duan et al., 2016; Adeyemo et al., 2017).
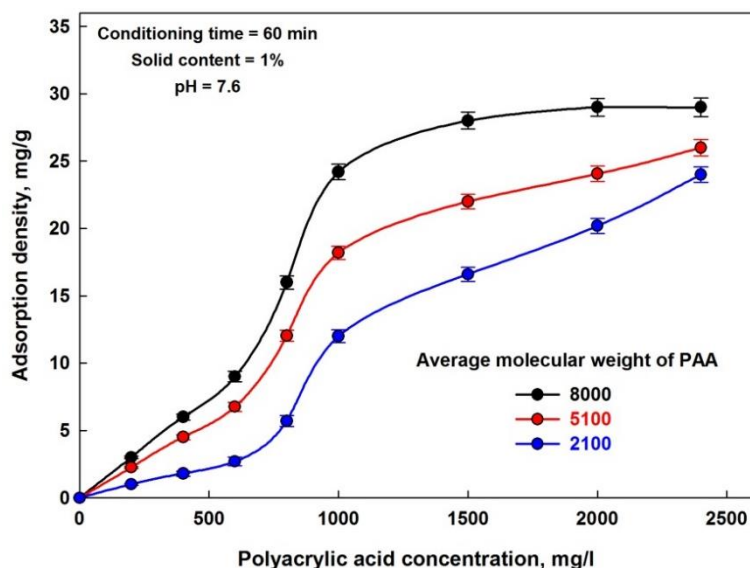

Fig. 2. Effect of polyacrylic acid concentrations on their adsorption

3.3. Zeta potential measurments

There is a debate about the potential–determining ions and the sign of the surface charge of calcium carbonate slurries. The sign of the surface charge of calcite in aqueous solutions has been a matter of discussion for decades already and still ongoing (Moulin and Roques, 2003; Moncho-Jordá et al., 2004; Lakshtanov et al., 2018). Fig.3 shows the zeta potential of calcium carbonate as a function of pH and ionic strength. The surface charge of calcium carbonate was found to be positive over the pH (5 - 12) range. It seems that a slight majority of publications are in agreement with these results (Madsen and Hubbard, 2002). According to the species distribution diagrams, the concentration of (HCO_3^- + CO_3^{2-}) exceeds the concentration of Ca^{2+} in solutions open to atmospheric CO_2 (other species concentrations are negligible), which implies that the surface of calcium carbonate is more rich in calcium ions than in carbonate ions at equilibrium. The equilibrium pH of calcium carbonate suspensions is very much dependent on the partial pressure of CO_2 in solution (Madsen and Hubbard, 2002). The zeta potential of calcium carbonate in different ionic strengths showed a small difference at alkaline pH. While, the significant difference is occurred at pH less than 9, this is may be due to release of CO_2 from calcium carbonate or compression of the double layer with change of the ionic strength (Eriksson et al., 2007).

The effect of PAA concentration and its molecular mass on the zeta potential of calcium carbonate showed that the PAA reverses the surface charge of calcium carbonate to negative due to the adsorption of PAA molecules on calcium carbonate surface, Fig.4. However, there is a minimum in zeta potential at about 80 mg/l of PAA, after which subsequent addition of PAA leads to a slight increase in zeta potential. The isoelectric point is occurred at about 30 mg/l of PAA. The magnitude of the negative charge is increased with increasing the molecular mass of PAA. The influence of NaCl concentration on the magnitude of the charge is small in presence of PAA. Also, PAA/water, (no calcium carbonate) gave very small zeta potential < −1.25 mV and therefore the zeta potential values measured are considered to be accurate (Eriksson et al., 2007).
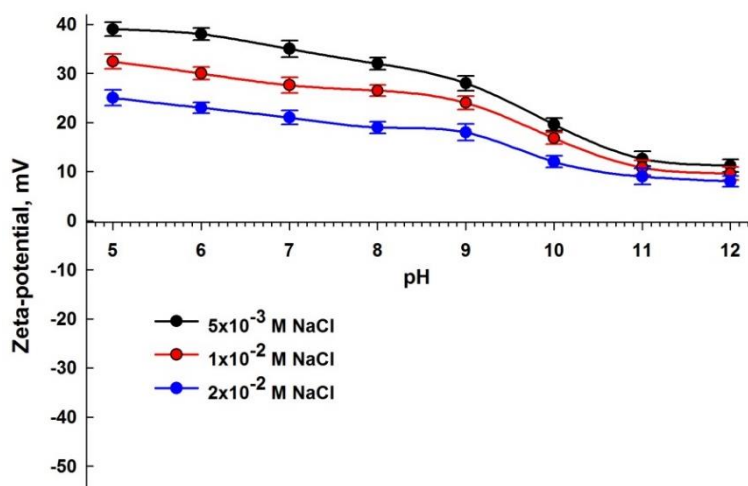
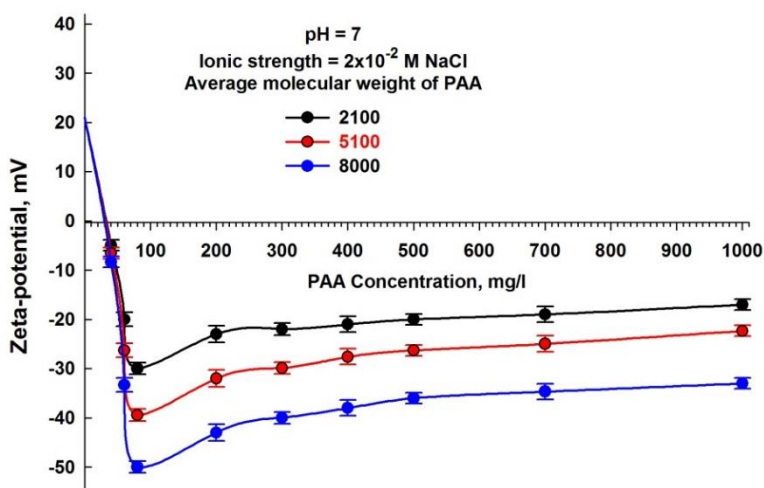Fig. 3. Zeta potential of calcium carbonate in different ionic strengths

Fig. 4. Zeta potential of calcium carbonate as a function type and concentration of PAA

3.4. Rheological properties of calcium carbonate suspension in the presence of PAA

The following results is a part of a project data, and so, the presented results are based on the optimized conditions such as time.

3.3.1. Effect of solid content on shear rate

The shear flow properties of aqueous calcium carbonate suspensions were investigated in the absence of polyelectrolyte. Fig.5 shows the viscosity as a function of the shear rate at different volume fractions for the calcium carbonate suspensions without polymer. The flow curves for these suspensions are different. The viscosity of the suspension without polymer decreased by increasing shear rate. This is in agreement with (Al-Quraisshi et al., 2020). This may be due to that as the particle concentration increases, the surface modified particles form a network structure and exhibited a negative tensile performance. It is reported that the modified CaCO3 particles were percolated only with a 30 wt.%, whereas the unmodified CaCO3 particles percolated with 40 wt.%. Above the threshold, the yield strength is decreased due to the formation of particle aggregates (Kim et al., 2020).

3.3.2. Effect of polyelectrolyte concentration

The relationship between the viscosity, at low shear rate $\approx 31 \ S^{-1}$, and polymer concentration at volume fraction of 20% is shown in Fig.6. The viscosity decreased drastically with increasing polymer concentration.

As mentioned before, Fig.3 and Fig.4, in the suspension without polymer, the particles had a positive charge, but they turned negative after the addition of PAA because the polymer is anionic in nature. Also, the absolute value of zeta potential is increased with increasing the polymer concentration and reached an equilibrium value where the change in zeta potential corresponded to the adsorption behavior. Therefore, it can be considered that the particles in PAA suspensions are electrostatically stabilized by the anionic charge of PAA (Van de Ven et al., 1977).
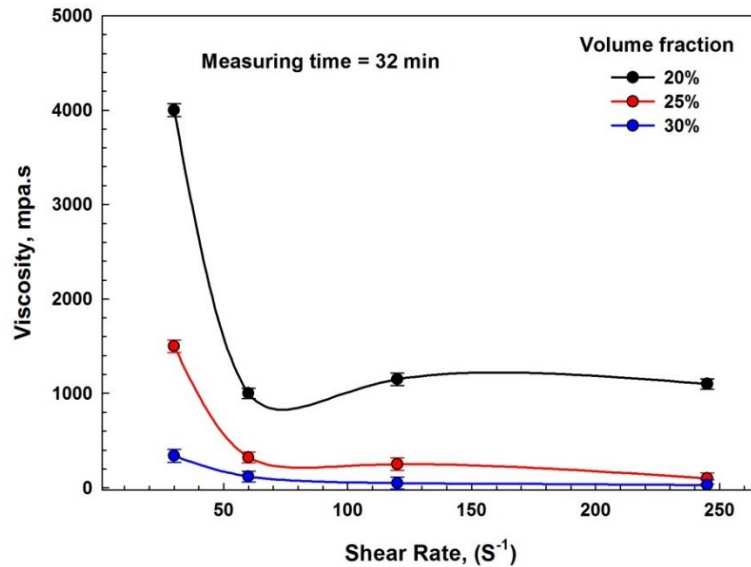

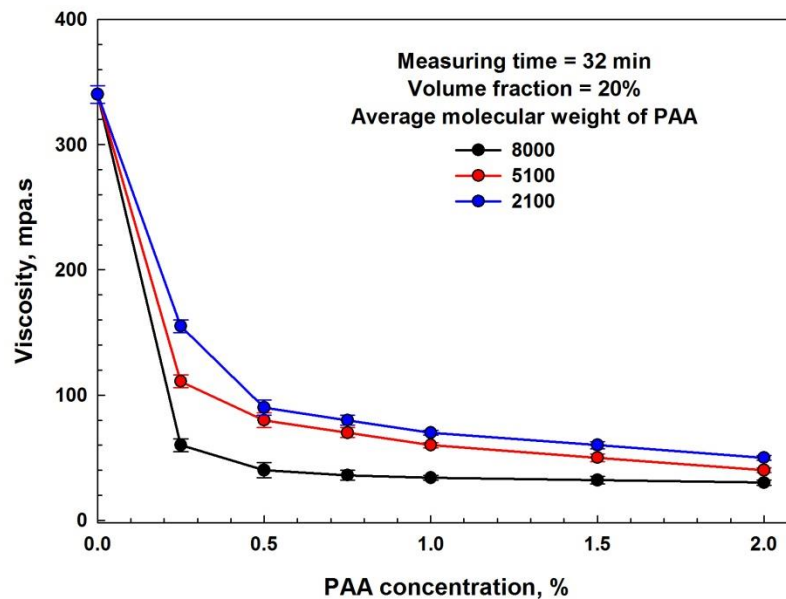Fig. 5. Viscosity against shear rate for $CaCO_3$ suspensions at various volume fractions without polymer

Fig. 6. Effect of polymer concentration on the viscosity of $CaCO_3$ suspension at lower shear rate

3.3.3. Relation between the polymer and flow behavior

Flow behaviour of a suspension in the presence of a polyelectrolyte is governed by the particle-particle interaction that depends on the electrostatic and/or steric forces induced by the polymer adsorption. We investigated the adsorbed amount of the polymer onto $CaCO_3$ particles and the surface charge of particles to evaluate the changes induced by the adsorbed particles, Fig.2. In Fig.7, the shear rate dependence of the viscosity of the suspensions is different. It can be considered that the change of flow by the addition of polymer reflects the dispersed state of particles in the suspension. In general, there are several reports showing that the equilibrium value of viscosity at high shear rate was not observed

in strongly flocculated suspensions but it was observed in weakly flocculate suspensions (Hunter, 1982; O'Brie and Mackay, 2000). According to results obtained, we can recognize that the particles in suspensions without polymers and in concentrated suspensions with PAA were aggregated despite the fact that the viscosity is reduced by the addition of PAA. A surface coating presenting amino acids, improved bonding to the polar groups within the polymer structure, hence improving the mechanical properties (Goodman, 2005). Thus, the coated calcium carbonate with polyacrylic acid (PAA) at the desired fineness and dispersibility and rheological properties for plastic, paper and paint industries could be prepared.
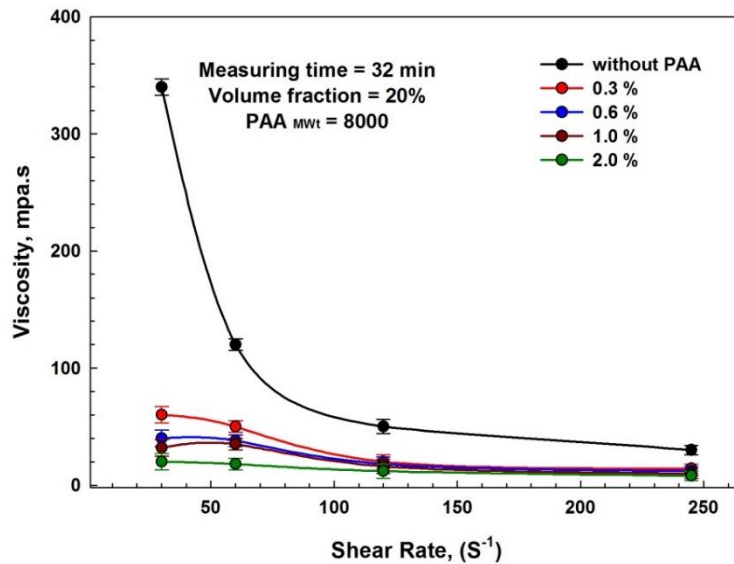
Fig. 7. Effect of shear force on the viscosity of $CaCO_3$ suspension in the presence of PAA

4. Conclusions

The effect of polyacrylic acid (PAA) of different molecular mass, on the surface properties and rheological behavior of concentrated aqueous suspensions of calcium carbonate. Shear flow properties of concentrated suspensions can be explained by the repulsive forces conferred by the polymer adsorbed to the particle surface. The adsorption kinetics indicates fast adsorption where the equilibrium can be achieved within 30 min. The zeta potential of calcium carbonate was found to be positive in the pH region investigated. The higher molecular mass of PAA enhanced the calcium carbonate bahavior.The species distribution in water is governed by the partial pressure of CO_2 in water and is the most important factor determining the surface charge of pure calcium carbonate surfaces at equilibrium. The effect of PAA on dispersibility is more pronounced by the steric hindrance behavior rather than the electrostatic behavior. The coated calcium carbonate with polyacrylic acid (PAA) at the desired fineness and dispersibility and rheological properties for plastic, paper and paint industries could be prepared.

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