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EARLY STAGES OF SOLIDIFICATION/STABILIZATION OF STORM WATER RUNOFF SOLID RESIDUALS IN CEMENT

Non-conventional DTA

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This paper presents a study of a cement-based solidification/stabilization process of storm water runoff solid residuals by non-conventional differential thermal analysis (NCDTA). The study was used to investigate the early hydration stages of a type I Portland cement containing the raw residual, two fractions of the residuals (coarse and fine), and two additives (quicklime and sodium bentonite). During these stages the fine fraction of the residuals retards the hydration reactions more than the coarse one, and both fractions have components that are reactive during the hydration process. When sodium bentonite is present in the pastes, the higher the initial cement content of the pastes, the lesser is the reactivity of the residuals. The presence of quicklime, which undergoes simultaneous highly exothermal hydration, accelerates the cement hydration reactions as well as those due to the presence of the residual solids. In these quicklime-containing compositions, the effect of sodium bentonite is similar to that when no quicklime is added, except when the whole residuals are used.

Keywords: *cement, non-conventional DTA, solid residuals, stabilization, storm water*

Introduction

The usual treatments for hazardous wastes are incineration, recycling, agriculture and landfill disposal. Landfill is currently the cheapest disposal option with the lowest cost [1].

Rainfall runoff from urban roadways often contains significant loads of heavy metals, which come from brakes, tires, frame and fuel. According to Sansalone and Buchberger [2] who performed several highway storm water residual collections in an experimental site located at Millcreek Expressway, I-75 in Cincinnati, the metal elements in water are present as dissolved and particulate-bound fractions. This can occur due to mainly pavement residence time, rainfall pH, solubility of the metal elements and the nature and quantity of present solids. Disposal of storm water runoff can contaminate groundwater and nearby surface waters. One of the disposal techniques is in land but it is necessary some care considering the presence of heavy metals, organic hazardous and pathogenic microorganisms. The soil pH and the sludge pH adjustment can reduce pathogen content and minimize the leaching potential of heavy metals. Pathogens and other contaminants have the potential to be spread from the landfill or land application sites unless sufficient precaution is taken to reduce their concentration in the sludge [3, 4].

Cement-based stabilization/solidification of toxic and hazardous wastes is a chemical treatment process, which aims to either bind or complex the components of a hazardous waste within the solid cement matrix [5–8].The addition of hazardous wastes to cement in the solidification process can affect the process in different ways. Accelerating chemicals generally shorten the induction period of cement hydration and increase the maximum rate of heat output, while retardants have opposite effects [9, 10]. These effects, which occur during the early stages of cement hydration, can be studied by NCDTA or other calorimetric devices [11] and are based on the fact that there is a fairly linear relationship between the degree of cement hydration and the total heat liberated from the pastes [12, 13].

According to Frey [8], who used conduction calorimetry, cadmium hydroxide has an accelerating effect on cement hydration due to its size similar and charge to calcium and it is used as a nucleation site for $Ca(OH)_2$ precipitation. Cadmium promotes early hydration of aluminate phases too. In high pH media,

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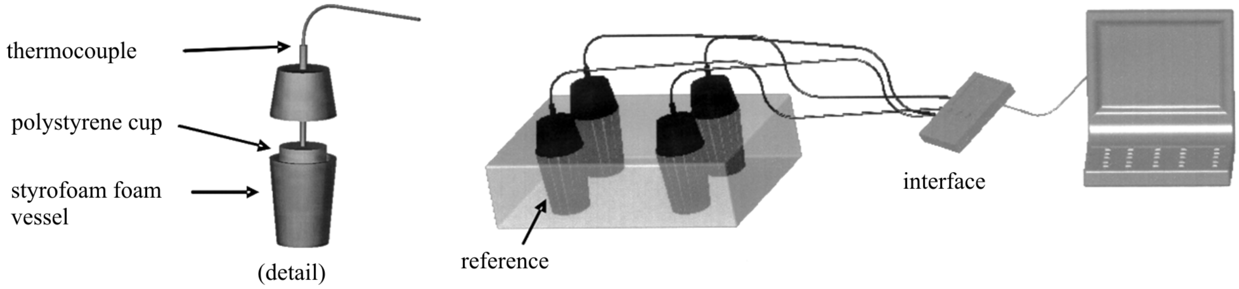


Fig. 1 Schematics of the NCDTA system

lead is dissolved and retards the cement hydration and it may slow down the nucleation of calcium hydroxide. For this reason, lead can not be used as a nucleation site, it is not coated effectively by hydrated calcium silicates (C–S–H) and can be leached from the system as well.

Portland cement, sodium bentonite, quicklime and the waste are used in this research. The addition of clay has the property to adsorb the waste and to fix it with the cement, decreasing the possibility to leach the waste. Lime applied to cement, according to Fang [14] can enhance the Portland cement hydration. This paper presents a method to analyze the solidification/stabilization process of the cement pastes containing storm water runoff residuals and additives by NCDTA and to evaluate the effects of the waste and additives on the early stages of cement hydration.

Experimental

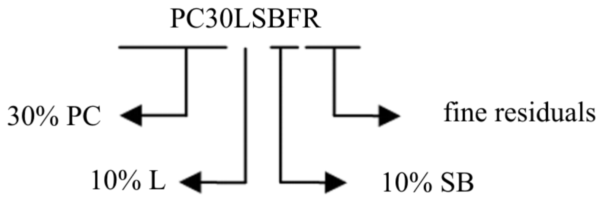
Materials and methods

The following materials are used: a Portland cement Type I, named as PC, a commercial non-treated natural sodium bentonite named as SB and a quicklime, named as L, which contains 94.1% of CaO according to the supplier. Storm water residuals were collected at interstate road (I-10), urban area in Baton Rouge, LA, USA in the experimental site located under the bridge of City Park Lake. The road has a Portland cement concrete pavement in this area. The samples were collected from pipe drainage into a sink with 2130 L capacity. The water was drained from the top and the solid waste was collected from the bottom of the sink, dried in a hot room at 60ºC, ground and separated in different size fractions. Three different particle size fractions were analyzed: total gradation (TR) samples with no separation; coarse fraction (CR) with particle size between 75 (Tyler 200) and 850 μm (Tyler 20); fine fraction (FR) with particle size lower than 75 μm.

NCDTA presents the same basic principle as the conventional Differential Thermal Analysis (DTA), but differs in the fact that there is not an externally controlled heating or cooling process as in DTA. The difference between the sample and reference temperatures (T_s–T_r), which is measured as a function of time, is due to the exothermic reactions that occur within the sample and the reference at ambient temperature. The higher is the inert content in total mass, the lower will be the instantaneous value of (T_s–T_r) for a same total generated heat. Thus, the total heat evolved up to a time *t*, on cement mass basis, was estimated by multiplying the integral of the NCDTA curve from *t*=0 to *t*=*t* by the rate between the total mass of the paste and its cement mass.

As shown in Fig. 1 each measuring device consists of a polystyrene cup inserted in a Styrofoam foam vessel. Both cup and vessel have their respective leads. The thermocouples are inserted into the samples through these leads. There are 3 units for samples and one for the reference. Thermocouples are inserted into the sample and reference. A Vernier Lab Pro interface connects the thermocouples to the computer, which acquires and processes the temperature data. The raw materials are weighted and left near each other and to the equipment 24 h before beginning an experiment to have the same initial ambient temperature. Samples were prepared with Portland cement type I (PC) by using masses equal to 20 and 30% of the residuals mass. Lime (L) and sodium bentonite (SB) masses, when used, were 10% of the residuals mass.

For each residuals fraction *R*, (where *R* can be FR – fine fraction; CR – coarse fraction and TR – total residuals), the following compositions were prepared: PC20R; PC20LR; PC20SBR; PC20LSBR; PC30R; PC30LR; PC30SBR; PC30LSBR. Below is shown an example of the way each sample was named:



The reference for all the NCDTA runs is a cement paste, with 0.5 water/cement mass ratio, prepared more than 90 days before beginning the experiments, in order to have a compatible and non-reacting reference for all the analyses. The mass of the samples containing the residuals is referred to the dried mass. To have good mixing of sample components, the water/residuals (W/R) mass ratio was different according to the particle diameter range: for the fine fraction, W/FR was 0.5; for the coarse fraction, W/CR was 0.3 and for the total gradation, W/TR was 0.2. The difference of the water/residuals ratio for each waste gradation is necessary to have good workability and homogeneous pastes when adding the water to the solid mixture of cement and additives. The use of the same W/R ratio for all gradations of the residuals was tested initially, but the final respective consistencies were completely different, with a too liquid paste for the samples with W/TR 0.5. In the case of the fines, with a W/FR ratio of 0.3 and 0.2, the final pastes could not be considered homogeneous by the difficulty of mixing. It was noted that the water was sorbed by the fine residual particles much more than by the coarse residual particles. A previous study of specific surface area (SSA) measurements of the solid residuals, performed according to Sansalone *et al*. [15] procedure, resulted in a range from 12 to 28 m^2 g^{-1} for the coarse fraction and from 30 to 3 m^2 g^{-1} for the fine fraction, which explains the higher water sorption by the latter residuals.

Results and discussion

Figure 2 shows the NCDTA curves of control pastes PC, PCL, PCSB, PCLSB, prepared without residuals, to see the influence of L and SB (separate and together) on cement hydration. Figure 3 shows the evolution of the respective accumulated total heat flow as a function of time. The water/total solids mass ratio was 0.5 in these samples and with an additive/cement mass ratio of 0.1, for each additive.

According to Dweck *et al*. [11], Zhou and Beaudion [13] and Gilliam and Wiles [16], the first peak, in similar calorimetric curves as shown in Fig. 2, for the PC case, is a combination of exothermic early reactions, as the calcium aluminate hydration, which begins to occur in the first minutes of mixture with the water. The second main peak, is due to calcium silicate hydration, forming hydrates (CSH) and calcium hydroxide (CH). The samples containing lime, because of its exothermal hydration, present an increase of the temperature in the early stages, which promotes an accelerating effect on cement hydration. PCL sample shows the highest peak, which occurs after 5 h of hydration.

PCSB on NCDTA curve shows that SB also accelerates the hydration, as can be observed by the reduction in time of the highest peak of temperature in about 1 h, compared to the PC case. The total evolved heat after 40 h of hydration, on cement mass basis, increases in the following sequence: PC<PCSB<PCLSB<PCL.

Pastes with fine fraction residuals were analyzed considering separately the samples with 20 and 30% of Portland cement and respective NCDTA curves are shown in Figs 4 and 5.

The same initial accelerating behavior was observed with 20 and 30% of Portland cement in PC20LFR and PC30LFR samples but with a lower highest temperature difference than PCL sample. Samples with SB and FR, PC20SBFR and PC30SBFR apparently did not present any exothermic peak considerably affected by the waste presence. The samples containing L show a high initial exothermal effect due to its hydration. This effect happens in the first hours in all the pastes containing it.

According to Cocke and Mollah in Spence [17] zinc can form hydroxides in solution in the pH>8, such as $Zn(OH)_4^{2-}$ and $Zn(OH)_3^{-}$, which can be adsorbed to the negative surface of the C–S–H at high pH. The same behavior can be expected from lead with adsorption by silicates and/or precipitates as sulfates forming a membrane that slows the hydration

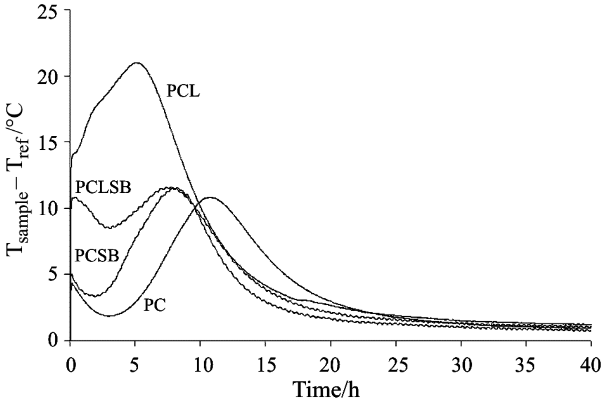


Fig. 2 NCDTA curves of the first control samples

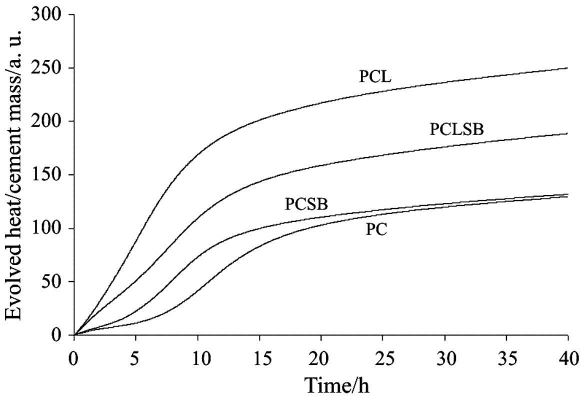


Fig. 3 Accumulated evolved heat of the first control samples

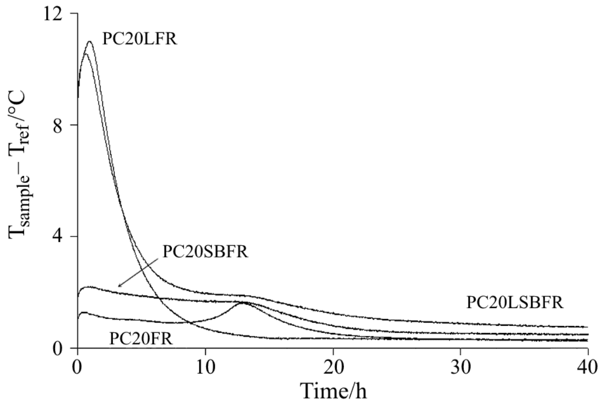


Fig. 4 NCDTA curves of FR pastes with 20% of PC

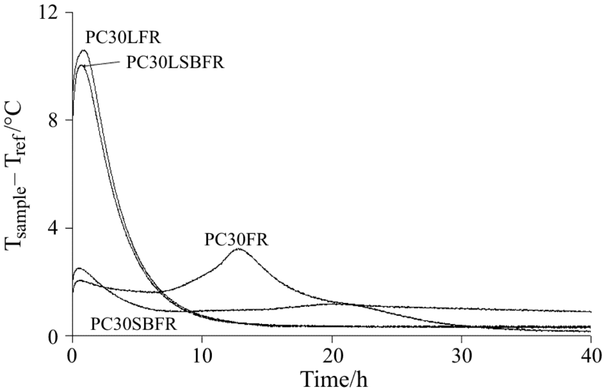


Fig. 5 NCDTA curves of FR pastes with 30% of PC

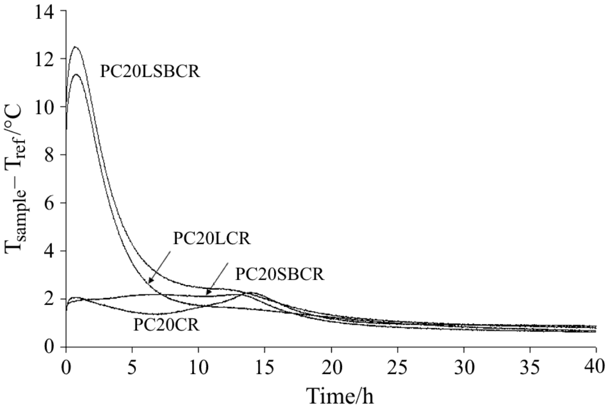


Fig. 6 NCDTA curves of CR pastes with 20% of PC

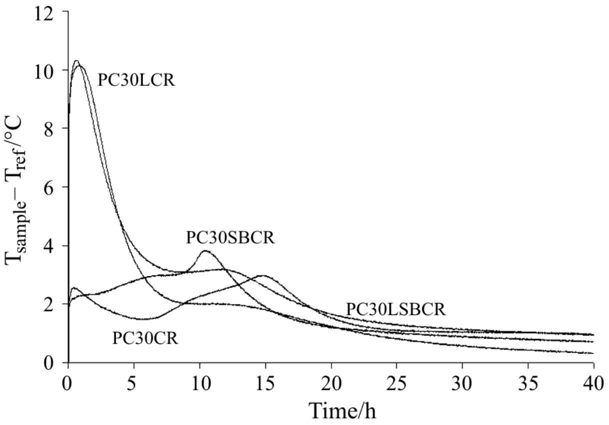


Fig. 7 NCDTA curves of CR pastes with 30% of PC

process. They also state that cadmium can stay in the C–S–H surface and retards the cement hydration. As the C–S–H formation contributes with the highest percent of energy release during the early stage of cement hydration [11], this retarding effect decreases the total evolved energy.

A chemical analysis of storm water residuals was performed. The equipment used is a PerkinElmer Élan 9000 ICP-MS analyzer. The results show that the concentrations of Cu, Zn, Cd and Mg were higher for FR than CR. Thus, the higher content of these metals present in the fine residuals may explain its higher retarding effect on cement hydration than CR, as will be further discussed.

The NCDTA curves of coarse fraction waste pastes with 20 and 30% of PC are shown respectively in Figs 6 and 7. It can be noticed that in PC20SBCR sample case, the calcium silicate hydration peak is not so well seen as in the case of PC30SBCR sample, which maximum exothermal effect ‘emerges’ after at 10.5 h of hydration. As SB accelerates the paste reactions since the beginning of the hydration, when there is 20% of cement, the lesser exothermal effect due to a lower calcium silicate content is probably hidden by other simultaneous exothermal effects by other reactions.

When CR and FR NCDTA results are compared, it is observed that the coarse residuals apparently have a different behavior than the fine ones. Besides the fact of the higher metal content previously discussed, the particle size of the material is an important parameter that may interfere the cement hydration in S/S processes [17]. The lower is the particle size of the waste, the higher is the probability of its reaction with cement and in the present case, it must be also considered that the fine residual particles have a compatible diameter range with that of cement. In the case of the coarse fraction, it seems that, in these early hydration stages, it also retards the cement hydration but in a lower degree than FR does, because of the probable lower reactivity of their particles.

Another point to be considered is the reduction of the water amount of reacting system. Because of the necessity to increase the W/FR ratio to 0.5, when compared to W/CR ratio of 0.3, this extra water differently influences the cement hydration. For lower ratios, non-reacting water amount is lower and according to Spence [17] the resulting temperature of the system is higher, which accelerates the cement reactions and a higher total heat is evolved, as shown in Figs 10 and 11, when comparing corresponding FR and CR cases.

As discussed before, the metals may have different retarding effects on cement hydration considering their concentrations and respective particle sizes, but other component effects also may be present. Sulfur analysis of FR, CR and TR fractions was performed in a Sulfur Element Analyzer Model SC-431 LECO, Inc. The results indicate that the FR has higher sulfur content than the other fractions, mainly as sulfates. According to Cincotto [18], the sulfate presence retards the C_3A hydration but if it is present as a sodium, magnesium (which is also in higher content in FR) , ammonium and some other sulfate compounds, it avoids the ettringite formation and reduces the cement hydration process. Another reason may be the zinc presence in the waste. Zn is the metal with the highest content in FR and zinc hydroxide is formed during the process, which in turn has a coating behavior on cement grains producing a retardant effect on its hydration [16, 18], its presence seems to be one of the main causes of FR paste behavior.

The NCDTA curves of pastes containing total gradation waste (TR) are shown in Figs 8 and 9. The samples containing SB show a little higher exothermal effect at the first hours when compared to the corresponding pastes without its presence, confirming its accelerating effect on the hydration reactions within the paste. As seen in the CR cases, when all other components of the paste are the same, the higher is the cement content, the higher is the exothermal effect shown in the corresponding NCDTA curve.

The total estimated accumulated heats evolved from each paste, on cement mass basis, with and without lime presence, at 40 h of hydration are shown, respectively, in Figs 10 and 11. Samples named 100NR (no residual sample), represent the first control samples evolved heat curves shown in Fig. 3. The other results were obtained from corresponding curves of the samples of Figs 4 to 9 and they were ordered by sets with and without SB, in pairs of samples with same fraction of residuals and same content of cement. As an example, the 20FR case of the PCSB set, corresponds to the sample originally named as PC20SBFR. Main conclusions are presented in the following item.

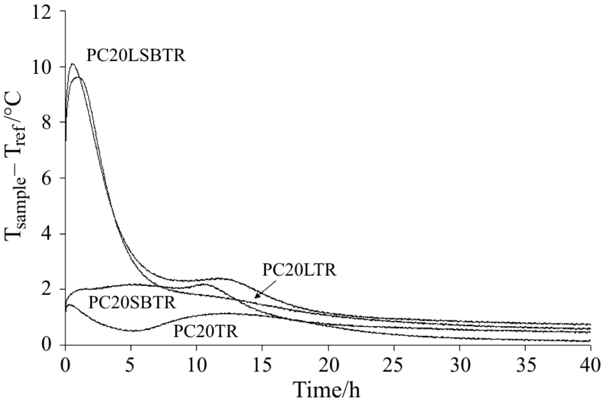


Fig. 8 Non-conventional DTA for total fraction samples with 20% of PC

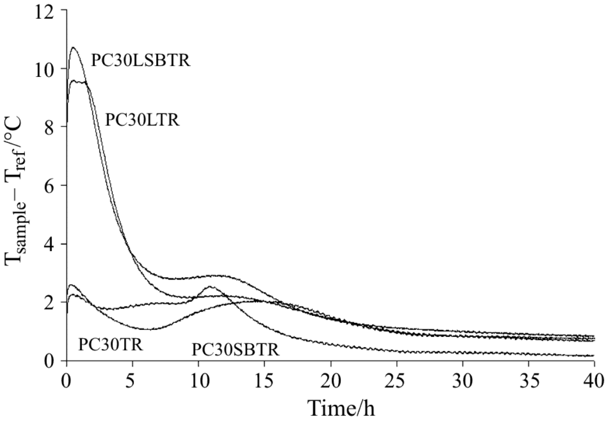


Fig. 9 Non-conventional DTA for total fraction samples with 30% of PC

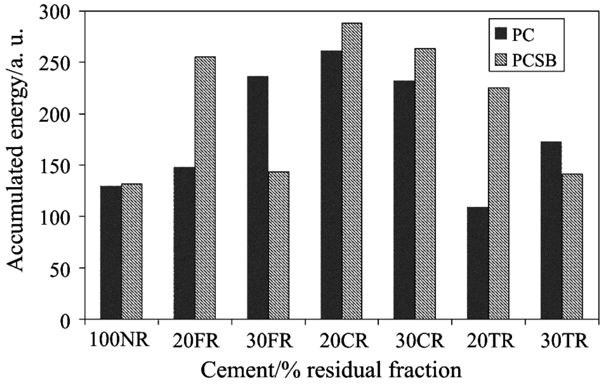


Fig. 10 Total evolved heat from pastes without lime at 40 h of hydration

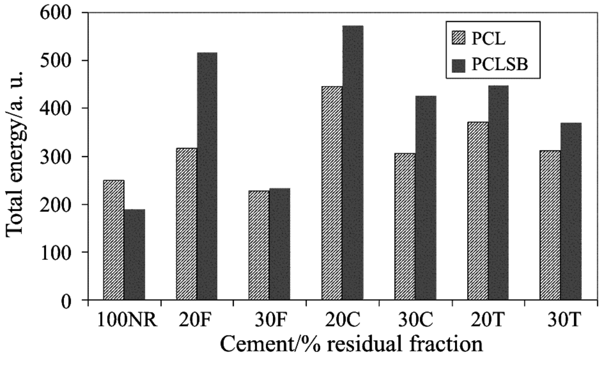


Fig. 11 Total evolved heat from pastes with lime at 40 h of hydration

Conclusions

The fine fraction of the residuals retards the occurrence of the several early hydration reactions more than the coarse one, due mainly to the higher concentrations of Cu, Cd, Zn, Mg and to the higher specific surface area of the particles.

Both fractions have components that are reactive during the hydration process. A higher water/solid ratio had to be used in FR than in CR samples, due to the higher water sorbing properties of the former. The lesser amount of water present in CR pastes contributed to their higher temperature levels during the early hydration stages, accelerating cement hydration reactions and increasing the accumulated evolved heat during their NCDTA analysis.

When sodium bentonite is present in the pastes, the higher is the initial cement content of the pastes, the lesser is the reactivity of the residuals, which have a retarding effect on cement hydration reactions.

The presence of quicklime, which undergoes simultaneous highly exothermal hydration, accelerates the early stage cement hydration reactions as well as those due to the presence of the residual solids. In these quicklime-containing compositions, the effect of sodium bentonite is similar to that when no quicklime is added, except when the whole residuals are used.

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