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CHARACTERIZATION OF HYDRAULIC MORTARS BY MEANS OF SIMULTANEOUS THERMAL ANALYSIS

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The properties of hydraulic mortars were studied by means of simultaneous thermal analysis (STA), according to a procedure proposed in the literature. Hydraulic limes, cement and/or slaked lime were mixed using different proportions of both inert and reactive aggregates, in order to test the effectiveness of such procedure in distinguishing the different degree of hydraulicity of such samples. The use of the normalized coordinates suggested in the literature results in overlapping of the clusters of different kinds of mortars. Modified coordinates are proposed, which give promising results in view of outlining a 'master curve' of hydraulicity.

Keywords: *cement, crushed brick, hydraulic binder, hydraulic lime, pozzolana, simultaneous thermal analysis*

Introduction

The physical-chemical characterization of ancient mortars nowadays is almost a regular step in the restoration of historic buildings, with a twofold aim: a) to supply analytical documentation of the constitutive materials and the building techniques; b) to achieve guidelines for the use of materials that are the most suitable. One of the most interesting aspects is to ascertain what kind of binder was used in the mortar, i.e. to distinguish between an air-hardening and a hydraulic system. Actually the latter shows in general lower porosity and, therefore, high strength and low permeability, both properties being relevant to produce the mortar for a restoration operation that fulfils the requirements of both compatibility and durability.

A great number of scientific papers [1–10] are available on the hydraulicity of ancient lime mortars, which use thermal analysis as a valuable analytical tool. They measure both the mass loss due to carbon dioxide, released by decomposition of the carbonates produced during the air-hardening of slaked lime, i.e. calcite and magnesite, and the mass loss due to the release of the water bound to hydraulic compounds, such as hydrated calcium silicates and aluminates. The general approach is that plotting such values, unmodified or arranged into normalized coordinates, should result in grouping the data into clusters according to the different typologies of mortars. As clearly underlined in [11], this simple approach is complicated by the great variety of mortars that can occur in the restoration of a historic building: different constitutive materials (e.g. slaked lime, hydraulic lime, pozzolanic and crushed bricks mortars), different conservation conditions, differences in the composition and proportion of aggregates with respect to binder. In particular the latter aspect proved to be critical [3], as the results of thermal analysis are affected by the accuracy in the separation of binder and aggregates.

Within this context, in order to validate the proposed normalization procedures, simultaneous thermal analysis was performed on several samples ad hoc prepared, according to simple recipes, so that a progressive degree of hydraulicity could be achieved. The coordinates suggested in [1] were the starting point to propose a new method of plotting data, which seems to improve the effectiveness and the reliability in grouping different mortars into clusters according to their properties.

Experimental

Materials

Different samples were prepared, with the aim of testing materials with progressive hydraulic properties. They are listed according to a presumed increasing hydraulicity of the binder and marked by letters related to their composition.

Binders

L	Slaked lime
LP	Lime plus Portland cement 3,25 (80/20 mass%)
LC	Lime plus cement 3,25R (70/30 mass%)
CL	Lime plus cement 3,25R (30/70 mass%)

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CB (Crushed brick) mixture of slaked lime and metakaolin
S Commercial mixture of slaked lime and Santorini earth
HL Hydraulic lime NHL3,5
P Portland cement 3,25
C Cement 3,25R (UNI-EN 459-1 Standard)

For all of the binding systems, but slaked lime, samples were prepared either without any aggregate (HL, C, LC, CL and CB) or using polyethylene pellets to reduce the shrinking during curing, whereas, because of the well known problems in carbonation of lime putty, samples L were prepared only in the form of mortars, using inert aggregates.

Furthermore, the following mortars were prepared using quartz aggregates, in order to investigate the influence on the STA results:

Mortars

LP with binder/aggregate volume ratio 1/3 and 1/10
CL and LC with binder/aggregate volume ratio 1/3
S with binder/aggregate volume ratio 1/3 and 1/10
CB with binder/aggregate volume ratio 1/3
HL with binder/aggregate volume ratio 1/3
C with binder/aggregate volume ratio 1/3

The results are presented in an order that follows in some way the sequence of samples preparation, which was regulated by the progression in the results of STA.

Methods

Samples were cured at 40°C and 99±1% relative humidity for at least 90 days and underwent thermal analysis as taken from the curing box.

As for the mortars, two different sets of samples were prepared [2, 3]: *i*) the material was just powdered, including binder and aggregates; *ii*) first the material was mildly pounded in order to separate binder from aggregates, then was sieved at 53 μm to enrich it into the binder and finally powdered.

Tests were performed using a simultaneous thermal analyzer Netzsch STA 409, heating rate 10°C min^{-1} in the range 30–1000°C, in static air.

Results were processed according to [1–3], measuring the mass loss in four consecutive temperature ranges:

- 30–120°C hygroscopic water
- 120–200°C water from hydrated salts
- 200–600°C water structurally bound to hydraulic components
- >600°C carbon dioxide from carbonates decomposition

The mass loss in the range 120–200°C was not significant within this work, as the samples ad hoc prepared did not contain soluble salts, so the relevant data will be referred to as H_2O_{abs} (30–120°C), H_2O (200–600°C) and CO_2 (600–1000°C).

It is worth underlining that such a sharp distinction of temperature ranges is just a working assumption, even though widely used and validated in the literature.

Results and discussion

The first step of the program was to analyze the simplest cases, i.e. samples made of binder alone, without any effect of the aggregates. The results of thermal analysis on binder samples are reported in Table 1: in columns 2–4 the percentage mass loss in the selected temperature ranges, in column 5 the inverse of the dimensionless

Table 1 Results of STA on binder samples

Sample ID	H_2O_{abs}/mass%	H_2O/mass%	CO_2/mass%	CO_2/H_2O	H_2O/H_2O_{abs}	CO_2/H_2O_{abs}
HL1	0.7	2.7	19.9	7.4	4.0	29.7
HL2	1.5	4.6	24.1	5.2	3.1	16.2
S	2.7	7.2	13.9	1.9	2.6	5.1
P	2.2	8.3	21.6	2.6	3.8	10.0
C	1.4	2.0	8.9	4.4	1.4	6.3
CL	2.1	2.3	20.3	9.0	2.4	9.5
LC	0.2	2.1	28.4	13.2	4.0	56.7
LP1	0.7	2.3	28.8	12.5	3.2	40.4
LP2	0.3	1.6	15.0	9.3	5.4	50.4
LP3	0.6	2.5	31.6	12.6	4.0	50.6
L1	0.3	1.6	28.7	17.7	4.8	84.4
L2	0.2	0.8	17.6	21.2	3.5	74.2
CB1	1.2	3.2	15.5	4.8	2.6	12.4
CB2	1.7	2.5	15.5	6.2	1.5	9.3
CB3	1.8	3.1	19.8	6.4	1.7	11.1

hydraulicity index from the literature, in columns 6 and 7 two proposed dimensionless coordinates.

Such data are presented in Fig. 1 according to the coordinates proposed in [1, 3], plots a–c on the left column. Hollow symbols are used for slaked lime, the solid ones for highly hydraulic binders, the grey ones for intermediate systems, the x for hydraulic mixtures of slaked lime and finely powdered metakaolin. As a general comment, the normalization of data proves to be only partially effective in grouping data according to their degree of hydraulicity. The best result is shown in plot b, were a sort of exponential ‘master curve’ of hydraulicity is outlined, though the scattering of points with respect to both abscissa and ordinate seems to be high even for samples of the same type.

In an attempt to improve the representation of data, the coordinates were modified according to some considerations on the relation between hydraulicity of mortars and their attitude to absorb hygroscopic water [3]. In fact, as a consequence of the curing procedure, all of the samples underwent STA in the same conditions, i.e. after at least 90 days of conditioning at 40°C and 99±1% humidity. So, taking advantage of such prerequisite, it is reasonable to assume that the amount of hygroscopic water, i.e. the mass loss measured during STA in the temperature range 30–120°C, is strongly affected by the presence of hydraulic compounds in the set binder. According to this assumption, the hygroscopic water H_2O_{abs} could be used as an additional parameter to emphasize the differences between air-hardening and hydraulic binders.

In Fig. 1 plots d–f on the right column show the effect produced on the representation of data by the use of H_2O_{abs} as normalizing factor for one or both of the coordinates proposed in the literature. The results seem to be very satisfactory, as the grouping into clusters of points corresponding to similar binders is improved with respect to both coordinates; furthermore, the overlapping of clusters of different types of binder is reduced. This is particularly clear in the case of mixtures of cement and slaked lime, diamonds and triangles in Fig. 1, as the order of the points from left to right follows the progression of cement content. The most effective adjustment proves to be the normalization of CO_2 by H_2O_{abs} shown in Fig. 1 plot f, as such parameters are in inverse dependence on the percentage of hydraulic compounds in the binder.

As reported in [2], one of the major problems that hinders the clustering of hydraulicity data of ancient mortars is the presence of aggregates, which affects the

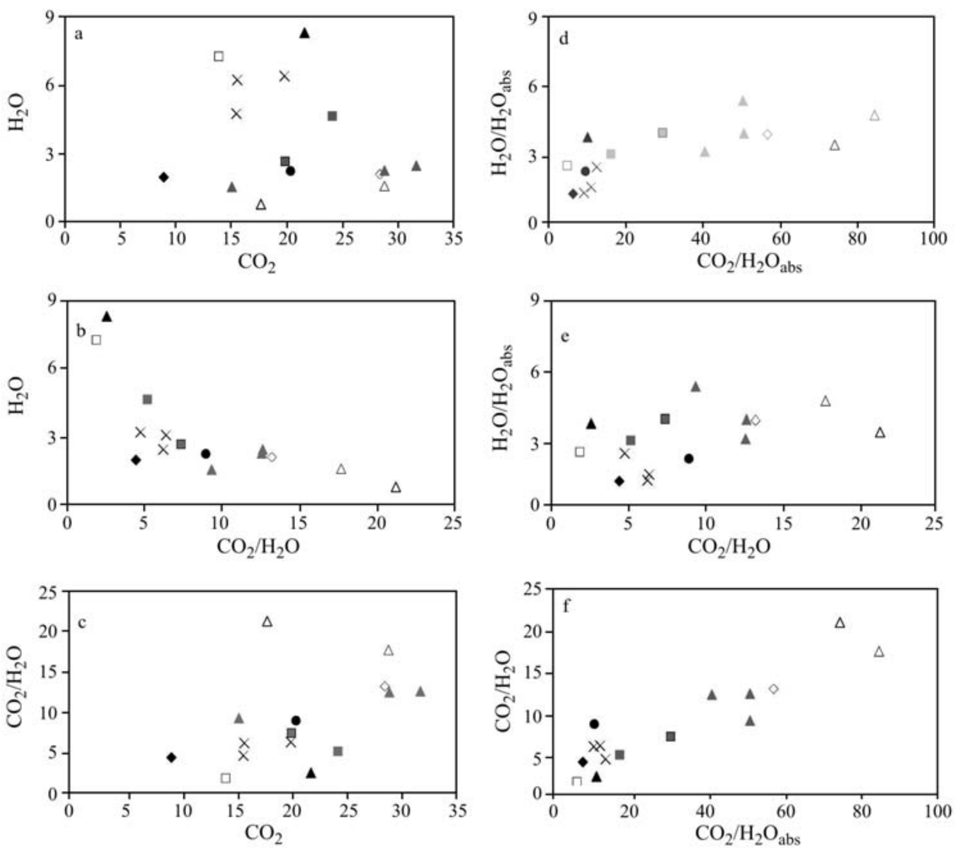

Fig. 1 Representation of hydraulicity of samples made of binder, without aggregates. a–c – coordinates proposed in the literature; d–f – modified coordinates; ■ – HL, □ – S, ▲ – P, ◆ – C, ● – CL, ◇ – LC, △ – LP, △ – L, × – CB

results of the STA either adding a misleading contribution to the mass loss of the binder (e.g. carbonatic aggregates) or diluting the true mass loss percentage of the binder (e.g. quartz). That's why it was a critical step to validate the coordinates proposed in this work, introducing the effect of aggregates, i.e. preparing and testing mortars with different aggregate to binder ratio, both before and after sieving.

The data of STA on different mortars are shown in Fig. 2. Again the results obtained using the coordinates from literature, plots a–c on the left column, are compared with results obtained using the modified coordinates, plots d–f on the right column. As already observed on the samples of binders, also in the case of mortars taking into account the hygroscopic water seems to improve the effectiveness of the clustering procedure. Again, the most effective adjustment proves to be the normalization of CO_2 by H_2O_{abs} shown in Fig. 2 plot f. In fact for hydraulic mortars such modified abscissa is strongly affected by the higher capacity of the binder, with respect to the aggregates, of absorbing hygroscopic water.

Comparison between the two columns in Fig. 2 evidence that, using the coordinates proposed in previous works [1–3], the objective of grouping different mortars into clusters according to their hydraulicity is best fulfilled by using H_2O *vs*. CO_2/H_2O, Figs 1b and 2b, respectively, whereas the results can be improved using the modified coordinates proposed in this work, the best being achieved by plotting CO_2/H_2O *vs*. CO_2/H_2O_{abs}, Figs 1f and 2f for binders and mortars, respectively.

The improvement of the clustering procedure is clearly pointed out in Fig. 3, where only data relative to a specific binder, i.e. the Santorini lime, are reported. Each point refers to a different composition of the sample: pure binder, mortars with binder/aggregate ratio 1/3 and 1/10. For mortars, further differentiation is present: *i*) sample as a tout venant, i.e. ground with the original ratio binder/aggregate; *ii*) sample enriched in binder by sieving. Even in the presence of only one binder, the use of the coordinates suggested in the literature, left column, Figs 3a–c, leads to a significant scattering of data, due to the influence of parameters others than hydraulicity of the binder. In particular, the sieving of samples proves to be quite ineffective in reducing the disturb produced by aggregates. On the contrary, the proposed coordinates allow a satisfactory clustering even for not sieved samples.

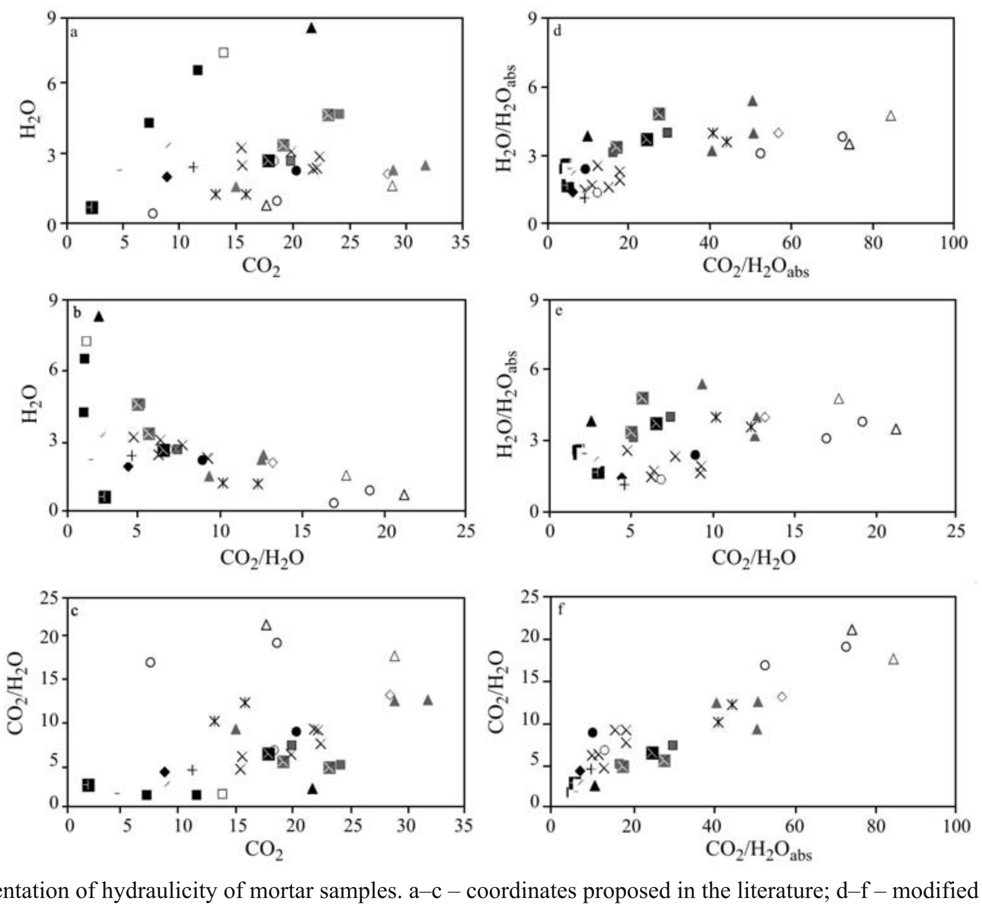

Fig. 2 Representation of hydraulicity of mortar samples. a–c – coordinates proposed in the literature; d–f – modified coordinates; ■ – HL, □ – S, ▲ – P, ◆ – C, ● – CL, ◇ – LC, △ – LP, △ – L, × – CB, ⊠ – HL+A, - – S+A, + – C+A, ○ – CL+A, ∗ – LP+A, ■ – L+A, / – CB+A

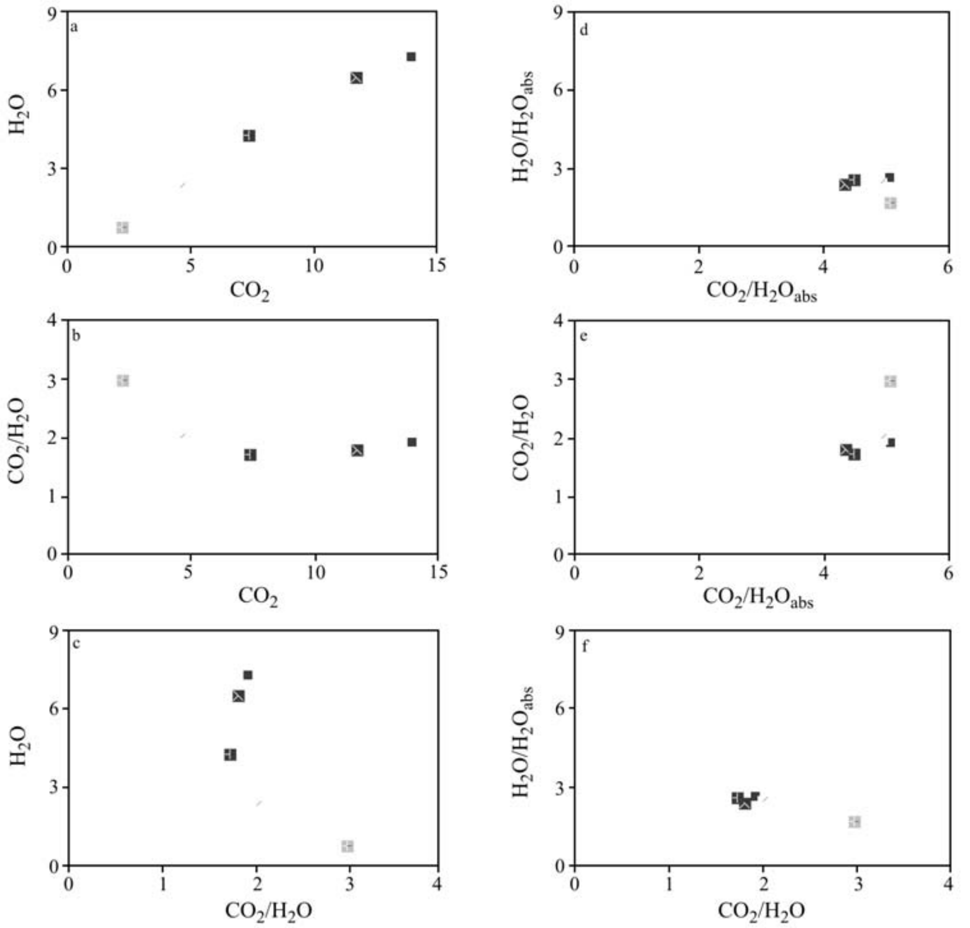

Fig. 3 Representation of hydraulicity of samples made of the same binder, Santorini lime, with and without aggregates. a–c – coordinates proposed in the literature; d–f – modified coordinates; / – S1f, ▦ – S2f, ■ – S3, ⊠ – S1, ▪ – S2

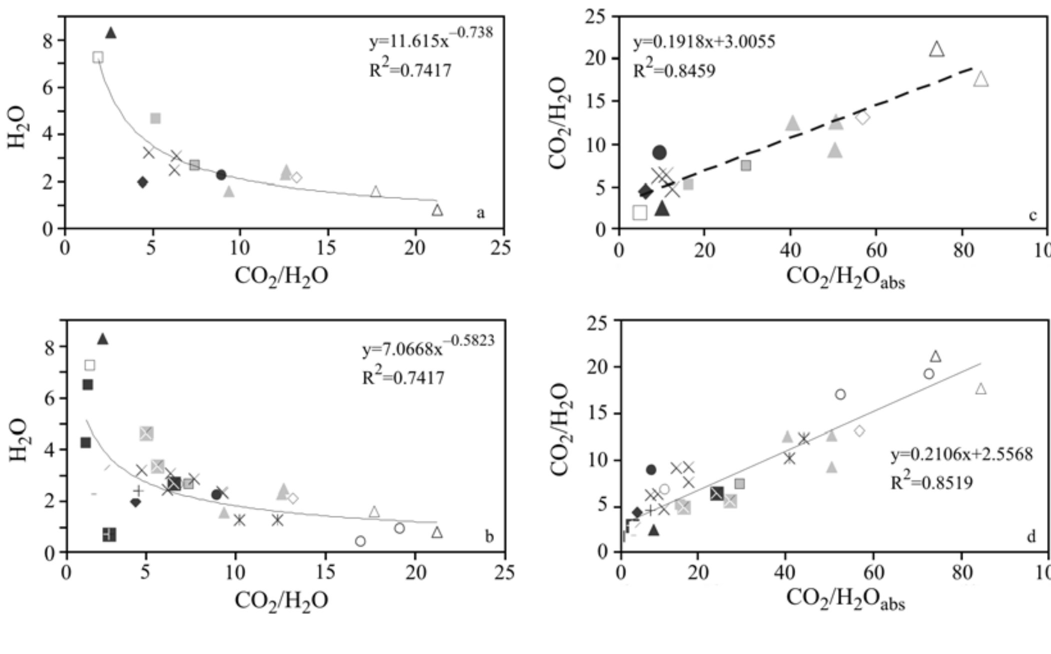

Fig. 4 Best fitting of the results of the simultaneous thermal analysis. a, b – coordinates proposed in the literature; c, d – modified coordinates; ■ – HL, □ – S, ▲ – P, ◆ – C, ● – CL, ◇ – LC, △ – LP, △ – L, × – CB, ⊠ – HL+A, - – S+A, + – C+A, ○ – CL+A, ∗ – LP+A, ■ – L+A, / – CB+A

As a final comment, the degree of hydraulicity of binders and, even more, of mortars seems to be properly represented taking into account the hygroscopic water H_2O_{abs}. Such improvement is highlighted by superimposing the best fitting curves to the plots, Fig. 4. Particularly, the presence of aggregates is better taken into account by using the new coordinates, as can be observed comparing the best fitting in Figs 4b with d.

Conclusions

A procedure proposed in the literature for evaluating the hydraulicity of ancient mortars by clustering of STA data, was applied to samples, ad hoc prepared with increasing hydraulicity from slaked lime to cement. The results evidence some problems: a) the scattering of data with respect to both abscissa and ordinate seems to be high; b) sometimes the coordinates are ineffective in grouping even mortars of the same type according to their hydraulicity; c) particularly the presence of aggregates within the analyzed samples significantly affects the position of points relative to the same binder.

The working assumption of this paper is that the hygroscopic water, H_2O_{abs}, can be used to improve the clustering of mortars according to their degree of hydraulicity. In fact, the capability of absorbing moisture from the environment increases with the hydraulicity of the binder. The results obtained confirm the effectiveness of such assumption, as the clusters of similar ad hoc prepared samples are better defined and separated each other. Furthermore, the normalized coordinates reduce the scattering of data due to the presence of the aggregates within the analyzed samples.

In order to be validated, the proposed procedure will be applied to a wider variety of mortars, ad hoc prepared with different types of binders and aggregates. As a following step, also historic samples will be analyzed and the degree of hydraulicity, pointed out by processing STA data, will be compared with the information achievable by other techniques, such as mineralogical petrographic analysis, scanning electron microscopy, IR and Raman spectroscopy.

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