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Performance Estimation of Copper-Free Solar Reflectors

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Abstract. Copper (Cu) has been an essential ingredient in the production of silvered-glass reflectors used in the concentrated solar power (CSP) systems. However, due to added material cost and the environmental burden induced by Cu mining, researchers have started to look for ways to develop copper-free coating systems for reflectors used in solar thermal applications. In this study, we employed accelerated aging tests to obtain the aging characteristics of reflectors with and without Cu and exposed reflectors outside for natural aging. Samples were subjected to Copper Accelerated Acetic Acid Salt Spray (CASS), Ultraviolet-Humidity (UVH) and UV tests, and the changes in the hemispherical and specular reflectance were measured and compared.

Keywords: Concentrated Solar Power, Point Focus Systems, Copper-Free Reflectors, Accelerated Aging, Finite-Difference Time-Domain.

1. Introduction

CSP systems suffer from aging due to various environmental loads such as ultraviolet (UV) radiation, temperature cycling, and abrasives (dust and sand). Thus, their long-term optical performance should be determined before large scale installations. Typical CSP reflectors include a copper layer in addition to silver to enhance corrosion resistance. Copper reflects the UV radiation that penetrates through the thin silver layer and provides shielding to the backside paint layers. Additionally, it serves as an adhesive layer between the paint layers and the silver as well as a sacrificial anode to provide protection against corrosion. However, high material costs associated with the use of copper layers in reflectors led to the development copper-free reflectors. Optical performance of copper-free reflectors could be performed naturally by deploying them outside; however, this procedure takes a long time and thus is not feasible for R&D applications. To rectify for that, accelerated aging tests are used where the substrates are subjected to predetermined and precalibrated loads representing the environmental forces. Accelerated aging tests provide a reliable framework for estimating the long-term performance in a short period and are extensively used for CSP tests [1]. In this study, two types of silvered-glass reflectors (with and without copper layers) were investigated for their corrosion resistance. To obtain their performance metrics (hemispherical and specular reflectance), three types of accelerated aging tests were utilized: 1) The Copper Accelerated Acetic Acid Salt Spray (CASS)-, 2) an Ultraviolet-Humidity (UVH)- and 3) an UV Chamber test. In addition to accelerated aging tests, some samples were exposed to outside conditions for 6 months at 1) Plataforma Solar de Almería (PSA) and 2) Almería city (Spain) to obtain their real-life performances. Our results show that copper-free reflectors display similar performance to conventional reflectors and provide design metrics for the next generation of CSP reflectors.

2. Descriptions of samples and tests

The dimensions of the reflectors are 10 cm x 10 cm with a thickness of 4 mm. 30 samples were tested in total; 15 with the state-of-the-art coating recipe (Type 1) and 15 copper-free (Type 2). All the samples were cut from a larger facet and therefore do not exhibit appropriate edge protection on all the four edges as it is the usual case for the whole facet mounted in the CSP field. Type 1 reflectors contain 29.6 µm protective paint, 32.4 µm primer coating, 41 nm Cu, and 168 ± 17 nm Ag layer. Type 2 reflectors contain 30.8 µm protective paint, 24.6 µm primer coating, and 159 ± 17 nm Ag layer. The compositions of the coatings are further given in Table 1. These data were provided by the manufacturer. The components of the coatings are similar except that the primer coating of Type 1 (with Cu) reflectors contain PbO, whereas its copper-free counterpart does not.

Table 1. The composition of coatings in terms of weight percentage.

Coating	**MgO**	**Al_2O_3**	**SiO_2**	**SO_3**	**CaO**	**TiO_2**	**Fe_2O_3**	**ZnO_2**	**BaO**	**PbO**
Type 1 Primer	10.21	1.39	17.24		44.77		6.5	2.88		17.01
Type 1 Protective	2.30	4.48	11.85	6.55	7.51	57.45			9.86	
Type 2 Primer	14.61	1.59	9.71		28.05	26.19	2.56	17.29		
Type 2 Protective	7.23	2.99	18.63	4.69	3.37	56.26			6.83	

2.1. Copper accelerated acetic acid salt spray (CASS)

The CASS test according to the standard ISO 9227:2006 [2] consists of exposing the samples to the spray of a salt (NaCl) solution with the addition of copper chloride ($CuCl_2$) and hydrochloric acid (HCl). The concentrations of NaCl and $CuCl_2$ are 50 ± 5 g/l and 0.205 ± 0.015 g/l, respectively. HCl is added until the pH of the solution is 3.1-3.3. The amount of condensation per area is 1-2 ml per hour on a surface of 80 cm². The temperature in the chamber is 50 ± 2°C. Samples were positioned in the chamber with an inclination of ≈25° to the vertical, front side up. The testing time in the CASS test was 240 hours. On one of the three samples of each type, a tape was glued on the glass side in order to have this side protected during the test.

2.2. UV light and humidity

The UV light and humidity test according to the standard ISO 11507 (Method A) [3] consists of the following cycle: in the beginning, samples were exposed during 4 hours at (60 ± 3) ºC to UV-radiation in a specific testing chamber (see Figure 1). For solar reflectors, the lamp type II (UVA-340) is used. It emits radiation in the wavelength-range of 290-400 nm with a peak emission at 340 nm, with a radiation of 0.77 $W/m^2/nm$. Afterwards, the samples were exposed during 4 hours at (50 ± 3) ºC to condensation (100 % relative humidity without irradiation). The total duration of one cycle was 8 hours. 3 samples of each type were tested with the front side (glass) facing towards the chamber interior. The testing time was 1000 hours. The test was carried out in the fluorescent/UV instrument from the company of Atlas.

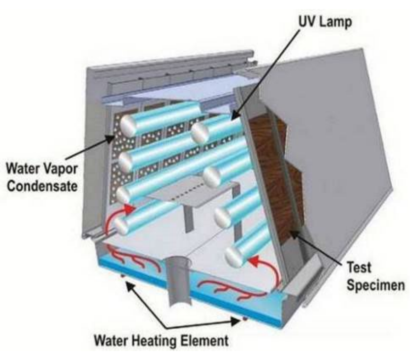

Figure 1. UV+water testing chamber.

Figure 2. UVA-Cube Dr. Hönle UV radiation chamber.

2.3. UV test

The resistance to UV radiation was tested by exposing the samples during 1000 hours to UV radiation under ambient temperature and humidity. The test was performed in the UVA-cube radiation chamber from Dr. Hönle (Figure 2). The samples were placed with the glass side facing upwards inside the chamber.

The acceleration factor compared to the global ASTM G173 spectrum [4] depends on the considered wavelength range. In the wavelength range from 270 to 400 nm, the intensity of the ASTM G173 spectrum is 92.7 W/m². The intensity of the Dr. Hönle UV radiation chamber in the same wavelength range is 301.3 W/m². Therefore, an acceleration factor of 3.3 is obtained. If the wavelength ranges from 270 to 300 nm is considered, a much higher acceleration factor of 1925 is obtained (the intensity of the UV chamber in this wavelength range is 6.70 W/m² compared to 3.48 mW/m² of the reference spectrum).

2.4. Outside exposure

The samples were placed on a platform of 1 m height, facing the south, tilted at a 45° angle with the normal to the ground. 6 samples were located at PSA and 6 were located at Almería. The samples were exposed to outside conditions from 16.02.2022 to 31.08.2022, (≈6 months or 4700 hours). Regarding the syntax of sample nomenclature: the first digit in front of the dot stands for the sample type and the number after the dot gives the exact sample number, 2.3 stands for the third sample of sample type 2. Sample numbers 1, 2 and 3 of each type were used for UVH; Samples 4,5 and 6 for CASS; 7,8 and 9 for exposure at the PSA; 10, 11 and 12 for exposure in Almería and 13, 14 and 15 for the UV experiments.

3. Measurements

Optical reflectance analysis was performed according to the actual SolarPACES reflectance measurement guideline [5]. The measurement process consisted of measuring the spectral hemispherical and the monochromatic specular reflectance. Nomenclature is based on the standard UNE 206009:2013 [6]. The hemispherical reflectance was measured in the wavelength range of $\lambda = [280, 2500]$ nm, using 5 nm intervals at an incidence angle of $\theta = 8°$ with a Perkin-Elmer Lambda1050 spectrophotometer with an integrating sphere of 150 mm diameter. Following ISO 9845-1 [7], the solar-weighted hemispherical reflectance, $\rho_{s,h}([\lambda_a,\lambda_b],\theta_i,h)$, can be calculated by weighting the spectral hemispherical reflectance, $\rho_{\lambda,h}(\lambda,\theta_i,h)$, with the solar direct irradiance. The monochromatic specular reflectance, $\rho_{\lambda,\varphi}(\lambda,\theta_i,\varphi)$, within a defined acceptance half-angle of $\varphi = 12.5$ mrad, was measured with a Devices & Services 15R-USB portable specular reflectometer. This instrument uses a parallel beam with an incidence angle of $\theta_i = 15°$ and a wavelength range of 635-685 nm, with a peak at 660 nm ($\lambda = 660$ nm). Each sample was measured at three points and the mean value with its standard deviation is given.

4. Results and discussion

4.1. Results of simulations

We estimated the optical performance of copper-free reflectors using numerical simulations. A typical commercial silver-glass solar reflector uses ≈150 nm silver (Ag) and ≈150 nm Cu as the reflector layer and coating layers with a total thickness range of 60-96 μm [8]. Accordingly, the reflectance of the plain Ag surface and Cu backed Ag surface calculated by a finite-difference time-domain (FDTD) algorithm are given in Figure 3. From the results, it is evident that the Cu layer has negligible effect on the reflectance except near ultraviolet range (0.3 μm). In fact, the spectrally averaged reflectance over the solar irradiance range (0.3 – 2.5 μm) is calculated to be 0.958 for both cases.

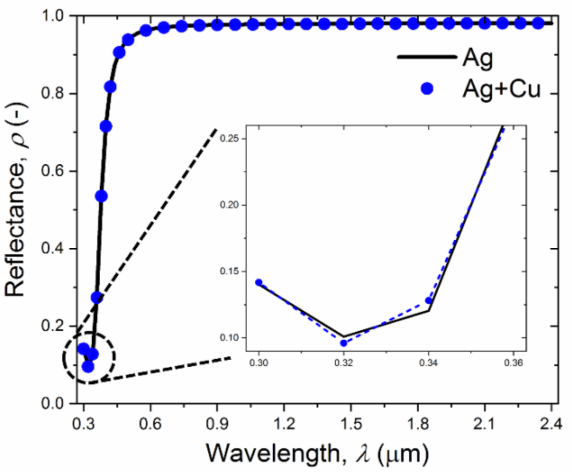

Figure 3. Simulated reflectance spectra of silver and silver backed by copper.

Experimental studies have shown that optical degradation (i.e., decrease in the reflectance) due to corrosion depends strongly on the thickness of the coating layers since corrosive agents need to penetrate through the coating layers to begin corroding the silver layer [8]. Since the thickness of Cu is two orders of magnitude smaller than the coatings, its effect on the corrosion resistance is expected to be negligible. Experimentally, the ratio of corroded area (A_c/A_{tot}) is related to time spent in the acceleration chamber (t_{age}) by [8]:

$$\ln\left(\ln\left(\frac{1}{(1-A_c/A_{tot})}\right)\right)=\ln b+c\ln t_{age} \tag{1}$$

where *b* and *c* are fitted parameters. Furthermore, the operational reflectance (*ρ)* and the non-corroded reflectance (ρ_{NC}) could be related to the corroded area by [8]:

$$\rho=\rho_{NC}(1-A_c/A_{tot}) \tag{2}$$

Treating the Cu layer as another anti-corrosive coating, the constants can be estimated for a standard reflector without copper (96.0 μm total coating), by interpolating the *ln b* and *c* of reflectors with thickest (96.15 μm) and thinnest coatings (60.15 μm). The parameters for reflectors with and without Cu presented in Table 2 [8]. These values could then be used to determine the change in reflectance during accelerated aging tests (Figure 4). Our numerical results show that the removal of the Cu layer has no significant effect on the initial reflectance performance. In fact, the difference is less than 0.001 after 2000 hours of operation. Using a conservative average aging factor of 100, this corresponds to 23 years of outdoor performance [9-10]. In other words, the optical degradation due to the removal of the copper layer is less than 0.1% for 23 years of normal operation in a solar-thermal facility, proving that copper-free reflectors could be deployed as effective reflective surfaces.

Table 2. Fitting parameters for standard and non-copper reflectors.

Reflector	**b**	**c**
Standard (With Cu)	2.60×10^{-13}	2.87
Without Cu	3.02×10^{-13}	2.87

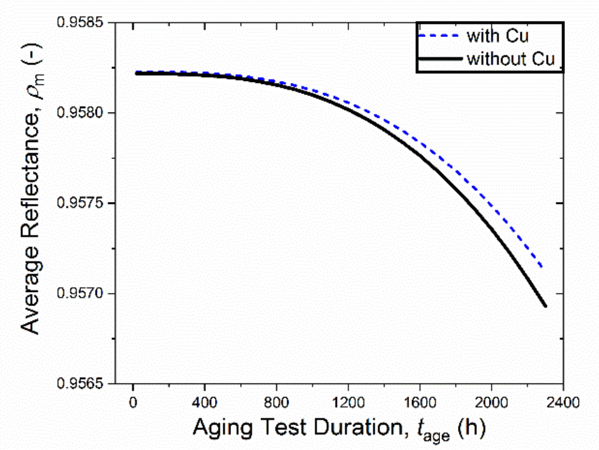

Figure 4. Average reflectance of reflectors with respect to time spent in the accelerated aging chamber.

4.2. Results of laboratory experiments

Before inspecting the reflectance, it is useful to look for any noticeable corrosion spots after the CASS test. Among six samples, only one (1.4) displayed a corrosion spot, while all others have shown only edge corrosion. It can be inferred that this corrosion is due to the inherent quality of the sample as it was absent from others. One average, Type 1 and Type 2 samples showed maximum original edge corrosion penetrations of 0.33 mm and 1.67 mm, respectively. As it was explained in the methodology section, the fact that there is no proper edge protection on the investigated samples, prohibits drawing a strong conclusion from this data, but still it should be seen as a first indicator of less corrosion resistance of the sample Type 2. The reflectance measurements of samples placed in the CASS chamber is shown in Figure 5.

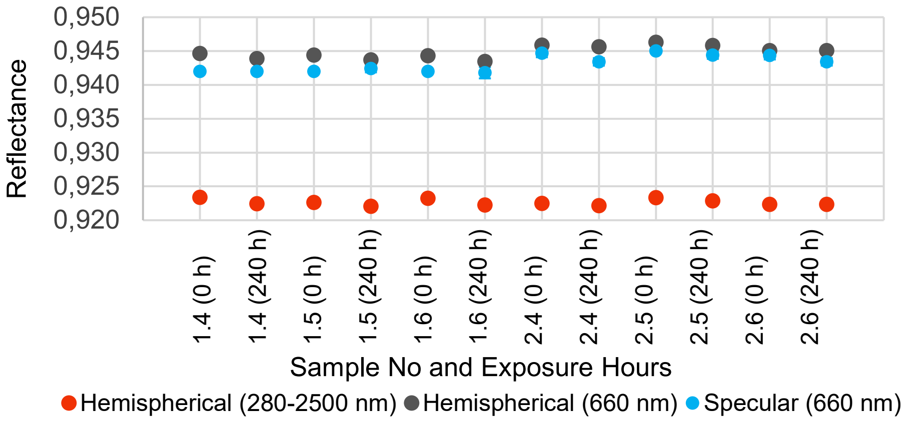

Figure 5. Optical measurements before and after CASS.

Figure 5 shows that the reflectors without copper have displayed a reflectance drop of 0.001 in hemispherical reflectance measurements whereas the maximum drop detected in samples without copper is half of this value. In terms of specular reflectance, copper free reflectors have shown a drop of 0.001 while other samples retained their reflectance. The changes in reflectance are generally within the error margin of the measurements so the performance difference of the samples with and without copper layer is deemed insignificant under the CASS test.

Six of the samples were subjected to UVH tests and their reflectance is measured before the test and after 1000 and 2000 hours in the chamber. The reflectance measurements of samples placed in the UVH chamber is shown in Figure 6.

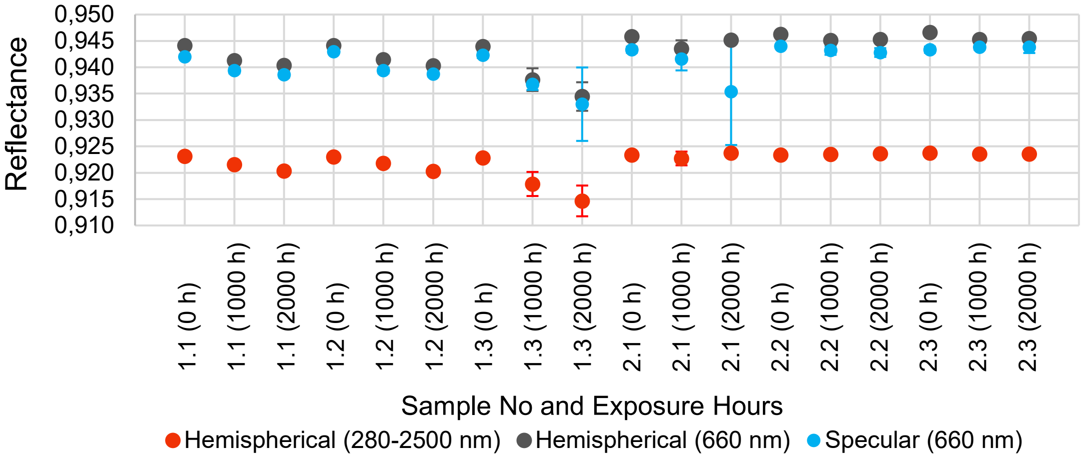

Figure 6. Reflectance measurements before and after UVH.

In Figure 6, it is observed that, after 2000 hours, the average hemispherical reflectance decreases as much as 0.005 for Type 1 and no change was observed for Type 2 samples. On the contrary, the reduction in the specular reflectance of both types are of the same order of magnitude, 0.006 for Type 1 and 0.003 for Type 2. In specular reflectance measurements, it is seen that most of the degradation happened during the first 1000 hours except for samples 1.3 and 2.1. However, the error margin in these particular measurements exceeds the reflectance drop. On the basis of UV-Humidity test, reflectors without Cu appear to be more resilient than their counterparts with Cu, but there needs to be further investigations to arrive a conclusion.

Reflectance measurements before and after UV test is presented in Figure 7. It is seen that Type 1 reflectors showed a reflectance loss around 0.001, while Type 2 reflectors did not show any degradation. Due to the UV protective feature of Cu layer, the opposite is expected. It can be concluded that the effect of coatings is more significant than Cu for UV protection.

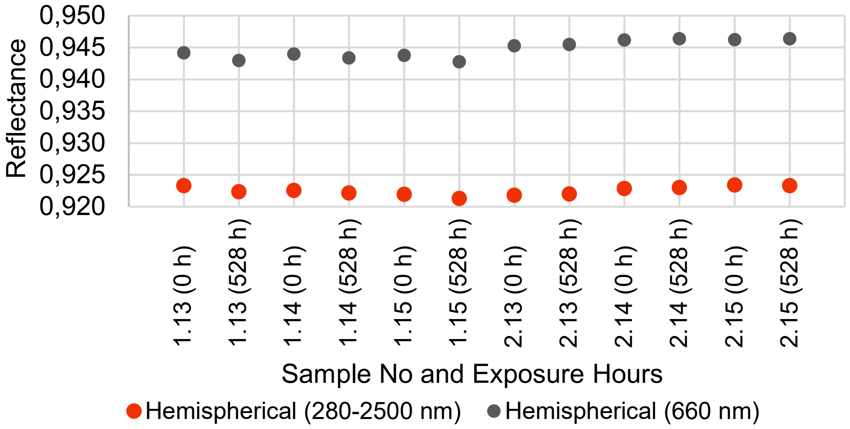

Figure 7. Reflectance measurements before and after UV

4.3. Results of outdoor exposure tests

Figure 8 shows the reflectance measurements before and after outside exposure at PSA. Over the solar spectrum (280-2500 nm), the hemispherical reflectance of Type 1 samples dropped up to 0.001 while Type 2 samples retained their initial values. In monochromatic (660 nm) hemispherical reflectance measurements, Type 1 and Type 2 samples experienced drops of 0.002 and 0.001, respectively. In terms of specular reflectance, however, the opposite is observed; the reflectance of Type 1 dropped by 0.001 and that of Type 2 dropped by 0.002.

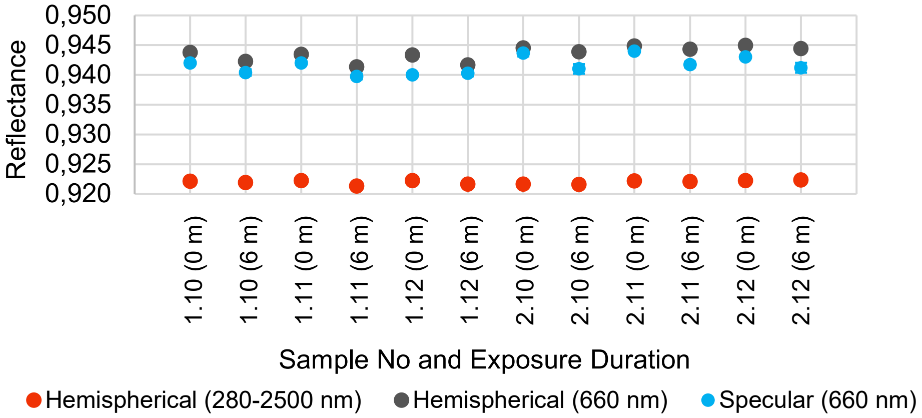

Figure 8. Reflectance measurements before and after outside exposure at PSA.

In Figure 9, reflectance measurements before and after outside exposure at Almería are shown. On average, both types of reflectors have displayed the same amount of optical degradation. Over the solar spectrum, the average hemispherical reflectance drop is measured as 0.001. The monochromatic hemispherical and specular reflectances dropped by 0.002.

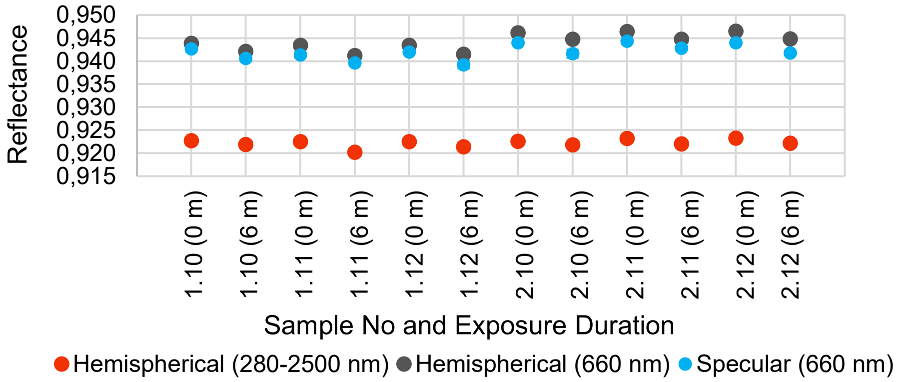

Figure 9. Reflectance measurements before and after outside exposure at Almería.

5. Conclusion

Most silver-glass reflectors used in CSP industry include a copper layer. The harmful effects of copper production on the environment, amplified by the requirement of large number of reflectors by CSP, pushes researchers to consider alternative reflector designs without copper. In order to evaluate the long-term performance of reflectors with and without copper, we performed accelerated aging tests consisting of CASS, UVH and UV, and exposed reflectors outside for naturally aging. Our results show that elimination of the copper layer does not cause a significant performance reduction in the reflectors (optical degradation) after state-of-the-art accelerated aging testing. However, it cannot be assumed so far that this statement still holds true after further, more complex combinations of artificial aging tests. Regarding the outdoor exposure it has to be stated that the duration of six months can be regarded as short and more data is needed to arrive at a reliable lifetime assessment. Still, the observed performance of the novel coating type is regarded as promising. The results of this study are expected to influence further testing campaigns and in a second step the design priorities for the next generation of copper-free reflective surfaces.

Data availability statement

Measurement data can be accessed through the corresponding author.

Author contributions

EEA designed the experiments, performed numerical calculations, partly attended the accelerated aging tests, and wrote the paper. GK prepared the samples. FW and RSM carried out accelerated aging and outdoor tests. AAG and TOÖ helped with the experimental and numerical planning. AAG, TOÖ and DB guided the work. All authors commented on the final version of this manuscript.

Competing interests

The authors declare no competing interests.

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