Development of Superhydrophobic Coatings on Concrete Surfaces

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Abstract: ***Durability of concrete is a most concerned problem among civil engineers all over the World. The durability of concrete is affected by intrusion of water and other chemicals through pores and capillaries of the surface of concrete. Once this water permeation is arrested by proper coating, the durability of concrete will be increased to many fold. Therefore keeping this in mind, various coating (36 No's) are developed to develop Superhydrophobicity using Silane, Siloxane, Silicone, Poly vinyl alcohol (PVA) as binders and as filler material Nano Silica, Silica Fume, Micro Silica, TiO_2, etc are added and applied & sprayed on surface of cement mortar specimens of size 100mm x 100mm x 10mm. Superhydrophobicity of the coating was seen with a drop of water on that. Few coatings performed very well and resembles water droplet on a Lotus Leaf and the rest of the coatings does not provide the necessary Superhydrophobicity but were hydrophobic. The Coatings with water drops are shown in photographs to actually witness the technology of the coating.***

Keywords: Superhydrophobicity, Silane, Siloxane, Silicone, PVA, Microsilica, Nanosilica, Waterproofing, Durability

1. Introduction

Concrete surface is usually hydrophilic porous and contain many capillaries, fissures, microcracks and other defects. Water or any other aggressive liquids and gases can easily penetrate through these surface defects and will lead to undesirable consequences. The penetrated chemicals or other aggressive species will react with concrete and form new chemical compounds and thus internal stresses formed and as a result of this the concrete cracks. Therefore, the problem of durability of concrete raises. The Durability of concrete depends on its own overall absorption and permeability of aqueous solutions. The cumulative effect of such penetration, permeation, absorption and capillary sorption etc eventually cause expansion, cracking, scaling and crumbling of concrete. Therefore it is important to synthesize water-repellent hydrophobic or superhydrophobic coating to concrete surface in order to make the concrete more durable and in particular to produce Ultra-durable concrete [1, 2]. It can be noted that superhydrophobic concrete surfaces prevents discolouration and staining of concrete by chemical contacts. Superhydrophobic coating also provides scratch free concrete surface. Hydrophobic and superhydrophobic material are surface protection materials and capable of increasing the angle of contact between the water droplet and the surface of concrete. It has been reported that the chloride ion penetration has been reduced by 2.12 to 7.0 times depending on the product [3]. Among various methods to protect concrete surface, impregnation of hydrophobic material is least harmful and highly efficient to inhibit capillary water absorption. It has been proved [4] that hydrophobic agents could be effective for more than 10 years when applied as 6 months old concrete surfaces. These hydrophobic materials and coatings are in use for bridges in UK, USA and Germany since 1986, to avoid chloride ion penetration [5].

In the present research work various combinations of hydrophobic and superhydrophobic coatings are developed using the materials such as silane, siloxane, polyvinyl alcohol, latex, sodium silicate, etc with and without additives such as nanosilica, silica fume, TiO_2, ZnO, microsilica, glass powder. These synthesised coatings were applied on concrete tiles to observe for hydrophobicity and superhydrophobicity of the coatings.

2. Theory of Superhydrophobicity

The hydrophobicity of a material can be defined as its ability to repel water and it depends on the chemical composition of the concrete surface and the surface geometry (micro - and - nano structural morphology). The contact angle between a drop of water and the surface is generally used as an indicator of hydrophobicity or wettability. When the contact angle is more than 90˚, then it indicates hydrophobicity, while if the contact angle is less than 30˚, then it denotes hydrophilicity, which is the tendency of a surface become wet or to absorb water [6].

The most important role of hydrophobic agents is the reduction of concrete water absorption. It is also critical that this reduction be effective for many years; and as a result of this the hydrophobic agent sufficiently penetrate the concrete. The minimum penetration 2mm is required. The fig.1 shows hydrophobic and superhydrophobic nature of water droplets and the conditions required.

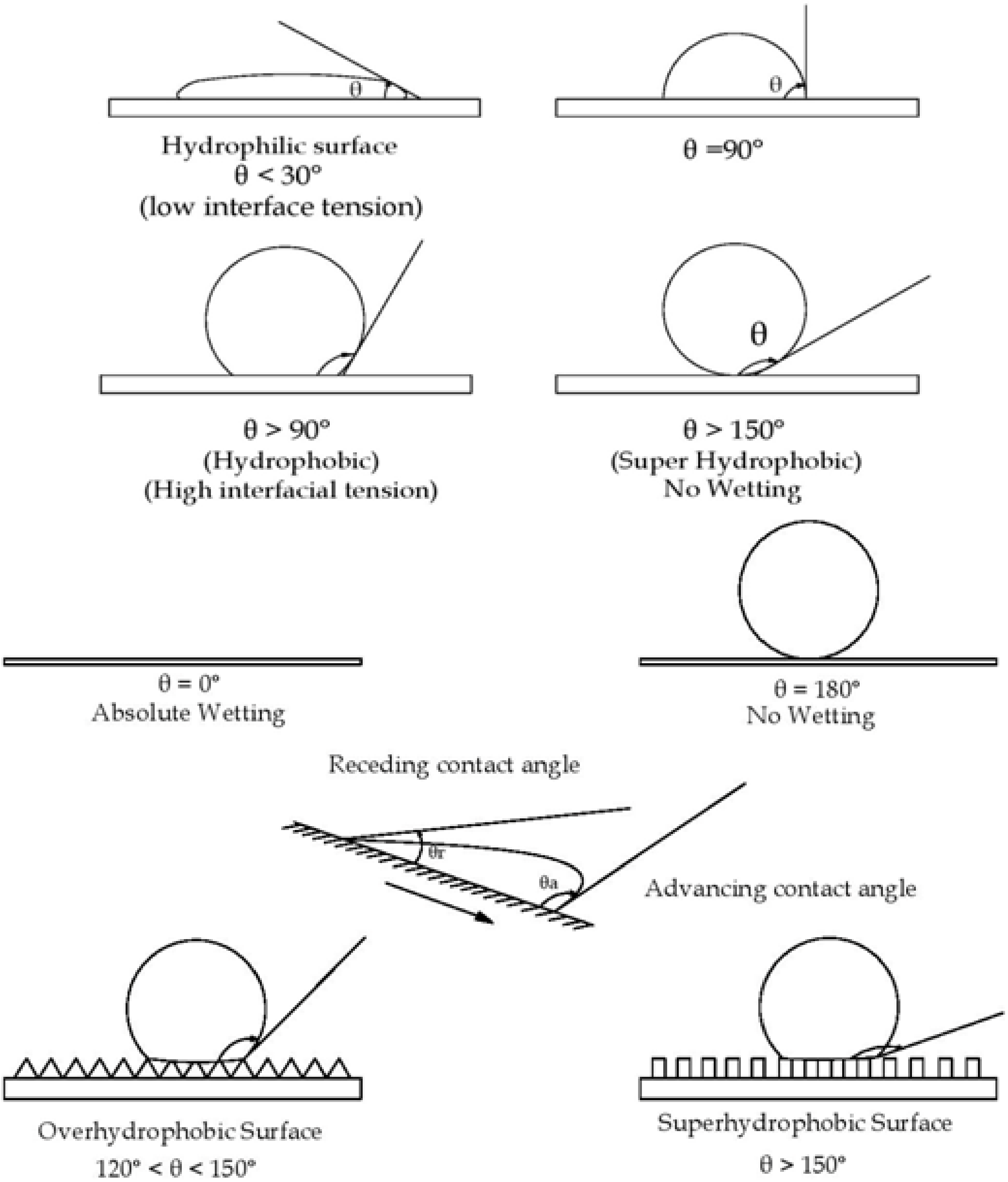

Fig:1 Hydrophobic, Overhydrophobic, Superhydrophobic and Hydrophilic surfaces.

As it has been stated earlier, concrete is an example of a hydrophilic mesoporous material which absorbs water. The Superhydrophobicity corresponds to contact angle between 150˚ and surfaces with intermediate properties (with high contact angles between 120˚ and 150˚) above this typical values for hydrophobic materials are called "over hydrophobic". The water contact angle with a solid surface can be measured by goniometer or tensiometer.

Superhydrophobic surfaces with roughness patterns imposed over large roughness patterns as shown in fig.1 have generated interest due to their potential in industrial applications (mainly for self cleaning). These surfaces mimic the "***Lotus Leaf***" surface, which is well known for its superhydrophobicity and self cleaning properties [7].Mimicking living nature for engineering applications is called "biomimetics" and this biomimetic approaches can be used to synthesize hydrophobic and superhydrophobic concrete.

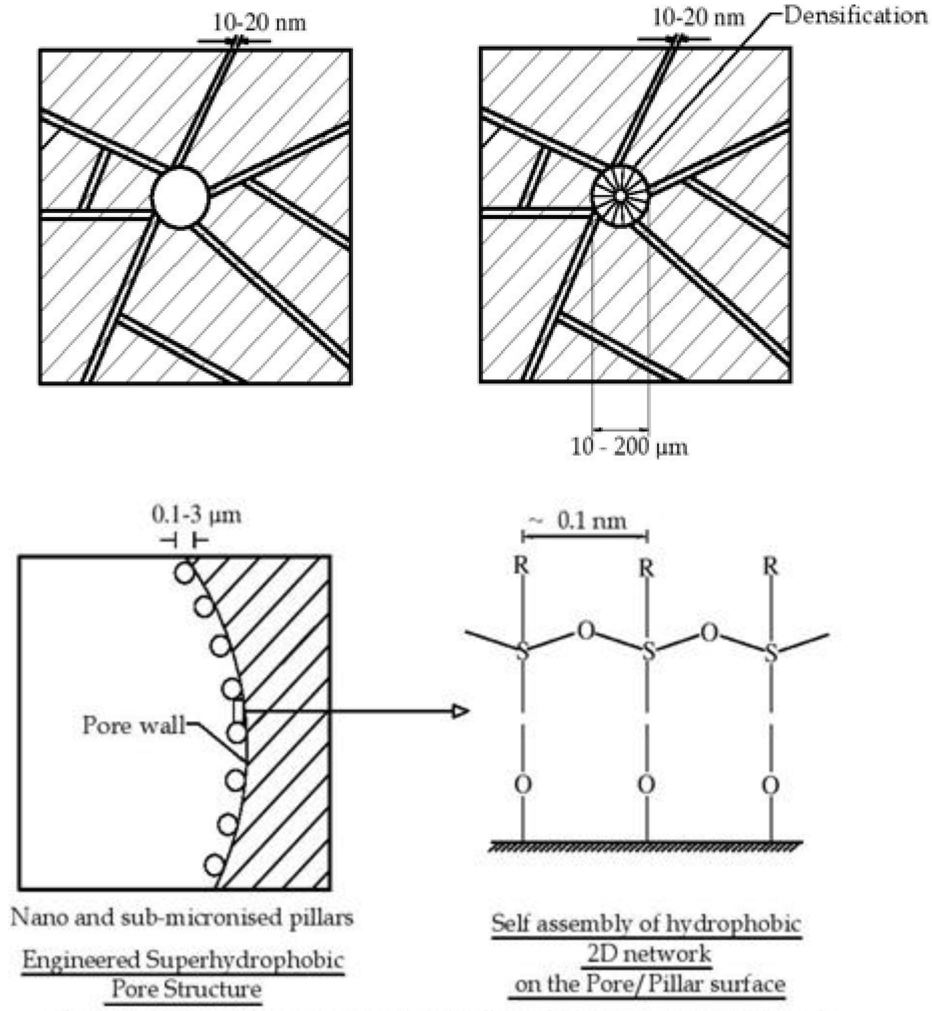

Fig:2 Working of Superhydrophobic hybridization of Concrete Walls

The fig.2 shows the modification of porewall surface due to superhydrophobicity and two directional networks on pores of concrete

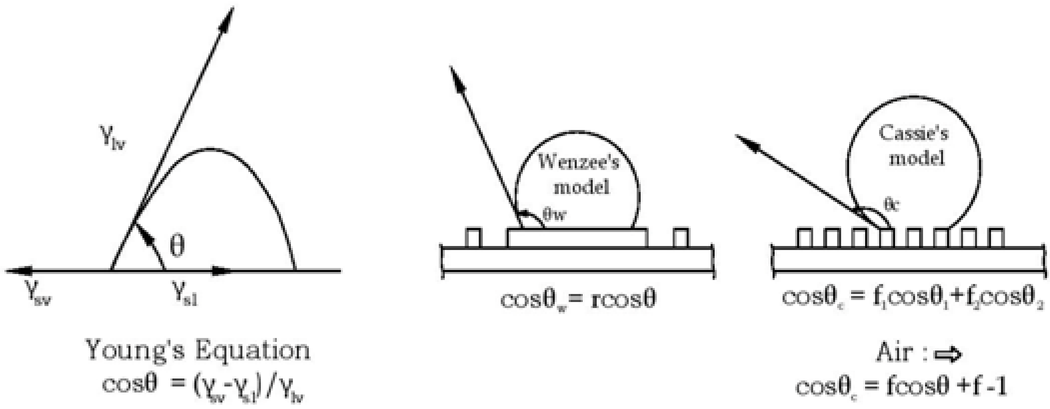

Fig:3 Phenomenon of Wetting and Contact angle

The fig.3 explains the phenomena of wetting and contact angle for hydrophobicity and superhydrophobicity on concrete surfaces with water droplet [8].

Due to high water absorption, the contact angles for uncoated specimens were very small (0-20˚). The uncoated specimens absorb most of the water since portland cement based materials are highly hydrophilic. Coatings formulations with hydrophobic material and sub micronised and nano-sized particles of silica fume, nano silica, TiO_2, etc will increase contact angle as indicated in fig.3. This is due to the fact that micro-nano roughness of hierarchical structure required for superhydrophobicity effects. Increased water to cement ratio increases pores on surface of concrete and this increased porosity with diluted emulsion reduce contact angle to a greater extent. This is because the coating material will be absorbed in the pores and voids and thus lower contact angle.

3. Wettability: Contact angles and Sliding

Wettability is one of the important properties of solid surfaces from fundamental practical aspects. The surface energy and surface roughness are the two important factors dominate wetting property or wettability of a concrete surface. When the surface energy is lowered, the hydrophobicity is enhanced. However even a material with lowest surface energy (6.7 mJ/m^2 for a surface with regularly aligned closed hexagonal packed group) gives a water contact angle of only around 120˚. For higher hydrophobicity, providing a proper surface roughness is required. Infact, surfaces with a water contact angle of more than 150˚ were developed by introducing proper roughness on materials having low surface energies. Contact angles of water is usually used as common criterion for the evaluation of hydrophobicity of concrete surface; but this alone is insufficient for the evaluation of sliding properties of water droplets on surfaces. A surface with high contact angle does not always show a sliding angle which is defined as the critical angle where water droplet with certain weight begins to slide down the inclined plate. Therefore, when we discuss hydrophobicity, the sliding property of water droplets should be evaluated separately from the contact angle, as per fig.1. Referring to fig.3, the contact angle θ, of a liquid droplet on a flat solid surface is given by young's equation

$$\boxed{\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}} \quad \text{----- (1)}$$

where γ_{sl}, γ_{sv} and γ_{lv} are the interfacial free energy per unit area of solid-liquid, solid-gas and liquid-gas interfaces respectively. However this equation is applicable only for flat surfaces and not to a rough surface. Wenzel proposed a theoretical model describing the contact angle θ' at a surface roughness.

The young's equation is modified as follows fig.3 [9]

$$\boxed{\cos\theta' = \left(\frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}\right) = \cos\theta} \quad \text{----- (2)}$$

The roughness factor is defined as the ratio of the actual area of a rough surface to the geometric projected area. This equation indicates that the surface roughness enhances the hydrophobicity of hydrophilic surfaces and also enhances hydrophobicity of hydrophobic ones because it is always greater than 1.0 [9].Cassie proposed an equation describing the contact angle θ' at a heterogenous surface composed of two different materials for surface area fraction f_1 and f_2, with contact angles θ_1 and θ_2 then the contact angle on surface can be expressed by the following equation.

$$\boxed{\cos\theta' = f_1 \cos\theta_1 + f_2 \cos\theta_2} \quad \text{---- (3)}$$

4. Principles of Hydrophobicity

The best hydrophobicity can be achieved by applying hydrophobic material coatings on concrete surface. Hardened concrete has pores distribution of various diameters randomly depending upon water to cement ratio of the concrete mixture, hydration. Majority of the pores in ordinary concrete have diameters in the range of 0.05-1.0µm [1], and the water penetrates through these pores with applied pressure or by capillary rise. Once hydrophobic coating is applied on concrete surface, the coating penetrate through the pores and gets coated on the inner walls of the pores with a thin layer of molecules of fatty acids/wax emulsion/latices etc as illustrated in fig.4. The end result in last two cases in production of hydrophobic surfaces exhibiting high contact angles to water. The force P required to force water into the pore of radius r is given by equation 4.

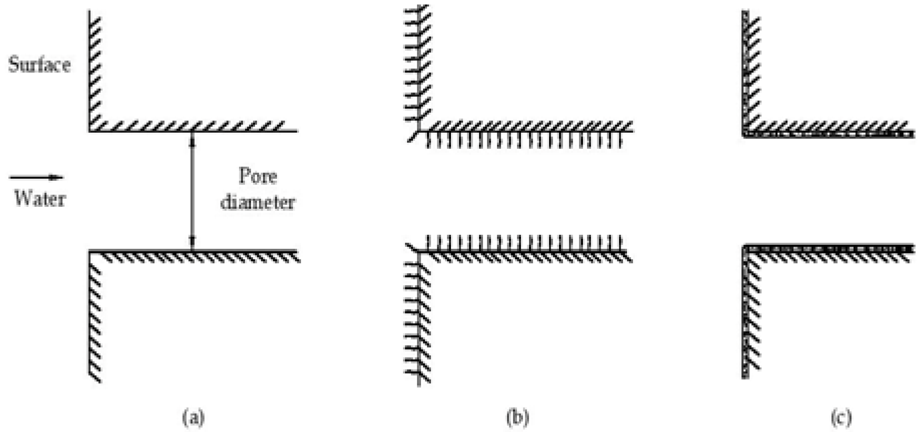

Fig 4: Capillary pore without hydrophobic agent-(a) lined with molecular hydrophobizing agent-(b) and lined with a coalesced emulsion layer-(c) (Rixom and Mailvaganam,1999), Ref.1

$$\boxed{P = -2\gamma\cos\theta/r} \quad \text{----- (4)}$$

where γ is the surface tension of water (72 dyn.cm^{-1} or 0.072N/m) and θ is the contact angle of water (i.e. about 120˚ for hydrophobic). For a pore with radius 0.5µm (largest capillary), the required pressure becomes to an equivalent of a hydrostatic head of 14m water.

Hydrophobizing Agents

The chemical admixtures used to produce hydrophobizing agents are able to form a thin hydrophobic layer within the pores and voids and on the surface of concrete in one of the three ways:

1) Reaction with hydration products
2) Coalescence from globular particles form (emulsion)
3) Distribution in concrete matrix in a very divided form.

The Chemicals used for all three categories are shown in Table 1.

Table 1: Examples of chemicals used for hydrophobizing of concrete surfaces [10]

	Mechanism	*Chemicals*
1.	Reaction with cement hydration products	• Stearic acid $C_{17}H_{35}\ COOH$ • Oleic acid $C_{17}H_{33}\ COOH$ • Caprylic $C_7H_{15}\ COOH$ • Capric $C_9H_{19}\ COOH$, acids. • Vegetable and animal fats • Butyl Stearate (ester)
2.	Coalescence from emulsion	• Wax emulsion
3.	Finely divided minerals	• Calcium stearate • Aluminium stearate • Bitumen

Superhydrophobicizing

As discussed earlier, the control of surface wettability is an important factor. For superhydrophobicity, the water contact angle θ must be more than 150˚ as illustrated in fig.1. In Superhydrophobic Surfaces, to which water either does not adhere or only meekly adheres are often prepared by hydrophobic modification of rough surfaces or through roughening of hydrophobic surfaces [11-13]. But these superhydrophobic and superhydrophilic surfaces can be converted or affected by light, heat, electric field or solvents [14-16].

Titanium dioxide (TiO_2), silica fume, nano silica, micro silica along with hydrophobic materials such as silane, siloxane, silicone mixed and coated for super hydrophobicity on concrete panels. These coatings are applied by brush and also by sprayer as shown in Fig.5 and Fig.6.

Figure 5: Coating by Brush

Figure 6: Coating by Sprayer

Several coatings with different compositions (36 coatings) were developed and studied for superhydrophobicity as shown in Table 2.

Table 2: List of Compositions of Coatings

S.No.	SPECIMENS	REMARKS
1	Silicone emulsion [Sprayed]	Hydrophobic
2	Silane [Sprayed]	Superhydrophobic
3	Latex [Sprayed]	Hydrophobic
4	Silane [Brush Applied]	Hydrophobic
5	Silicone Emulsion +NanoSilica [Sprayed]	SuperHydrophobic
6	Siloxane + TiO_2 + NanoSilica [Brush Applied]	Hydrophobic
7	Siloxane + TiO_2 [Brush Applied]	Hydrophobic
8	Siloxane +Nano Silica[Brush Applied]	Hydrophobic
9	Siloxane [Brush Applied]	Hydrophobic
10	Silane +Nano Silica [Brush Applied]	Hydrophobic
11	Silane +Nano Silica +TiO_2 [Brush Applied]	SuperHydrophobic
12	Silane +TiO_2 [Brush Applied]	SuperHydrophobic
13	Latex [Brush Applied]	Hydrophobic
14	Latex + TiO_2 [Brush Applied]	Hydrophobic
15	Latex + Nano Silica + TiO_2 [Brush Applied]	Hydrophobic
16	Latex + Nano Silica [Brush Applied]	Hydrophobic
17	Poly Vinyl Alcohol (PVA) [Sprayed]	Hydrophilic
18	PVA + Nano Silica [Sprayed]	Hydrophilic
19	PVA +Silica Fume [Sprayed]	Hydrophilic
20	PVA +TiO_2 [Brush Applied]	Hydrophilic
21	PVA +TiO_2 +Nanosilica [Brush Applied]	Hydrophilic
22	PVA +Nano Silica +TiO_2 +Silica Fume [Brush Applied]	Hydrophilic
23	PVA + Silica Powder [Brush Applied]	Hydrophilic
24	PVA + Silica Powder+ Micro Silica [Brush Applied]	Hydrophilic
25	PVA + Micro Silica [Brush Applied]	Hydrophilic
26	PVA +Micro Silica +TiO_2 [Brush Applied]	Hydrophilic

27	PVA +Micro Silica +TiO_2 +Nano Silica [Brush Applied]	Hydrophilic
28	Silicone Emulsion +Silica Fume [Brush Applied]	Superhydrophobic
29	Silicone Emulsion +Silica Fume +Tio_2 [Brush Applied]	Superhydrophobic
30	Silicone Emulsion +Tio_2 +Silica Fume +ZnO [Brush Applied]	Superhydrophobic
31	Sodium Silicate sol [Brush Applied]	Hydrophilic
32	Sodium Silicate Sol +Nano Silica [Brush Applied]	Hydrophilic
33	Sodium Silicate Sol +Nano Silica +Silica Fume [Brush Applied]	Hydrophilic
34	Sodium Silicate Sol +Nano Silica +Silica Fume +Tio_2 [Brush Applied]	Hydrophilic
35	Sodium Silicate Sol +Nano Silica +Silica Fume +Tio_2 +A. Clay [Brush Applied]	Hydrophilic
36	Sodium Silicate Sol +Nano Silica +Silica Fume +A. Clay +ZnO [Brush Applied]	Hydrophilic

Silicone emulsion and silane based agents with nano SiO_2 and silica fume proved to be Superhydrophobic coating and acted like lotus leaf coating. This can be seen from Fig.7.

Figure 7: Superhydrophobic Coatings

5. Conclusions

- For hydrophobic surface coatings, the contact angle shall be >120˚.
- For Superhydrophobic surface coatings, the water contact angle shall be >150˚.
- Water contact angles less than 20˚, is considered as hydrophilic.
- Silicone Emulsion and silane with Nano silica, Silica fume with TiO_2 performed well as superhydrophobic material on concrete surface.
- Optimisation of these coatings with weight percentages are yet to be carried out.

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