

Influence of internal curing using lightweight aggregates on interfacial transition zone percolation and chloride ingress in mortars

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ABSTRACT

The microstructure of the interfacial transition zone (ITZ) between cement paste and aggregate depends strongly on the nature of the aggregate, specifically its porosity and water absorption. Lightweight aggregates (LWA) with a porous surface layer have been noted to produce a dense ITZ microstructure that is equivalent to that of the bulk cement paste, as opposed to the more porous ITZ regions that typically surround normal weight aggregates. This ITZ microstructure can have a large influence on diffusive transport into a concrete, especially if the individual ITZ regions are percolated (connected) across the three-dimensional microstructure. In this paper, the substitution of LWA sand for a portion of the normal weight sand to provide internal curing (IC) for a mortar is examined with respect to its influence on ITZ percolation and chloride ingress. Experimental measurements of chloride ion penetration depths are combined with computer modeling of the ITZ percolation and random walk diffusion simulations to determine the magnitude of the reduced diffusivity provided in a mortar with IC vs. one with only normal weight sand. In this study, for a mixture of sands that is 31% LWA and 69% normal weight sand by volume, the chloride ion diffusivity is estimated to be reduced by 25% or more, based on the measured penetration depths.

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1. Introduction

Lightweight aggregate (LWA) concretes have generally exhibited excellent performance under severe weathering conditions [1]. One of the reasons cited for this is the high integrity “contact zone” formed between the LWA and the neighboring hydrating cement paste [1]. More recently, the terms interfacial zone and interfacial transition zone (ITZ) have been adopted to replace contact zone. For normal weight aggregates, due to the inherent size differences between cement and aggregates, a “wall effect” exists, so that there is a deficiency of cement particles near the aggregate surface relative to their concentration in the bulk (non ITZ) cement paste. Direct microstructural examinations by scanning electron microscopy (SEM) have revealed that for LWA with a porous outer layer, this wall effect does not exist and a nearly continuous uniform microstructure of hydration products abuts and partially penetrates the LWA [2,3]. As an example, Fig. 1 shows SEM micrographs of blended cement mortars with and without internal curing [4]. A nearly continuous microstructure is observed near the porous LWA particle, along with the ability for the cement hydration products to penetrate into the LWA surface pores and irregularities.

The formation of these ITZ around normal weight aggregates will also be influenced by curing conditions. Due to a wall effect that causes inefficient “packing” of the cement particles near the aggregates, the ITZ regions will initially have a higher water-to-cement ratio (w/c) and a larger interparticle spacing than the bulk cement paste [5]. If sufficient curing water is not readily available at early ages, the concrete will undergo self-desiccation, with the bulk cement paste regions imbibing water from the largest pores within the ITZ, resulting in less hydration, greater porosity, and larger empty pores being present in the ITZ (bottom micrograph in Fig. 1) [6]. If such a concrete later resaturates during its environmental exposure, such porous ITZ regions would likely provide less resistance to ionic and fluid transport.

When each normal weight aggregate in concrete is surrounded by such a porous ITZ, their percolation or connectivity across the three-dimensional microstructure may become an issue for transport and durability [7]. This percolation has been extensively examined using a hard core-soft shell (HCSS) model developed at the National Institute of Standards and Technology (NIST) [7,8], in which the aggregates are considered as hard core (impenetrable) spherical particles and the ITZ as surrounding concentric soft (penetrable) shells. The HCSS model has been extended to examine spalling of high-performance concretes containing polymeric fibers [9], to adapt the protected paste volume concept to internal curing [10], and most recently to document the influence of water-cement ratio (w/c) and cement particle size distribution on particle

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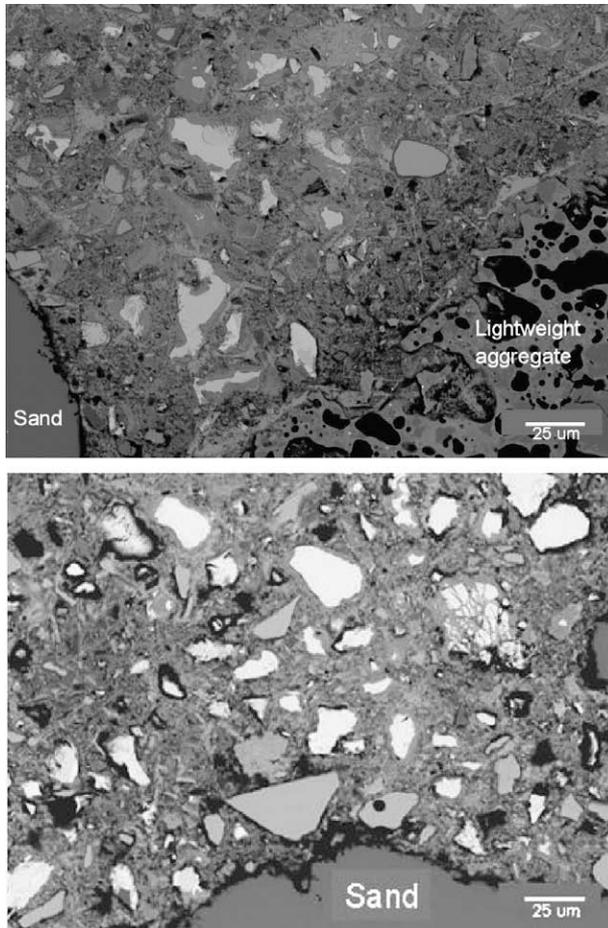


Fig. 1. SEM micrographs of blended (20% slag) cement mortars with $w/c = 0.30$, cured under sealed conditions for 120 d [4]. Top micrograph is for a mortar with internal curing (0.08 extra units of water supplied by LWA sand) while bottom micrograph is for a mortar with normal weight sand only. Dark regions within LWA sand in top micrograph correspond to pores.

spacing in fresh cement paste [11]. In this paper, the model will be further adapted to consider a mixture of normal weight sand particles, with an accompanying ITZ, and LWA where no distinct ITZ is present, in a fashion similar to that previously employed for macro-defect-free cements containing both inert and reactive particles [12]. It should be noted that controversy exists in the literature regarding the existence of ITZ percolation in concrete [13], despite microstructural examinations that have validated the existence of such percolated pathways in concrete [14].

Previously, experimental and computer modeling efforts have quantified diffusion rates of ions diffusing within these ITZ regions relative to those diffusing in the bulk paste [15–18]. For example, Bretton et al. [15] conducted model experiments using a cylindrical aggregate surrounded by cement paste and concluded that the ITZ exhibits a chloride ion diffusion coefficient that is 12–15 times that of bulk paste, for a $w/c = 0.5$ cement paste cured for 10 d and an assumed ITZ thickness of 100 μm . Bourdette [16] has estimated a lower ratio of ITZ to bulk paste diffusivity of 3 for a $w/c = 0.4$ mortar cured for 3 months, assuming an ITZ thickness of 120 μm . Conversely, Otsuki et al. [17] have projected that the diffusion coefficient for the ITZ could be over 100 times that of the bulk paste for concretes with w/c ranging between 0.4 and 0.7, assuming an ITZ thickness that is a function of aggregate size and varies between zero and about 80 μm . Based on a multi-scale microstructural model, Bentz [18] arrived at diffusivity ratios ranging from 0.7 to about 21 for an assumed ITZ thickness of 15 μm and degrees

of hydration ranging from 0.62 to 0.88. In that study, values of less than one, indicating that the ITZ is more resistant to diffusion than the bulk paste, were obtained only for low $w/c = 0.3$ concretes containing silica fume. For these concretes, the very small silica fume particles can concentrate in the ITZ regions leading to an ITZ microstructure that is ultimately denser than that of the bulk paste [5,18]. The larger values near 20 were observed for $w/c = 0.5$ concretes and are in reasonable agreement with those of Bretton et al. discussed above. Based on these results, the general consensus would be that for many conventional concretes, the ITZs could indeed provide a preferential path for the ingress of deleterious species such as chloride ions.

As a further concrete example, the lack of distinct and more porous ITZ regions in lightweight aggregate concretes could contribute to Thomas' observation of apparent diffusion coefficients that are reduced by as much as 70% due to the incorporation of LWA [19]. Furthermore, his results indicated that the greatest reductions in concrete diffusivity were achieved when both the coarse and fine aggregates were totally replaced with their lightweight counterparts, as opposed to a total replacement of the coarse aggregates combined with a normal weight sand. While it is only natural to question whether porous LWA might not be expected to actually increase transport rates, one can observe in Fig. 1 that the pores contained in the LWA appear to be discrete and may not be percolated across the aggregate particle. In fact, this lack of three-dimensional percolation has been confirmed by X-ray microtomography studies at NIST for several commercially available LWA. This discontinuity is also in agreement with the experimental observation of Zhang and Gjorv that the permeability of high-strength lightweight concrete is more dependent on the properties of the cement paste than the porosity of the LWA [20]. Recently, Pyc et al. have performed mass measurements that suggest that once the pores in LWA empty while supplying water to the hydrating cement paste during curing, they are not subsequently resaturated, even upon complete immersion of the specimen [21]. If these pores in the LWA remain empty, ionic diffusion through them is a moot point and instead they may potentially function as part of an effective air void system to provide freeze thaw resistance to the concrete [10]. Of course, it is critical that the pre-wetted LWA be provided an opportunity to empty prior to exposure to chloride ions. In the current study, this was achieved by employing sealed curing for 7 d or 28 d for the specimens containing pre-wetted LWA, prior to immersion in Cl^- solutions.

In typical internal curing (IC) applications, only a fraction of the normal weight aggregates are replaced by LWA [22]. Such a replacement can still substantially reduce the total volume of ITZ paste and could also have a significant influence on its three-dimensional percolation and chloride ion transport, as illustrated

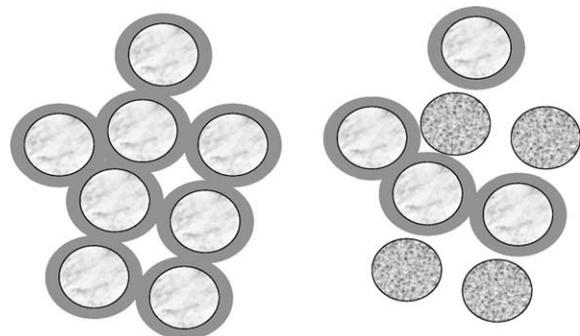


Fig. 2. Comparison of model mortars with normal weight sand particles only (left) with their surrounding ITZs and with a 50:50 blend (volume basis) of sand and LWA (right). Both the volume fraction of ITZ (grey) paste and its percolation are reduced by the incorporation of the LWA.

schematically in two dimensions in Fig. 2. The impetus for the current study was an observation made during a recent study on the effectiveness of viscosity modifiers in reducing the ingress of chloride ions into mortars (VERDiCT: Viscosity Enhancers Reducing Diffusion in Concrete Technology) [23]. In that study, three methods for introducing a polyoxyalkylene alkyl ether viscosity modifier into the mortar were explored, namely direct addition to the mixing water, application as a topical curing solution, and incorporation via pre-wetted lightweight fine aggregates. The latter technology, FLAIR (Fine Lightweight Aggregates as Internal Reservoirs), had been previously applied to introduce shrinkage-reducing admixtures (SRA) into a mortar, mitigating the air detrainment observed when the SRA was added directly to the mixing water [24]. As shown in Fig. 3, while all three methods of VERDiCT introduction generally reduced the depth of chloride penetration into a w/c = 0.4 mortar, by far the most successful was when an aqueous solution of the viscosity enhancer was utilized to pre-wet the lightweight fine aggregates. Based on these results, the current study using LWA pre-wetted with water only was initiated to separate out the beneficial effects of IC from those of VERDiCT.

2. Experiments and modeling

For this study, mortars with a water-to-cement ratio (w/c) of 0.4 were prepared. The actual batch mixture proportions employed for mortars with and without IC are provided in Table 1. The replacement of normal weight sand by LWA in the mortar was performed to provide an extra 0.08 units of curing water per mass of

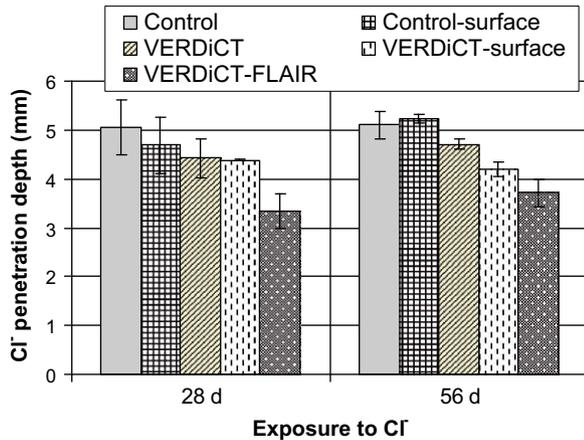


Fig. 3. Penetration depth as determined by spraying with AgNO₃ vs. Cl⁻ exposure time (28 d or 56 d) for mortar cylinders first cured for 28 d and then exposed to chloride solutions. Labels of *surface* and *FLAIR* indicate 28 d curing in a curing solution composed of a mixture of hydroxides and the VERDiCT admixture, or cured for 28 d under sealed conditions, respectively. Error bars indicate ± one standard deviation in the measured average penetration depth [23].

Table 1
Mixture proportions for control and IC mortars.

Material	Control mortar (g)	IC mortar (g)
Portland cement	1757.3	2300
Water	702.9	920
F95 fine sand	985.0	954.0
ASTM C778 [25] graded sand	748.6	836.1
ASTM C778 20–30 sand	748.6	788.2
S16 coarse sand	1457.7	982.2
LWA (pre-wetted)	–	1100.7

cement, while maintaining an overall volume fraction of 55% for the sand or sand/LWA blend in each mortar. The LWA, an expanded shale, was obtained from a lightweight aggregate manufacturer. It has a saturated-surface-dried (SSD) specific gravity of 1.80 and a total water absorption capacity of 22% by mass; 20.3% water or about 93% of the total water is released from the LWA during desorption in a 93% RH environment [22].

After mixing each mortar, cylindrical specimens 50 mm in diameter by 100 mm in height were prepared. After curing for 1 d in the molds and subsequently curing for either 7 d or 28 d, the cylinders were exposed in individual sealed plastic bottles to 1 M chloride ion solutions. The control mortar was cured in a solution of NaOH/KOH/Ca(OH)₂, to avoid leaching of alkalis from the mortar into the curing solution. For the mortar with IC, sealed curing in double plastic bags (7 d or 28 d) was employed, to promote water movement from the lightweight fine aggregates to the surrounding cement paste, as discussed previously. Isothermal calorimetry measurements were conducted at 25 °C during the first 7 d of curing on replicate sealed mortar specimens weighing between 7 g and 7.5 g.

A silver nitrate spraying method [26,27] is being employed for quantifying the chloride ion ingress into the control and IC mortar cylinders after exposure times of 28 d, 56 d, 180 d, and 365 d. At each exposure time, two cylinders are removed from their chloride solutions and broken down the middle (lengthwise) using a universal testing machine. For each specimen, one of the two created faces is sprayed with silver nitrate (AgNO₃), the specimen is photographed, and image processing software is used to visually assess the penetration depth of the chloride ions (example of results previously obtained using this technique are provided in Fig. 3).

The sieve size distributions of the different sands and the LWA had been previously measured. For the mortar with IC, different portions of the four normal weight sands were replaced by LWA as indicated in Table 1, in order to maintain a similar overall fine aggregate size distribution. The specific sieve size distributions were used as input into the HCSS computer program to determine the volume fraction of percolated ITZ paste as a function of ITZ thickness for the two mortars. For these simulations, the computer codes [8] were modified so that ITZs were only present surrounding the normal weight sand particles and not the LWA. While the simulations were conducted for a range of ITZ thicknesses, in general the ITZ thickness would be expected to be near the median particle diameter of the cement [5–7], about 12 μm for the cement employed in this study. A computational volume of 20 mm × 20 mm × 20 mm was employed for each simulation conducted in this study, requiring over 750,000 individual sand/LWA particles. For the ITZ thickness of 12 μm, random walk diffusion studies were executed to estimate the relative diffusivity of the mortars with and without IC. The “ant” step size was set at 6 μm and the simulations were conducted using 10,000 ants, each taking 100,000 random steps [8]. Given the early ages at which the experimental specimens were exposed to chlorides, for these simulations, the diffusivity of the ITZ regions (surrounding the normal weight aggregates only) was first set to be 20 times greater than that of the bulk cement paste, as discussed above. To better understand the influence of this parameter, a second set of simulations was conducted with a more conservative diffusivity ratio of 5:1. In the simulations, no diffusion was allowed within either the normal weight sand or the LWA particles.

In a separate experiment, the absorption/release of chloride ions by/from the LWA and coarsest (silica) sand were monitored by exposing 100 g of dry aggregate to 500 mL of either distilled water or a one molar solution of chloride ions. Within the experimental variability of the measurement of chloride ion concentration, the results indicated no significant absorption or release of chloride ions during a 28 d evaluation period by either the LWA

Table 2
Measured penetration depths of chlorides into mortars, via AgNO_3 spraying technique.

Curing time (d)	Exposure to Cl^- (d)	Penetration depth (mm) for control mortar	Penetration depth (mm) for IC mortar	$l_{\text{IC}}/l_{\text{cont}}$	$D_{\text{IC}}/D_{\text{cont}}$
7	28	6.7 (0.6) ^a	5.0 (0.4)	0.75	0.56
7	56	6.3 (0.3)	5.3 (0.1)	0.84	0.70
28	28	5.06 (0.33)	3.67 (0.39)	0.73	0.53
28	56	5.11 (0.53)	4.36 (0.30)	0.85	0.73

^a Numbers in parentheses indicate standard deviation in penetration depth between replicate specimens.

or the normal weight sand employed in this study. This suggests that any reduction in chloride penetration depth is not being caused by absorption of the chloride ions by the LWA (or sand).

3. Results and discussion

The measured penetration depths for chloride ingress into the various mortars with and without IC are summarized in Table 2. In every case, the penetration depth measured by the AgNO_3 spraying technique is significantly less for the mortars with IC than for their equivalent control mortars with no IC. While the exact analytical solution for ingress/binding of chloride ions from a fixed solution volume into a cylindrical mortar specimen is quite complex [28] even when fluid sorption (imbibition) and reaction/binding are neglected, it contains terms of the form Dt/l^2 , where D is the diffusion coefficient, t is the exposure time, and l is the penetration depth. This implies that for a fixed exposure time, the ratio of the

penetration depths for the IC and control mortars should be equivalent to the square root of the ratio of their diffusivities, or conversely that the ratio of their diffusivities is given by the ratio of their penetration depths squared, recognizing that the multi-mode transport/reaction occurring in the real material is being mapped onto much simpler Fickian diffusion. These ratios for the various curing conditions and chloride exposure periods have been included as the last two columns in Table 2. They suggest that the diffusion coefficient for chloride ions in the IC mortar may be only about 55–75% of that for the control mortar, a significant reduction. In many real world degradation scenarios, concrete service life is proportional to diffusion coefficients, so reducing the diffusion coefficient by a factor of two, for example, could effectively double the service life of the concrete [23].

Could such a significant reduction in diffusion coefficients be explained simply by the absence of ITZ regions surrounding the lightweight aggregates in the IC mortar? According to the simulation results provided in Fig. 4, the volume fraction of percolated ITZ paste (defined as the volume fraction of ITZ paste that is continuous across the microstructure) for the IC mortar is only 60% of that for the control mortar for an assumed ITZ thickness of 12 μm . However, the random walk simulations for these two mortar microstructures indicate that this reduced ITZ volume/percolation would produce only about a 22% reduction in diffusivity for the mortar with IC vs. the control mortar without LWA. By contrast, if a 5:1 ratio is assumed for the diffusivity of the ITZ relative to the bulk paste, the projected reduction in diffusivity is only 10%. But these simulations did not account for any possible further reductions in bulk paste (and ITZ) diffusivities due to enhanced hydration provided by the IC water. For example, for a $w/c = 0.4$ cement paste, previously developed equations [29] would indicate about a 32% reduction in the diffusivity of a cement paste, if its degree of hydration were increased from 75% to 80%, due to the availability of extra IC water for instance. Even an increase from 77% to 80% would produce a 13% reduction in diffusivity. Enhanced hydration of the mortar with internal curing at later ages is supported by the isothermal calorimetry results presented in Fig. 5 that indicate

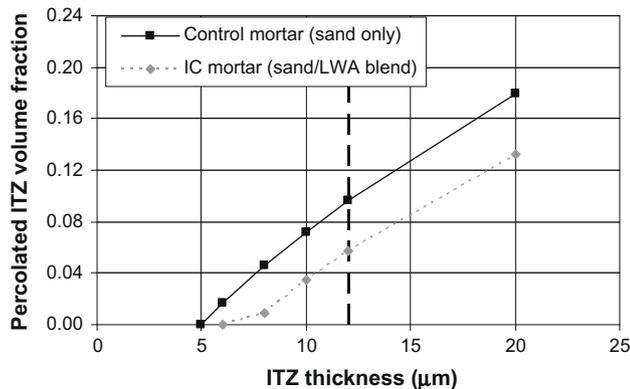


Fig. 4. Simulation results for the volume fraction of percolated ITZ paste as a function of ITZ thickness for the control and IC mortar mixtures of Table 1. Dashed vertical line indicates an ITZ thickness of 12 μm , the median particle diameter of the cement used in this study.

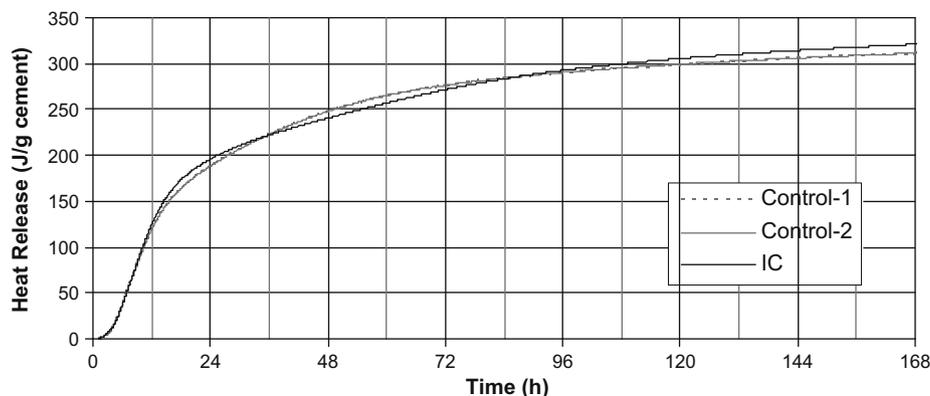


Fig. 5. Isothermal calorimetry results (25 °C) for mortars without (Control) and with IC. Results for two replicates for the control mortar are shown to provide an indication of repeatability.

about a 5% increase in heat released (or degree of hydration) at a curing age of 7 d for the IC mortar relative to the control mortar, both cured under sealed conditions. Fig. 1 also qualitatively indicates the enhanced hydration and denser microstructure achieved at later ages (120 d) in mortars with IC. Thus, the combination of decreased ITZ volume fraction/percolation and enhanced hydration could easily produce an IC mortar with a diffusivity that is about 55% to 75% of that of the control mortar (e.g., $0.78 \times 0.68 = 0.53$ or $0.9 \times 0.87 = 0.78$).

These results have been obtained for mortars with a 55% sand volume fraction. The absolute reduction in diffusion coefficients will likely be different for concretes that typically contain 60–70% aggregates (coarse and fine) by volume fraction. The ITZ regions in a conventional concrete will be highly percolated [7] so that it may take a larger replacement by lightweight aggregates to substantially reduce the volume fraction of percolated ITZ paste. Still, some reduction will surely be achieved along with enhanced hydration so that one would expect the IC concrete to have a lower diffusion coefficient than its control counterpart. Furthermore, the simulation and experimental techniques presented here should be equally applicable to concrete as to the mortars examined in this study, as will be pursued in future research.

4. Conclusions

In this study, the mortar prepared with IC and then cured under sealed conditions exhibited chloride ion penetrations depths that were significantly reduced with respect to the control mortar. Modeling results indicate that this reduction in diffusion coefficient is likely due to both a significant reduction in the volume fraction of percolated ITZ paste and enhanced long term hydration in the mortar with IC. Thus, based on the results of this study, it appears that in addition to providing significant reductions in early-age autogenous shrinkage and strength enhancement at ages of 28 d and beyond [4,30], IC may also produce mortars and concretes with significantly enhanced resistance to the penetration of chloride ions and other deleterious species.

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