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Corrosion Resistance of Steel Rebar in Simulated Concrete Pore Solution in Presence of Trisodium Phosphate and Zn^{2+}

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Abstract - **The inhibitive performance of Trisodium Phosphate (TSP) in controlling corrosion of rebar steel immersed in simulated concrete pore solution prepared in well water in the absence and presence of Zn^{2+} has been evaluated by the weight loss method. The formulation consisting of 250 ppm of TSP and 50 ppm of Zn^{2+} offers 95 % inhibition efficiency to rebar steel. Potentiodynamic polarization and electrochemical impedance studies confirmed that a TSP -Zn^{2+} system function as an anodic inhibitor and the formulation controls the anodic reaction predominantly. Surface analysis by CV, SEM and AFM confirmed the formation of protective layer on the rebar steel surface.**

Keywords: **Rebar Steel, Corrosion Inhibition, Trisodium Phosphate, Well Water, Synergistic Effect, Simulated Concrete Pore Solution.**

I. INTRODUCTION

The corrosion of metals in many industries is a severe problem. Proper design and preparation of concrete consistent with relevant standards and timely maintenance would assure them a long and efficient life in aggressive media. However, these requirements not always possible and adhered too. In this state, the use of inhibitors is one of the most practical methods for protection of metal against corrosion, especially in acidic media [1]. They have been increasingly used as concrete admixtures for new structures and restorative applications for repairing existing reinforced concrete during the recent years. There are many corrosion-inhibiting systems commercially available [2]. It includes a wide list of organic and inorganic compounds [3] containing the functional groups such as aldehydes [4], amines [5,6], phosphates[7,8] etc. Trisodium phosphate has the hetero atom like oxygen. Such compounds are expected to have good inhibition efficiency.
The present work is undertaken

1. To evaluate the inhibition efficiency (IE) and corrosion rate(CR) of the Trisodium phosphate-Zn^{2+} system in controlling corrosion of rebar steel immersed in simulated concrete pore solution(SCPS) prepared in well water, in the absence and presence of Zn^{2+} by the weight loss method;
2. To study the mechanism of corrosion inhibition by polarization curves; and AC Impedance spectral studies;
3. To evaluate the protective film formed on the metal surface by CV, SEM and AFM spectral studies; and
4. To propose the mechanism of corrosion inhibition based on the above results.

II. EXPERIMENTAL SECTION

Metal Specimens

Rebar steel specimens were used in the present study with Composition (wt %): 0.05 S, 0.05 P, 0.5 Mn, 0.2 C, and the rest iron were used for the study. Rebar specimens of size 0.7x1.0 cm were used for weight loss study, specimens of exposed area 1 × 1 cm (square the rest being covered with lacquer) with stem were used for electrochemical study. The surface preparation of the mechanically polished specimens were carried out using different grades of emery paper and then degreased with acetone.

Preparation of Simulated Concrete pore solution (SCPS)

In numerous studies of rebar corrosion, saturated $Ca(OH)_2$ has been used as a substitute for pore solution [9]. A saturated calcium hydroxide solution is used in present study, as SCP solution with the pH ~ 12.5. The environment chosen is SCPS prepared in well water and the Physico-chemical parameter of well water is given in Table 1**.**

TABLE 1 PARAMETERS OF WELL WATER

Parameters	Value
pH	8.2
Conductivity	$1770\mu\Omega^{-1}cm^{-1}$
Total Dissolved solids	1204 ppm
Total Hardness	402 ppm
Chlorides	665 ppm
Sulphate	214 ppm
Total Alkanity	390 ppm
Magnesium	83 ppm
Potassium	55 ppm
Sodium	172 ppm
Calcium	88 ppm

Weight-Loss Method

The polished and pre weighed Rebar specimens in triplicate were suspended in 100 ml of the simulated concrete pore solution prepared in well water containing solutions with and without the inhibitor at different concentrations for 1day. Then the specimens were washed, dried and weighed. The weight loss was calculated using a Shimadzu balance, model AY62. The parameter of the well water is given in Table.1. From this data, inhibition efficiency (IE) was calculated by the following equation [1]:

$$IE = 100\,[1-(W2/W1)]\,\% \quad \text{---- (1)}$$

Where,
W1, W2 are the corrosion rate (mmy) in the absence of inhibitor and in the presence of inhibitor.

Determination of Corrosion Rate

From the change in weights of the specimen, corrosion rates were calculated using the following equation (2):

$$\text{Corrosion Rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2\text{)} \ \text{X} \ \text{Period of immersion (days)}} \quad \text{--- (2)}$$

Potentiodynamic Polarization and AC Impedance Measurements

Polarization studies were carried out in a CHI-Electrochemical workstation with impedance, Model 660A. A three–electrode cell assembly was used. The working electrode was rebar steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as Corrosion Potential (E_{corr}),Corrosion Current (I_{corr}) and Tafel slopes (anodic= b_a and cathodic=b_c) and LPR values were calculated. During the polarization study, the scan rate (v/s) was 0.01; hold time at Ef(s) was zero and quit time was 2. In AC impedance measurements, the real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The Rt (charge transfer resistance) and Cdl (double layer capacitance) values were calculated. AC Impedance spectra were recorded with initial E (v) = 0; High frequency (Hz) = $1x10^5$, Low frequency (Hz) = 1; Amplitude (v) = 0.05 and Quit time (s) =2.

Surface Analytical Techniques

The specimens in presence and absence of inhibitor medium are analyzed using CV, SEM and AFM spectral techniques**.**

III. RESULTS AND DISCUSSION

Weight-Loss Method

Evaluation of Improvement of IE of Zn^{2+} with TSP

The inhibition efficiency of Trisodium phosphate (TSP) in controlling corrosion of rebar steel immersed in simulated concrete pore solution prepared in well water for a period of one day in the absence and presence of is given in Table 2. It is found that Trisodiumphosphate (TSP) alone has some inhibition efficiency. As the concentration of TSP increases inhibition efficiency also increases. 50 ppm of TSP has 60.6 % inhibition efficiency and 250ppm of TSP + Zn^{2+}has 75.4 %.

TABLE 2 CORROSION RATE(CR) AND INHIBITION EFFICIENCY (IE) BY TRISODIUM PHOSPHATE-ZN^{2+} SYSTEM TO REBAR STEEL IMMERSED IN SCPS PREPARED IN WELL WATER FOR ONE DAY

Inhibitor TSP (ppm)	**Zn^{2+}**			
	0ppm		50ppm	
	CR(mdd)	**IE%**	**CR(mdd)**	**IE%**
0	1.44	-	1.24	65.8
50	0.57	60.6	0.35	75.4
100	0.52	63.6	0.19	86.8
150	0.49	65.8	0.16	88.7
200	0.39	73.1	0.11	92.3
250	0.35	75.4	0.07	95.0

When Zn^{2+} is added to TSP the corrosion inhibition efficiency increases to a great extent that is 95%. This suggests that a synergistic effect exists between Zn^{2+} and the inhibitor namely TSP. When TSP and Zn^{2+} are mixed, Zn^{2+} - TSP complex is formed. It is transported towards the metal surface.

On the metal surface Zn^{2+} -TSP complex is broken. The released TSP combines with Fe^{2+} (formed on the metal surface due to corrosion process) resulting in the formation of Fe^{2+} - TSP complex. Fe^{2+} - TSP complex is more stable than the Zn^{2+} - TSP complex.

The released Zn^{2+}combines with OH- formed by cathodic reaction and Zn $(OH)_2$ is precipitated on the cathodic site of a metal surface. The Zn^{2+} -TSP complex bond is strong enough to carry the complex towards the metal surface and it is weak enough to break in the presence of Fe^{2+}. This accounts for the breaking of TSP-Zn^{2+}complex and the formation of Fe^{2+}- TSP complex.

Analysis of Potentiodynamic Polarization Curves

Polarization study has been used to know if a protective film is found on the metal surface. If a protective film is formed on the metal surface [10], the linear polarization resistance (LPR) increases and corrosion current decreases [11-15]. The polarization curves of rebar steel immersed in the absence and presence of inhibitors are shown in figure.1.

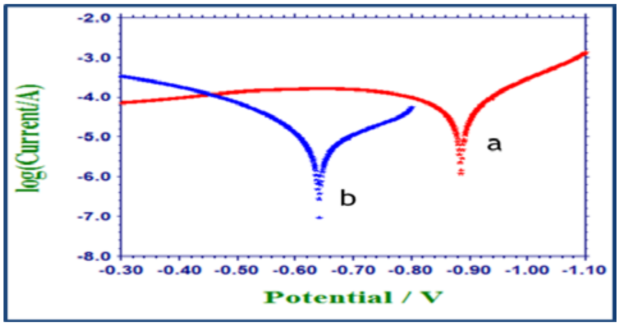


Fig.1. Polarization curves of rebar steel immersed in various test solutions
(a) SCPS(b) SCPS + 250ppm of TSP

The various corrosion parameters such as corrosion potential, corrosion current, linear polarization resistance (LPR) and Tafel slopes, derived from the polarization curves are given in Table.3.

TABLE 3 CORROSION PARAMETERS OF REBAR STEEL IMMERSED IN SIMULATED CONCRETE PORE SOLUTION OBTAINED BY POLARIZATION STUDY

System	E_{corr} mV Vs SCE	Bc mV/ decade	ba mV/ decade	LPR ohmcm^2	Icorr A/cm^2
SCPS	-888	148	278	650.5	6.455×10^{-5}
SCPS + 250 ppm of TSP+50ppm of Zn^{2+}	-643	183	108	4167.8	7.100×10^{-6}

When rebar steel is immersed in simulated concrete pore solution prepared in well water the corrosion potential was -888 mV vs SCE (saturated calomel electrode). When TSP (250 ppm) and Zn^{2+}(50 ppm) were added to the above system the corrosion potential shifted to the anodic side -643 mV vs SCE; that is noble side. This indicates that the TSP - Zn^{2+} system controls anodic reaction predominantly [16, 17]. This indicates that the passive film is formed on the metal surface in presence of inhibitor. Further, the LPR value increases from 650.5 ohmcm^2 to 4167.8 ohmcm^2; When rebar steel is immersed in well water the corrosion current I_{corr} is 6.455×10^{-5}A/cm^2. When 250ppm of TSP with 50 ppm of Zn $^{2+}$ it decreases to 7.100×10^{-6}A/cm^2. This significant reduction in corrosion current indicates a decrease in corrosion rate in the presence of inhibitor. When a passive film is formed on rebar steel surface, in presence of inhibitor system, the electron transfer from the metal surface towards the bulk of the solution is difficult and prevented. So rate of corrosion decreases and hence corrosion current decreases in presence of inhibitor system. Thus the decreasing order of corrosion is as follows,

SCPS+ Inhibitor < SCPS

Analysis of AC Impedance Spectra

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film formed on the metal surface. If a protective film on the metal surface, the charge transfer resistance (R_t) increases, double layer capacitance value (C_{dl}) decreases and the impedance log(z/ohm) value increases[18,19]. The AC impedance spectra of rebar steel immersed in SCPS prepared in well water in the absence and presence of inhibitors are shown in Fig 5.2.3 (Nyquist plot) and Fig 5.2.4(a,b) (Bode plot). The AC impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) and impedance value log(z/ohm) are given in Table 4.

TABLE 4 IMPEDANCE PARAMETERS OF REBAR STEEL IMMERSED IN SCPS OBTAINED BY AC IMPEDANCE SPECTRA

System	Nyquist plot		Bode plot
	R_t ohm cm^2	C_{dl} F/cm^2	Impedance value log (z/ohm)
SCPS	56.12	8.909×10^{-8}	1.93
SCPS + 250 ppm of TSP+50ppm of Zn^{2+}	71.92	6.952×10^{-8}	2.03

The AC impedance spectra of rebar steel immersed in SCPS prepared in well water in the absence and presence of inhibitors are shown in Fig.2. (Nyquist plot) and Fig.3.(a,b) (Bode plot).

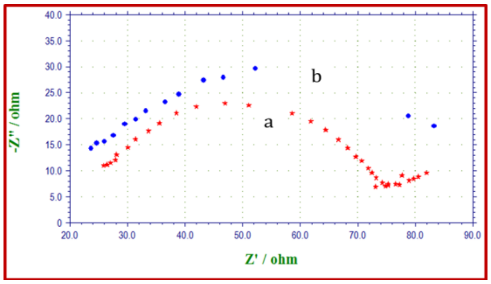


Fig.2. AC Impedance spectrum of rebar steel immersed in various test solutions (Nyquist plot); a) SCPS prepared in well water b) SCPS + 250ppm of TSP

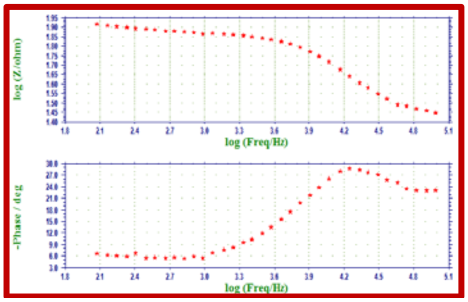


Fig.3.a. Bode plots of rebar steel immersed in SCPS prepared in well water

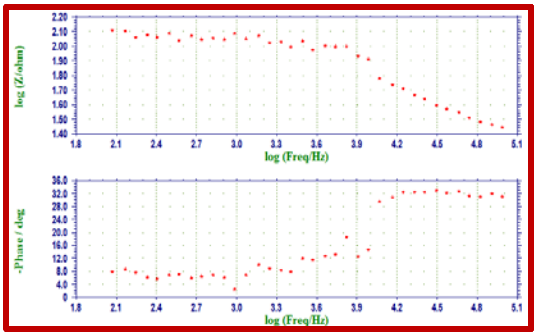


Fig.3.b. Bode plots of rebar steel immersed in SCPS + 250 ppm of TSP+50ppm of Zn^{2+}

Analysis of Cyclic Voltammetry

Cyclic voltammograms have been used to investigate the corrosion behaviour of metals.

In the present study, cyclic voltammograms were recorded by measuring the working electrode, rebar steel, in 3.5% NaCl solution]. The cyclic voltammetry parameters are given in Table 5.

TABLE 5 CYCLIC VOLTAMMETRY PARAMETERS (TSP + ZN^{2+})

Sample	Ep (mV)	Peak ip (mA)	Pitting Corrosion product(mV)	Pitting Potential (mV)
Control (rebar steel)	930	12.29	-	-1.11
Blank (SCPS)	250	2.21	-450	-1.15
Inhibitor system (TSP+ Zn^{2+})	1040	2.42	-380	-1.1

The cyclic voltammogram of rebar steel immersed in 3.5% NaCl is shown in Fig.4.a. The cyclic voltammogram of rebar steel, which has been immersed in SCPS for one day and dried is shown in Fig.4.b.. and the cyclic voltammogram of rebar steel electrode deposited with the above protective film is shown in Fig.4.c.

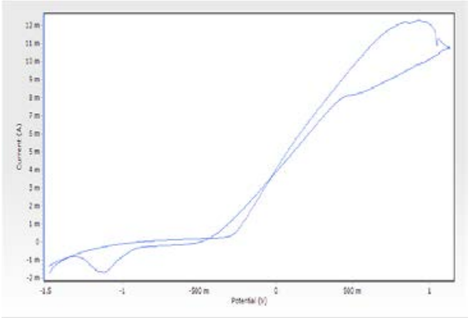


Fig.4.a. Cyclic voltammogram of polished rebar steel electrode immersed in 3.5% NaCl.

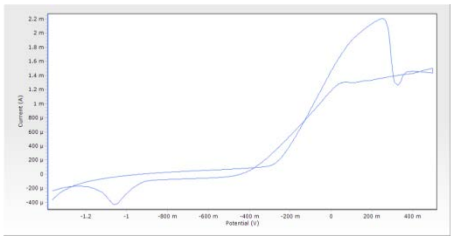


Fig. 4.b. CV of rebar steel in 3.5% NaCl solution after its immersion in SCPS for 1 day

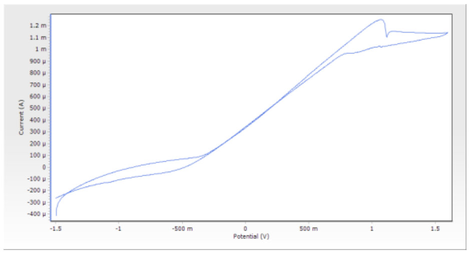


Fig.4.c. CV of rebar steel in 3.5% NaCl solution after its immersion in SCPS + 250 ppm of TSP + 50 ppm of Zn^{2+} for one day

It is observed that during anodic sweep, dissolution of metal does not take place. This indicates that the protective film is stable and compact. Electrons are not transferred from the metal surface, and a passive region is observed. During cathodic sweep, the peak corresponding to reduction of pitting corrosion product appears at -380 mV. However, the peak due to reduction of iron oxide to iron appears at -1.3 V. The current density increases from 12.29 mA to 2.42 mA. The increase in current density may be explained as above. It is observed from the Fig.4.a, 4.b, 4.c that the pitting potentials for the three systems at -1.11 mV, -1.15 mV, and -1.1 mV respectively. That is when rebar steel electrode is immersed in the SCPS medium; the pitting potential is shifted to more negative side (active side, i.e., -1.15 mV).

It accelerates corrosion because the protective film formed is porous and amorphous. When the electrode is immersed in the inhibitor medium, the pitting potential is shifted to the noble side, i.e., -1.1 mV. This indicates that the passive film found on the metal surface in the presence of inhibitors is compact and stable. It can withstand the attack of chloride ion present in 3.5% NaCl.

SEM Analysis of Metal Surface

SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of rebar steel, the SEM Micrographs of the surface are examined. The SEM images of rebar steel specimen immersed in the SCPS for one day in the absence and presence of inhibitor system are shown in Fig.5.a, 5.b.(Magnifications X50)

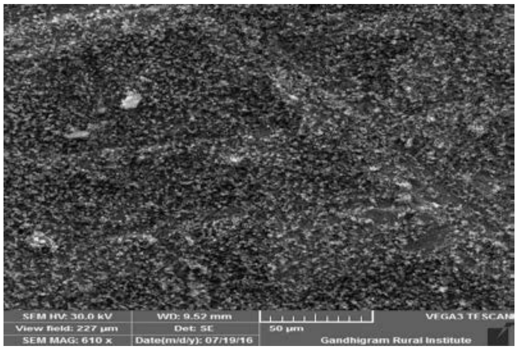


Fig.5.a. SEM of Rebar Steel immersed in SCPS

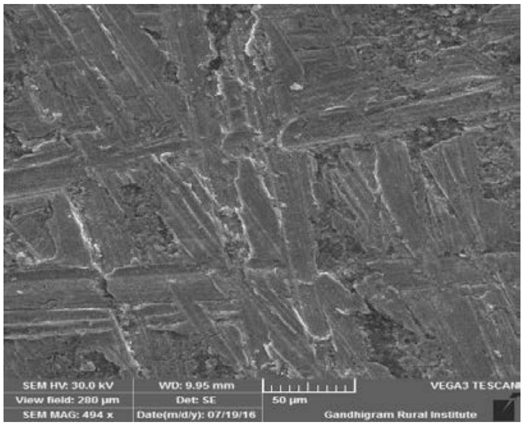


Fig.5.b. SEM of Rebar Steel immersed in SCPS + TSP 250ppm + Zn^{2+} (50ppm)

The SEM Micrographs of rebar steel surface immersed in SCPS shown in Fig 56.a. shows the roughness of the metal surface whereas the roughness is reduced in the rebar Steel immersed in SCPS containing TSP 250ppm+Zn^{2+}(50ppm) which creates a thin protective film, and it inhibits the rebar steel corrosion.

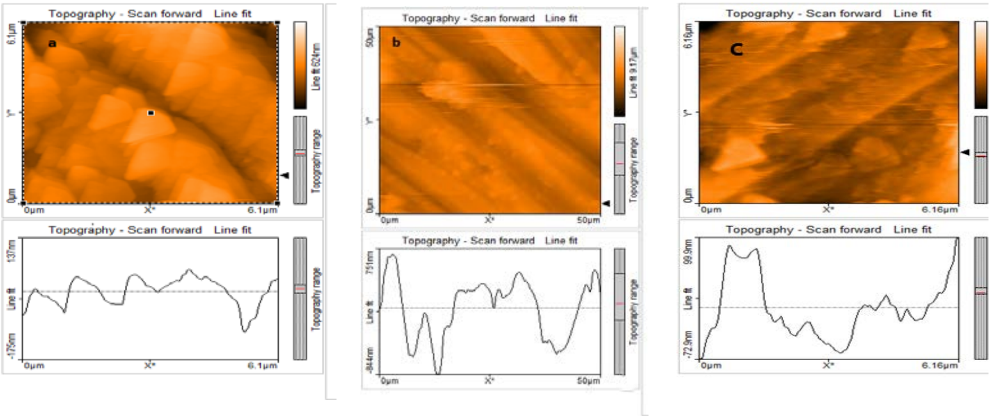
Atomic Force Microscopy Characterization

Atomic force microscopy is a powerful technique for gathering roughness statistics from a variety of surfaces. AFM instrument operating in contact mode in air. The scan size of all the AFM images are 50µm areas at a scan rate of 1µm/second, direction of scanning is down, line by line scanning rate is 256. The varying scan rate depends upon the frequency and scanning area of the sample.

The two dimensional (2D) and cross – sectional profile and histogram images of surface for polished rebar steel surface, rebar steel surface immersed in SCPS and rebar steel surface immersed in SCPS containing the formulation of 250 ppm of TSP and 50 ppm of Zn^{2+} are shown in Fig 6 (a,b,c),

TABLE 6 AFM DATA FOR REBAR STEEL SURFACE IMMERSED IN INHIBITED AND UNINHIBITED ENVIRONMENTS

Samples	**RMS Roughness Rq(nm)**	**Average Roughness Ra (nm)**	**Maximum Peak to Valley height (nm)**
Polished rebar steel (Control)	45.871	34.049	44.518
Rebar Steel immersed in SCPS	455.63	390.81	433.29
Rebar steel in SCPS + 250 ppm of TSP + 50 ppm Zn^{2+}	21.204	17.934	24.013



(a) (b) (c)

Fig.6 AFM cross sectional images of the surface of
a) Polished rebar steel (control) b) Rebar steel immersed in SCPS (blank)
c) Rebar steel immersed in SCPS containing 250 ppm of TSP + Zn^{2+} 50 ppm

The value of $R_{RMS,}$ R_a and peak to valley height for the polished rebar steel surface are 45.871nm, 34.049 nm and 44.518nm respectively, which shows a more homogeneous surface, with some places in which the height is lower than the average depth. Fig 6 (a) displays the uncorroded metal surface. The slight roughness observed on the polished rebar steel surface is due to atmospheric corrosion. The RMS roughness, average roughness and P-V height values for the rebar steel surface immersed in SCPS are 455.63 nm, 390.81 nm and 433.29 nm respectively. These data suggest that rebar steel surface immersed in SCPS has a greater surface roughness than the polished metal surface. This shows that the unprotected rebar steel surface is rougher and is due to the corrosion of the rebar steel in SCPS. Fig.6 (b) displays the corroded metal surface with few pits. The presence of rebar steel immersed in SCPS and 250 ppm of TSP reduces the R_q by a factor of 21.204 from 455.63 nm and the average roughness is significantly reduced to 17.934 nm, when compared with 390.81 nm of rebar steel surface immersed in SCPS prepared in well water. The maximum peak to valley height also reduced to 24.013 nm from 433.29 nm. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} - TSP complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of rebar steel, and the formation of the film on the metal surface, which is protective in nature.

IV.CONCLUSION

In presence of Trisodium phosphate-Zn^{2+} system, the corrosion resistance of rebar steel immersed in SCPS solution prepared in well water increases. Hence, it is recommended that when concrete admixtures are prepared, Trisodium phosphate and Zn^{2+} may be added to the admixture, to increase the lifetime of steel rebar.

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