

## Sodium tungstate – Zn<sup>2+</sup> as corrosion inhibitor for carbon steel

*The inhibition efficiency of a sodium bisulphite (SBS) in combination with a bivalent cation like Zn<sup>2+</sup> in controlling corrosion of carbon steel was investigated by weight – loss method. A formulation consisting of Zn<sup>2+</sup>, sodium tungstate, ST, and SBS can be used as a potent inhibitor to prevent the corrosion attack to carbon steel in neutral aqueous media. The ternary system ST (20ppm), Zn<sup>2+</sup> (50ppm) and SBS (10ppm) is effective and has 95% I.E. The protective film consists of Zn(OH)<sub>2</sub> and complexes of Fe<sup>2+</sup> / Fe<sup>3+</sup> and Zn<sup>2+</sup> with SBS and ST. These complexes formation are confirmed by UV-Visible, FTIR and atomic force microscopic (AFM) spectra. The surface morphology of the protective film on the metal surface is also characterized by AFM.*

**Key words:-** Corrosion inhibition, carbon steel, sodium tungstate, sodium bisulphite, Zn<sup>2+</sup>, UV-visible and FTIR spectra, atomic force microscopy, mechanism.

### 1. INTRODUCTION

Due to its low cost, availability etc., carbon steel is considered as in wide area of practical applications such as water pipelines [1, 2], cooling water systems [3], boilers etc, due to its low cost, availability etc. However they are susceptible to different forms of corrosion induced by chloride and so on. One of the most important methods in corrosion protection is to use inhibitors [4, 5], inhibitors should be of low toxicity and easily biodegradable in order to meet environmental protection requirements. Tungstate is an environmentally friendly inhibitor and has been extensively studied for its application in the protection of iron, zinc and aluminium substrates in neutral, acidic and alkaline solutions. Normally it is not feasible to use tungstate alone as a corrosion inhibitor due to its low inhibition ability at low concentrations of tungstate and high cost. In most causes, the combinations of tungstate with co-inhibitors were described in the literature [6-10]. However previous literature has not reported the use of tungstate as the corrosion inhibitor for carbon steel with more than one co inhibitors. Phosphates in the form of polyphosphates control the corrosion of ferrous metals [11]. They act as cathodic inhibitors [12, 13].

The objectives of the present study are as follows

a) To study the synergistic inhibition of corrosion of carbon steel using sodium tungstate and zinc ions (elevator 1)

b) To study the synergistic inhibition of carbon steel using sodium tungstate, zinc ions and inorganic additives. Here, the aim is to reduce the amount of

sodium tungstate as well as zinc ions by introducing inorganic additive as second elevator. In the present study, cheaply and abundantly available inorganic salt such as sodium bisulphite used as inorganic additive.

c) To investigate the nature of the protective film formed on the metal surface by using FTIR spectroscopy and atomic force microscopy. The mechanistic aspects of corrosion inhibition are studied in a holistic way, based on the results obtained from the classical weight-loss method and different surface examination techniques mentioned above and UV – visible absorption spectra of the solution.

### 2. EXPERIMENTAL

#### 2.1. Preparation of carbon steel samples

The composition of all carbon steel samples used in this study was as follows: sulphur – 0.026 %, phosphorus – 0.06 %, manganese - 0.4 %, carbon – 0.1 % and the rest iron.

The carbon steel specimens of the dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish and then degreased with acetones. They were used in the weight loss method and surface examination studies.

#### 2.2. Weight - loss method

Determination of surface area of the specimens were determined with specimens and the length, breadth and the thickness of carbon steel specimens and the radius of the hole were determined with the help of a vernier calliper of high precision and the surface areas of the specimens were calculated.

#### 2.3. Weighing the specimens before and after immersion

All the weighing of the carbon steel specimens before and after immersion were carried out using a ANAMED™ Electronic balance–AE 240 dual range

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balance with readability of 0.01 mg in 40 g range and 0.1 mg in 200g range. This balance has reproducibility (standard deviation) of 0.02 mg in 40 g range and 0.1 mg in 200g and was supplied by instrument AG, CH-8606 Greifensee, Switzerland.

#### 2.4 Determination of corrosion inhibition efficiency

The weighed specimens in triplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of different test solutions. After immersion, the samples were taken out, washed and weighed. From the change in weight of the specimens corrosion inhibition efficiency (*I.E*) was calculated using the equation.

$$I.E. = 100 [1 - (W_2/W_1)], \text{ in } \%$$

Where:

$W_1$  – corrosion rate in the absence of inhibitor, and

$W_2$  – corrosion rate in the presence of inhibitor.

#### 2.5 UV- visible absorption spectra study

The possibility of formation of Zn<sup>2+</sup> - sodium bisulphite complex, Zn<sup>2+</sup>- sodium tungstate complex, Fe<sup>3+</sup> - sodium bisulphite complex, Fe<sup>3+</sup>- sodium tungstate complex in solutions was examined by mixing the respective solutions and recording their UV-visible absorption spectra using Hitachi U-3400 spectrophotometer.

#### 2.6 Surface examination study FTIR spectra

After two days of immersion in corrosion media, the samples were taken out of the test solutions and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so was to make it uniform throughout. FTIR spectrum of the powder (KBr pellet) was recorded using Perkin – Elmer 1600 FTIR spectrophotometer with a resolving power of 4 cm<sup>-1</sup>.

#### Surface morphology (AFM)

Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces (14). AFM is becoming an accepted method of roughness investigation (15-19)

All atomic force microscopy images were obtained on a pico SPM 2100 AFM instrument operating in contact mode in air, the scan size of all the AFM images are 30 μm X 30μm areas at a scan rate of 2.4 lines per second.

### 3. RESULT AND DISCUSSION

#### 3.1 Analysis of weight – loss method

Corrosion inhibition efficiency (*I.E*) of carbon steel in aqueous environment(100ppm Cl<sup>-</sup>) in the absence and presence of inhibitors obtained by weight

loss method are given in table 1 at pH = 7. It is observed that sodium tungstate (ST) has some efficiency in controlling corrosion of carbon steel. For 50 ppm - Zn<sup>2+</sup> alone, inhibition efficiency is -25%. When 50 ppm Zn<sup>2+</sup> is added to 5 ppm sodium tungstate, *I.E* is 75%. So there is a synergistic effect between sodium tungstate and Zn<sup>2+</sup>. Upon addition of various concentrations of sodium tungstate with 10 ppm sodium bisulphite (SBS) in *I.E* is observed due to increase in rate of deposition of complex on metal surface. After reaching a high *I.E*, there is a decrease in *I.E* due to desorption of formed complex from metal surface into the bulk of the solution.

#### 3.2 Analysis of Influence of duration of immersion on the inhibition efficiency of sodium tungstate – Zn<sup>2+</sup> - sodium bisulphite system

It is observed that from Table - I as the duration of immersion decreased. This is due to the fact that the protective film formed on the metal surface , probably Fe<sup>2+</sup>/Fe<sup>3+</sup> - active principle complex, is broken by the corrosive environment and the film is dissolved.

Table I - Corrosion inhibition efficiency of carbon steel in chloride aqueous environment (chloride = 100 ppm), in the presence and absence of inhibitor obtained by the weight – loss method

**Inhibitor system:** Sodium tungstate + Zn<sup>2+</sup> + NaHSO<sub>3</sub>

**Immersion period:** I day, III day, V day, VII day; pH=7

S.No	Concn. of ST (ppm)	Concn. of Zn <sup>2+</sup> (ppm)	Concn. of SBS (ppm)	I.E. %			
				I day	III day	V day	VII day
1.	0	0	0	-	-	-	-
2.	5	0	0	3	2	1	1
3.	0	50	0	-25	-30	-35	-33
4.	5	50	10	75	70	60	58
5.	10	50	10	80	75	65	55
6.	15	50	10	85	76	68	53
7.	20	50	10	95	79	70	50
8.	25	50	10	85	65	65	48
9.	30	50	10	80	60	63	45
10.	5	50	-	40	30	28	26

#### 3.3. Analysis of UV – visible spectra

It seems that there is an increase in absorbance (Figures I andii ). This suggests that there will be the formation of complexes with carbon steel.

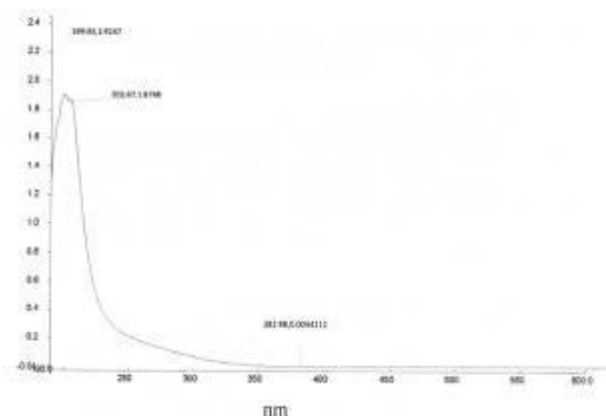


Figure i - UV – visible absorption spectrum of 25 ppm SBS + 25 ppm ST + 50 ppm Zn<sup>2+</sup>

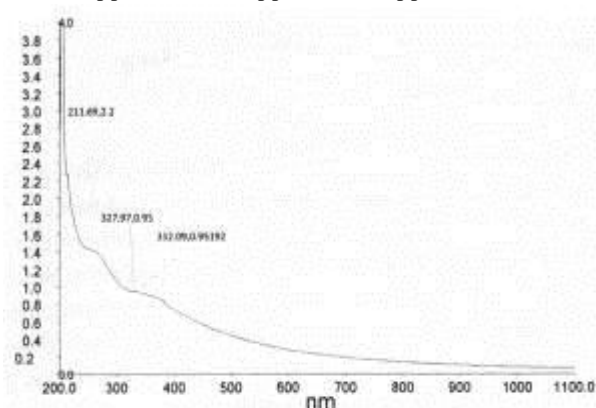


Figure (ii) - UV – visible spectrum of 25 ppm SBS + 25 ppm ST + 50 ppm Zn<sup>2+</sup> + 100 ppm Fe<sup>2+</sup>

### 3.4 Analysis of FTIR spectra

The FTIR spectrum of pure sodium bisulphite is shown in figure iii. The bisulphite stretching frequency of sodium bisulphite appears at 2877 cm<sup>-1</sup>. The FTIR spectrum of pure sodium tungstate is shown in figure iv. The WO<sub>4</sub><sup>2-</sup> stretching frequency appears at 1639 cm<sup>-1</sup>. The FTIR spectrum (KBr Pellet) of the film formed on carbon metal surface after immersion in the aqueous solution containing 100 ppm Cl<sup>-</sup> + 25 ppm sodium bisulphite + 25 ppm sodium tungstate + 25 ppm Zn<sup>2+</sup> is shown in figure V. The bisulphite stretching frequency of sodium bisulphite is shifted from 2877 cm<sup>-1</sup> to 2862 cm<sup>-1</sup>. This suggests that bisulphite is coordinative Fe<sup>3+</sup> resulting in the formation of Fe<sup>3+</sup>-HSO<sub>3</sub><sup>-</sup> complex. The WO<sub>4</sub><sup>2-</sup> stretching frequency is shifted from 1639 cm<sup>-1</sup> to 1635 cm<sup>-1</sup> due to the formation of Fe<sup>3+</sup> - WO<sub>4</sub><sup>2-</sup> complex. The band at 1365 cm<sup>-1</sup> due to Zn(OH)<sub>2</sub> is shifted to 1363 cm<sup>-1</sup> formed on the cathodic sites of the metal surface.

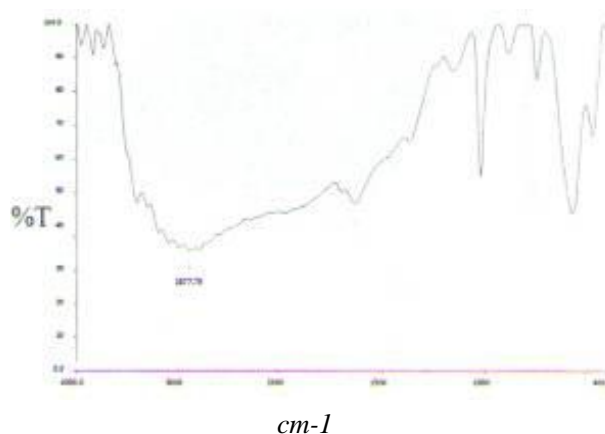


Figure (iii) - FTIR spectrum of pure SBS

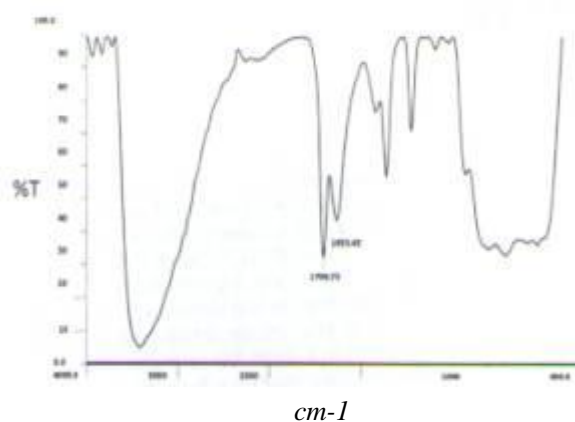


Figure-(iv) FTIR spectrum of pure ST

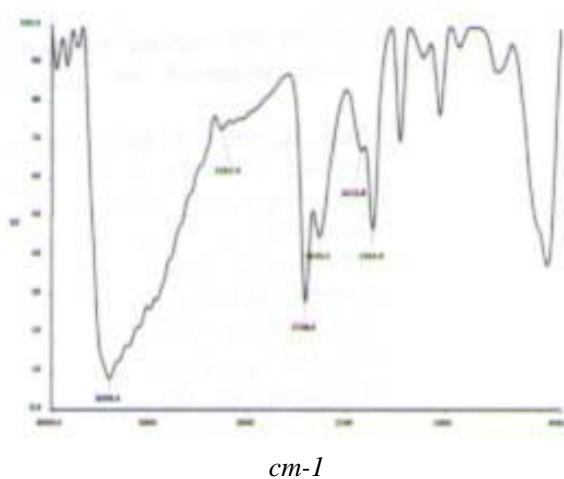


Figure (v) - FTIR spectrum of film formed on the carbon steel surface after immersion in the aqueous environment containing 100 ppm Cl<sup>-</sup> + 25 ppm SBS + 25 ppm ST + 25 ppm Zn<sup>2+</sup>

### 3.5. Analysis of atomic force microscopy

AFM is becoming an accepted method of roughness investigation [20-24]. All atomic force microscopy images were obtained on a pico SPM 2100 AFM instrument operating in contact mode in air.

The scan size of all the AFM images are 5µm X 5µm areas at a scan rate of 2.4 lines per second.

Table II - AFM parameters for carbon steel surface immersed in inhibited and uninhibited environments

Samples	RMS (Rq) Roughness (nm)	Average (Ra) Roughness (nm)	Maximum peak-to-Valley height (P-v) (nm)
Polished metal (control)	195	159	776
Carbon steel immersed in Cl <sup>-</sup> (100ppm)+SBS (25ppm)+ST (25ppm)+Zn <sup>2+</sup> (25ppm)	81.7	69.8	301.6

The two dimensional (2D), three dimensional (3D) AFM morphologies and the AFM cross – sectional profile for polished carbon steel surface (reference sample), and carbon steel immersed in aqueous solution containing 100 ppm (Cl<sup>-</sup>) + 25ppm (SBS) + 25ppm (ST) +25ppm (Zn<sup>2+</sup>), are shown as Figure vi (a,b), Figure vii (c,d) .

AFM image analysis was performed to obtain the average roughness, R<sub>a</sub> (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, R<sub>RMS</sub> (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to valley height in five adjoining sampling heights) [25]. R<sub>RMS</sub> is much more sensitive than R<sub>a</sub> to large and small height deviations from the mean [26].

The Table II shows the various parameters obtained for carbon steel immersed in different environments.

The value of R<sub>RMS</sub>, R<sub>a</sub> and P-V height for the polished carbon steel surface (reference sample) are 195nm, 159nm and 776nm respectively, which shows a more homogeneous surface, with some places in where the height is lower than the average depth. Figure vi (a), Figure vii (c) displays the uncorroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. The R<sub>RMS</sub> roughness, average roughness and P-V height values for the carbon steel immersed in aqueous solution containing 100ppm Cl<sup>-</sup>, 25ppm

(SBS),25ppm (ST), 25ppm (Zn<sup>2+</sup>) are reduced to 81.7nm, 69.8nm and 301.6nm.

These parameters confirmed that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe<sup>2+</sup> – SBS-ST complex and Zn(OH)<sub>2</sub> on the metal surface and there by inhibiting the corrosion of carbon steel.

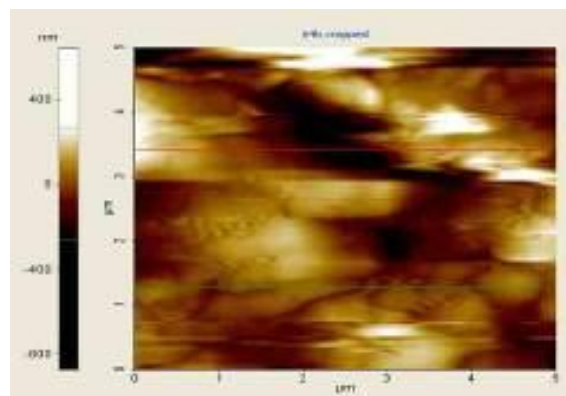


Figure vi (a) – 2D AFM images of polished carbon steel surface (control)

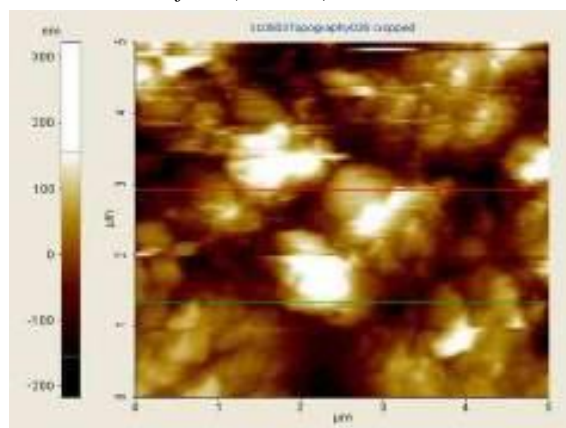


Figure vi (b) -2D Carbon steel immersed in Cl<sup>-</sup> (100ppm), SBS(25ppm), ST (25ppm), Zn<sup>2+</sup> (25ppm).

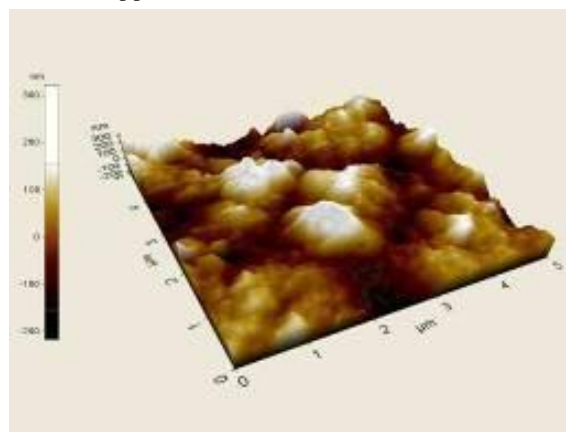


Figure vii (c) – 3D AFM images of polished carbon steelsurface (control).

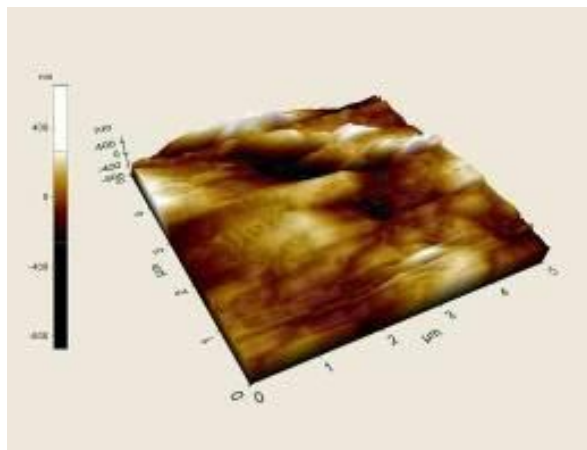


Figure vii (d) – 3D Carbon steel immersed in Cl<sup>-</sup> (100ppm), SBS (25ppm), ST (25ppm), Zn<sup>2+</sup> (25ppm).

### 3.6. Corrosion process

In order to explain the experimental results, the following mechanism of corrosion inhibition is proposed. The mechanistic aspect of the inhibition of carbon steel in aqueous solution has 100ppm Cl<sup>-</sup> by ST – Zn<sup>2+</sup> and SBS can be explained in terms of complexation.

i) Before immersion of carbon steel in aqueous environment, ST, Zn<sup>2+</sup> and SBS, zinc ions form complexes, viz, Zn<sup>2+</sup>, ST and SBS ions.

ii) During the dissolution of iron, the pH increases at the metal/electrolyte due to oxygen reduction. Thus Zn(OH)<sub>2</sub> precipitate may take place at cathodic sites thus decreasing the rate of further oxygen reduction.

iii) Addition of SBS reduces metal dissolution; this may be due to adsorption and complex formation at the surface with the combined application of Zn<sup>2+</sup> and SBS, the corresponding anodic and cathodic reactions of the metal can be generalized as follows. Zn<sup>2+</sup> inhibited the local cathodic region and the local anodic region was inhibited by SBS.

iv) The Zn<sup>2+</sup> – SBS complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe- SBS complex, which is more stable than Zn<sup>2+</sup> – SBS. The released Zn<sup>2+</sup>, causes Zn(OH)<sub>2</sub> precipitation at the local cathodic sites. Thus the protective film consists of an Fe- SBS complex and Zn(OH)<sub>2</sub>.

(v) The film formed on the metal surface of the carbon steel consists of oxides / hydroxides of iron and zinc. It is also likely to comprises of complexes of Fe<sup>2+</sup>/Fe<sup>3+</sup> and Zn<sup>2+</sup> with ST as well as with SBS.

(vi) The FTIR spectrum of the surface film suggests, the formation of these complexes and the presence of Zn(OH)<sub>2</sub> in the surface.

## 4. CONCLUSION

A formulation consisting of Zn<sup>2+</sup>, ST and SBS can be used as a potential corrosion inhibitor of carbon steel in neutral.

1. SBS plays an excellent synergistic role in the ST – Zn<sup>2+</sup> - SBS system.
2. The ternary system ST (20ppm) – Zn<sup>2+</sup> (50ppm)-SBS (10ppm) is effective and has 95% I.E.
3. Significant synergism was attained by the combined application of ST – Zn<sup>2+</sup>-SBS.
4. This new inhibitor formulation is more environment – friendly.
5. Both ST and SBS form stable complexes with metal ions in the metal surface.
6. The protective film consists of Zn(OH)<sub>2</sub> and complexes of Fe<sup>2+</sup> / Fe<sup>3+</sup> and Zn<sup>2+</sup> with SBS and ST.
7. UV-visible spectra confirm the formation of these complexes.
8. The protective film formation was also confirmed by atomic force microscopy study.

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## ИЗВОД

### НАТРИЈУМ ВОЛФРАМАТ–Zn<sup>2+</sup> КАО КОРОЗИОНИ ИНХИБИТОР ЗА УГЉЕНИЧНИ ЧЕЛИК

*Ефикасност инхибиције натријум-бисулфитом (SBS) у комбинацији са двовалентним катјоном као што је Zn<sup>2+</sup> у контроли корозије угљеничног челика истражена је методом губитка масе. Формулација која се састоји од Zn<sup>2+</sup>, натријум-волфрамата, ST, и SBS може да се користи као снажан инхибитор у спречавању корозије угљеничног челика у неутралној воденој средини. Тернарни систем ST (20 ppm), Zn<sup>2+</sup> (50 ppm) и SBS (10 ppm) је ефикасан и има инхибирајућу ефикасност од 95%. Заштитни филм се састоји од Zn(OH)<sub>2</sub> и комплекса Fe<sup>2+</sup>/Fe<sup>3+</sup> и Zn<sup>2+</sup> са SBS и ST. Формирање ових комплекса је потврђено UV-Visible, FTIR и AFM спектрима. Морфологија заштитног филма на металној површини је окарактерисана применом микроскопије засноване на међуатомским силама (AFM).*

**Кључне речи:** *Инхибиција корозије, угљенични челик, натријум-волфраMAT, натријум-бисулфит, Zn<sup>2+</sup>, UV-Visible и FTIR спектри, микроскопија заснована на међуатомским силама, механизам.*

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