

# Estimation of Corrosion Products and Inhibitor Films Contributions to Total Protective Effect

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## Abstract

Film of corrosion products (CP) often has got certain protective properties and leads to significant decrease in corrosion rate. In case of corrosion prevention an inhibitor is adsorbed on CP film, but corrosion retardation is usually connected only with the presence of inhibitor layer on metal surface without taking into account protectiveness of CP film. Such omission leads to inaccurate estimate of the inhibitor`s protective effect. To exclude this mistake, three different methods for separate estimation of CP and inhibitor films contributions to the total corrosion protection are used in this research. Comparison of the method results is conducted by example of hydrogen sulfide corrosion (HSC) inhibition.

**Keywords:** corrosion inhibitor, film, interfacial effects, hydrogen sulphide, amine

## Introduction

Film of corrosion products (CP) starts to form on a metal surface immediately at the moment of its contact with corrosive aggressive environment. This film often has got certain protective properties and leads to significant decrease in corrosion rate.<sup>1-7</sup> A corrosion inhibitor is adsorbed on the CP film as usual, but corrosion retardation is generally connected only with presence of inhibitor`s phase layer on a metal surface without taking into account protectiveness of CP. That kind of assumption results in serious exaggeration of the inhibitor`s protective effect. Thus, separate estimation of CP and inhibitor protective property is of interest. However, this very subject has become an issue of study in a number of research papers only recently.<sup>8-10</sup>

The simple and informative method for such estimation of contributions to the total protective effect (initial method) is offered by Prof. V.I. Vigdorovich.<sup>8</sup> This method is based on analysis of corrosion and inhibition kinetics. CP contribution ( $Z_{CP}$ ) to the total protective effect ( $Z_2$ ) of “CP–inhibitor” superficial system is estimated by formula:

$$Z_{CP,\tau} = \frac{K_{bg,\tau \rightarrow 0} - K_{bg,\tau}}{K_{bg,\tau \rightarrow 0}}, \quad (1)$$

where  $K_{bg,\tau}$  is corrosion rate in background environment by  $\tau$  time.

The total protective effect ( $Z_2$ ) and inhibitor contribution ( $Z_{in}$ ) are expressed as follows

$$Z_{\Sigma,\tau} = \frac{K_{bg,\tau \rightarrow 0} - K_{in,\tau}}{K_{bg,\tau \rightarrow 0}}, \quad (2)$$

where  $K_{in,\tau}$  is corrosion rate in inhibited environment by  $\tau$  time.

$$Z_{in,\tau} = Z_{\Sigma,\tau} - Z_{CP,\tau}. \quad (3)$$

Unfortunately the initial method has got some significant shortages and the present paper is aimed to decide some of them.

## Experimental procedure

### Materials and media

Experiments were carried out on samples made of St3 low-carbon steel [UNS K01804], whose composition is (wt%): C – 0.18, Mn – 0.5, Si – 0.21, P – 0.04, S – 0.05, Fe as the residue. Steel electrodes were ground to emery paper, polished with diamond paste, and degreased with acetone before every test.

Standard medium, consisting of 0.25 g/L  $\text{CH}_3\text{COOH}$ , 0.5 g/L NaCl with initial pH 3.6, was used as aggressive electrolyte. Gaseous  $\text{H}_2\text{S}$  was permanently blown through the electrolyte during the test. This system was used as “background media”.

Tributylamine (TBA) was studied in the paper as effective inhibitor against hydrogen sulfide corrosion (HSC) of steel.<sup>9,11</sup> Amine was fed directly into the liquid phase, after which, the tested media was considered as “inhibited environment”.

## Corrosion tests

Corrosion rate in background media and inhibited environment was determined by linear polarization resistance (LPR) method using two-electrodes steel sensor and corrosion rate indicator under 10 mV electrode polarization in stirring condition (300 rev/min). Tests were carried out at room temperature and lasted up to 6 h.

Concentrations of Fe ions in solution after the test were determined by colorimetry (ISO 7990<sup>12</sup>).

Protective effectiveness of planar components of a superficial film was expressed through two indicators in the paper: protective effect and protection coefficient. Protective effect ( $Z$ ) was calculated by the following equation

$$Z = \frac{K_{\tau \rightarrow 0} - K_{\tau}}{K_{\tau \rightarrow 0}}, \quad (4)$$

where  $K_{\tau \rightarrow 0}$  and  $K_{\tau}$  are corrosion rates by initial and  $\tau$  time, respectively.

Protection coefficient ( $\gamma$ ) was expressed as follows

$$\gamma = \frac{K_0}{K_{\tau}}. \quad (5)$$

## Theoretical basic of methods for estimation

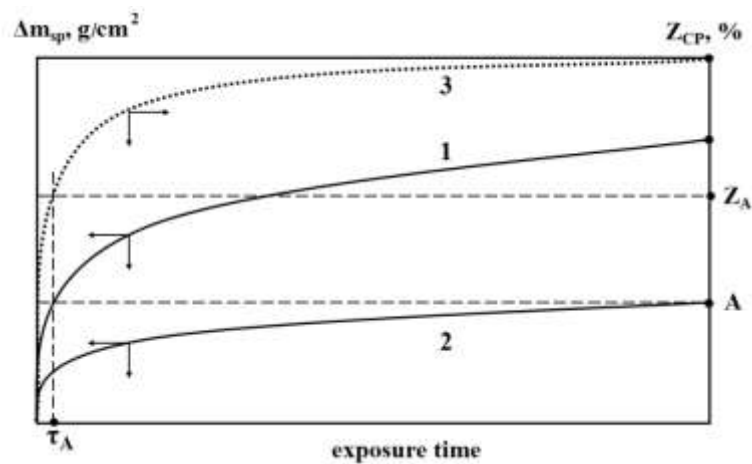
There are 3 method modifications which are considered in the paper.

### Modification 1 – Thickness Change Accounting

Corrosion rate is very high at the initial stage of destruction process. In case of HSC within the course of time, the rate value decreases due to formation of diffusion barrier to supply/removal of corrosion agents provided by the development of adhesive protective CP film. After a certain interval of time this film stabilizes and practically does not change with time, reaching, thus, a quasi-steady state.<sup>2</sup> It is therefore possible to estimate the protective effect of the formed CP film by the degree of corrosion rate reduction in time according to Equation (1).<sup>8</sup>

After addition of corrosion inhibitor in the environment it is adsorbed on the steel surface or the CP film and forms a protective layer and, thereby, slows down corrosion and growth rate of the CP film. Therefore, during corrosion inhibition the CP film of smaller thickness forms on the sample and such film has got considerably less protective properties than calculated by Equation (1).

To calculate  $Z_{CP}$  in the inhibited environment it is necessary to correlate  $Z_{CP}$  values and the thickness of the CP film formed in the background environment. The thickness of CP film will be directly proportional to specific weight losses of the sample in case of uniform growth of the CP film on the entire surface of corroded metal, i.e.  $h = const \times \Delta m_{sp}$ , where  $h$  is thickness of CP film and  $\Delta m_{sp}$  is specific weight losses of the sample. Such deduction immediately corresponds to the results received by W. Sun et al.<sup>2</sup> Next, we should simultaneously put on the diagram; the kinetics of specific weight losses of metal in background and inhibited environments and  $Z_{CP}$  calculated based on the data of background corrosion by Equation (1). After that it is possible to estimate  $Z_{CP}$  at corrosion inhibition at any time moment ( $\tau$ ) in the following way (Figure 1). Abscissa of intersection points of curve 1 and a perpendicular drawn from A point to OY axis determines  $\tau_A$  time in which the blank sample (curve 1) had the same specific weight losses and, hence, the same thickness of CP film as in A point in case of corrosion inhibition. Moreover, it is possible to calculate the protective effect of CP film at time  $\tau_A$  ( $Z_A$  point, Figure 1) from  $Z_{CP} - \tau$  relationship (curve 3). Thus, one can estimate the kinetics of  $Z_{CP}$  changes by means of calculating  $Z_{CP}$  in the inhibited environment at various  $\tau$  time.



**Figure 1:** Kinetics of specific weight loss of metal sample in background (1) and inhibited (2) environment and  $Z_{CP}$  (3).

The proposed method does not allow deducing the analytical dependence directly between  $Z_{in}$  value and corrosion kinetics in the background and inhibited environment. However, Equations (2) and (3) for calculation of the total protective effect inhibitor contribution ( $Z_{in}$ ) remains correct.

The latter equation does not contradict concepts underlying the present method since  $Z_{\Sigma}$  shows the total protective effect of «CP film –inhibitor» system, including redistribution of their contributions due to reduction of CP film thickness. One can determine the kinetics of contributions change by calculating  $Z_{\Sigma}$  by Equation (2) and then  $Z_{in}$  by Equation (3) for various  $\tau$  time.

### **Modification 2 – Film Dissolution Accounting**

It is necessary to consider not only CP film thickness reduction caused by an inhibitor additive but also dissolution of this film, result of which leads to changing of estimated protective properties of an inhibitor film. It was proved<sup>2</sup>, that up to a half of the iron consumed by corrosion ended up as iron sulfide on the steel surface and the other part of that dissolved and lost in the solution.

Therefore, consideration of CP film dissolution in a liquid phase is improvement for the 1<sup>st</sup> modified method. It is possible to obtain basing on a measurement of metal ions concentration in the test solution after experiment (iron ions in case of steel). The thickness of CP film ( $h$ ) will be directly proportional to specific weight loss of a sample ( $\Delta m_{sp}$ ) minus weight of the metal passed in a solution, *i.e.*  $h = const \cdot \Delta m_{sp} - C$ , where  $C$  is a parameter considering dissolution of CP film. It is further necessary to plot specific weight loss of metal minus the quantity of dissolved CP instead of simple  $\Delta m_{sp}$  on the “ $\Delta m_{sp} (Z_{CP}) - \tau$ ” graph. The latter value, in its turn, more precisely characterizes  $Z_{CP}$  because it expresses the total amount of corrosion products adsorbed directly on a metal surface.

### **Modification 3 – Additivity of Films Protection Coefficient**

The key methodological issue in estimation under the study, as is pointed out in the proper paper<sup>8</sup>, is in their definition and taking into account superficial films interaction. However, it is clear that full account for this kind of interaction is extremely difficult, some authors<sup>8</sup> even concluded that it was feasible to assume additivity of growing inhibitor and CP films (*i.e.* that there is no interaction).

Meanwhile, in a number of studies,<sup>8-9</sup> additivity of the films was estimated on basis of assumption about additivity of the its protective effects ( $Z$ ) only. However, this mathematical treatment of films additivity is highly disputable, thus the modification

considering the additivity of its protection coefficients ( $\gamma$ ) appears to be more successful (modification 3).<sup>14</sup>

$$Z_{\Sigma} = \sum_{i=1}^n Z_i, \quad (6)$$

$$\gamma_{\Sigma} = \prod_{i=1}^n \gamma_i, \quad (7)$$

where  $Z$  and  $\gamma$  indicate protective effect and protection coefficient, respectively;  $P$  is the product, while  $\Sigma$  and  $i$  are interlinear indexes representing the total and single indicators, respectively.

Equation (7) can be algebraically deduced on basis of well-known theoretical regularities. Protection coefficient in inhibited environment ( $\gamma_{in}$ ) is expressed as follows:

$$\gamma_{in} = \frac{K_{bg}}{K_{in}}, \quad (8)$$

where  $K_{bg}$  and  $K_{in}$  indicate corrosion rate in background and inhibited environments, respectively.

Corrosion rate in background environment is defined by presence of CP films on metal surfaces only. The rate decreases in time if the CP film possesses protective properties and vice versa, thus  $K_{bg} = K_{CP}$ . Based on a similar argument, we obtain that  $K_{in} = K_{\Sigma}$  as both CP and inhibitor films are present on metal in the inhibited environment ( $\Sigma = CP + in$ ). Therefore,

$$\frac{K_{bg}}{K_{in}} = \frac{K_{CP}}{K_{\Sigma}} \quad (9)$$

Furthermore, we express  $1/K_{\Sigma}$  multiplier from Equation (9) and then multiply both parts of the received equality by  $K_{bg}$ :

$$\frac{K_{bg}}{K_{\Sigma}} = \frac{K_{bg}}{K_{CP}} \cdot \frac{K_{bg}}{K_{in}}, \quad (10)$$

According to Equation (8), the latter expression represents special case of Equation (7), namely:

$$\gamma_{\Sigma} = \gamma_{CP} \cdot \gamma_{in} . \quad (11)$$

Then one attains Equation (12) expressing  $\gamma_{in}$  from Equation (11):

$$\gamma_{in} = \frac{\gamma_{\Sigma}}{\gamma_{CP}} . \quad (12)$$

The received Equation (12) is transformed by the substitution of the expression relating  $\gamma$  and  $Z$ :

$$\gamma = \frac{1}{1-Z} , \quad (13)$$

so one attains in this case:

$$\frac{1}{1-Z_{in}} = \frac{1-Z_{CP}}{1-Z_{\Sigma}} . \quad (14)$$

This is followed by finding the  $Z_{in}$  value for  $\gamma_i$  additivity case:

$$Z_{in} = 1 - \frac{1-Z_{\Sigma}}{1-Z_{CP}} = \frac{Z_{\Sigma} - Z_{CP}}{1-Z_{CP}} . \quad (15)$$

It follows from the Equation (15) that distinction between the considered approaches consists of  $1/(1-Z_{CP})$  multiplier presence at the  $Z_{in}$  calculation only.  $Z_{CP}$  grows eventually under condition of the more protective film formation and so does  $Z_{in}$  value as compared with the approach considering  $Z_i$  additivity.

On the other hand, the  $1/(1-Z_{CP})$  factor tends to 1 if a CP film does not possess protective nature. So, this factor does not influence  $Z_{in}$  value, which tends to  $Z_{\Sigma}$ . Both approaches produce similar estimations in this case only ( $Z_{in} \rightarrow Z_{\Sigma}$  if  $Z_{CP} \rightarrow 0$ ).

## Results and discussion

### Corrosion test result

Results of HSC kinetics study in liquid phase with (50, 500, 2000 mg/L) and without TBA are shown in Figure 2(a). All obtained correlations have inversely logarithmic characteristic which is evidence of permanent protective film formation. Addition of TBA to test solution considerably reduces corrosion rate which, undoubtedly leads to decrease in a CP film thickness in inhibited environment in comparison with background one. The total content of iron in tested solutions was measured during the tests (Figure 2(b)).

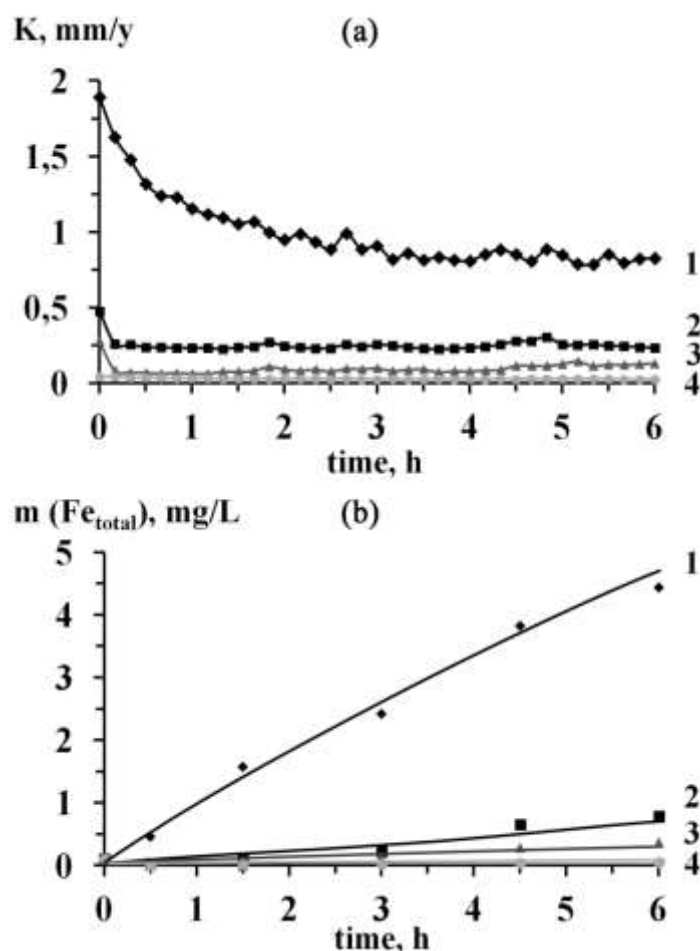
### Analysis of modifications 1 and 2

It is possible to calculate contributions of superficial films from above presented correlations in several ways. First we calculate  $Z_{CP}$  in background and inhibited environments from the received diagrams,  $Z_s$  and then  $Z_{in}$  are determined after  $Z_{CP}$ .

Received data (Figure 3) show that  $Z_{CP}$  in inhibited  $H_2S$ -containing liquid increases in the course of time, independent of inhibitor content and method of calculation. On the contrary,  $Z_{in}$  decreases in all cases. However contribution values strongly depend on  $C_{in}$  and have the similar trend of changes. For example,  $Z_{CP}$  starts to dominate at small inhibitor concentration – 50 mg/L (Figures 3(a) and 3(b)) after 1 or 2 hours (except in curve 2) although  $Z_{TBA} \approx 75\%$ . Therefore, CP film at such inhibitor concentration has greater contribution to the total protective effect, rather than inhibitor itself. It is significant that  $Z_{CP}$  value is almost identical at calculation according to the initial method<sup>8</sup> and modification 2 (curve 3), but  $Z_{CP}$  value is less in case of estimation according to modification 1 (curve 2). On the other hand,  $Z_{in}$  is greater according to calculation on the basis of modification 1 (curve 2).

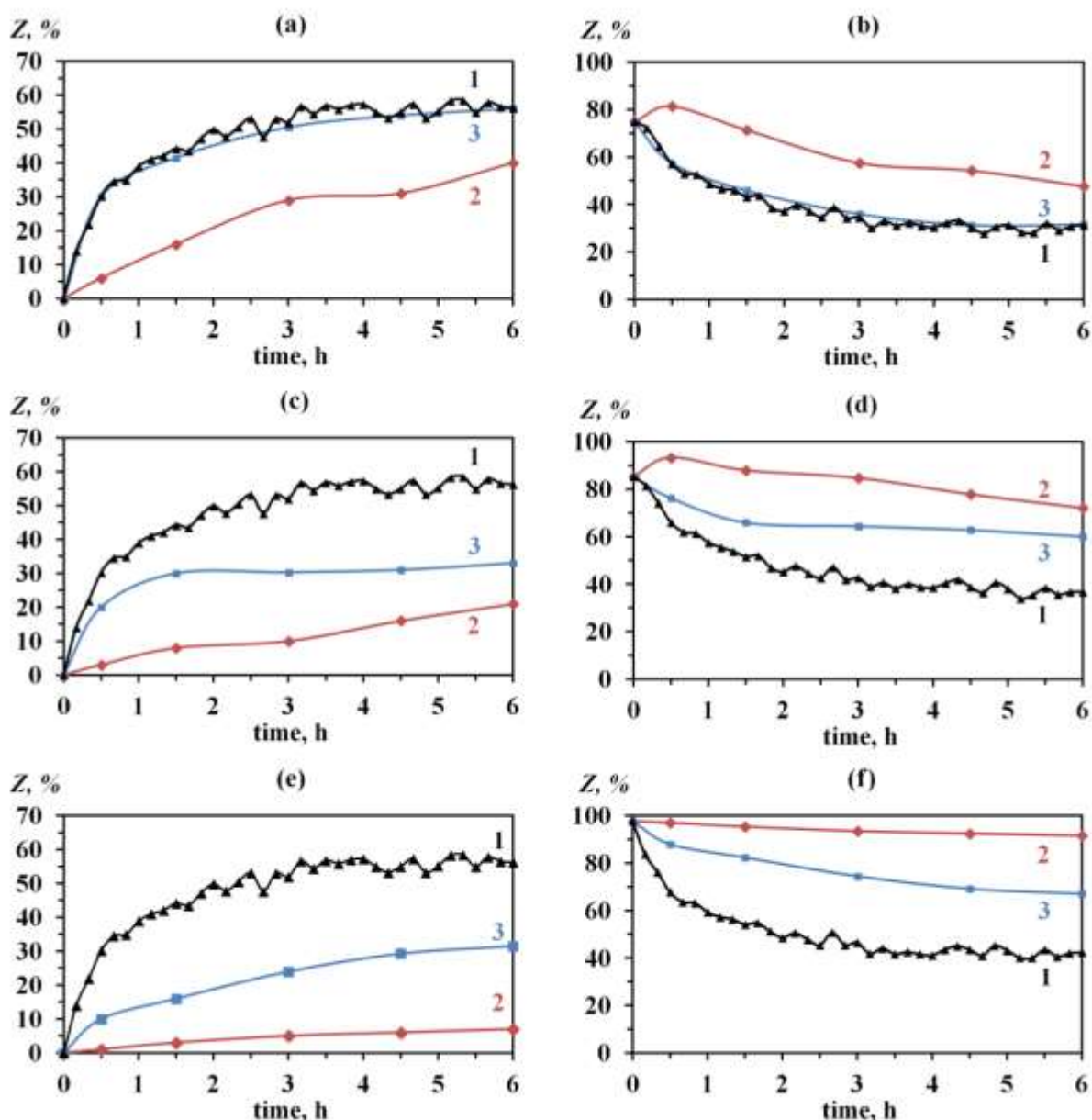
Similar results of  $Z_{CP}$  estimation by initial method are obtained in the range of average inhibitor concentration – 500 mg/L (Figures 3 (c) and 3(d)), but the  $Z_{CP}$  values calculated according to 1<sup>st</sup> and 2<sup>nd</sup> modification procedures are less than that with 50 mg/L of TBA. Therefore CP film demonstrates a minor contribution to the total protection.  $Z_{in}$  dominates during all test time (except initial method) and so it brings the main contribution to  $Z_s$ .





**Figure 2:** Time dependence of HSC rate (a) and the total Fe content (b) in background media (1) and in the presence of 50 (2), 500 (3) and 2000 mg/L of TBA (4).

Data received at high amine concentration (2 g/L) is logical continuation of the above mentioned results.  $Z_{CP}$  in this case calculated by initial method is considerably greater and  $Z_{in}$ , on the contrary, is less than the similar values defined by the modified methods. As consequence, the initial method testifies to the leading part of CP film in  $Z_s$ , and the modified methods give an opposite estimation. Such distinction can be explained by the fact that, initial method disregarding decrease of CP film thickness, considerably overestimates its contribution to  $Z_s$ .<sup>11</sup> Thus, this data follows that the higher protective effect a corrosion inhibitor has, the greater error of  $Z_{CP}$  estimation by calculation according to initial method.



**Figure 3:** Values of  $Z_{CP}$  (a, c, e) and  $Z_{in}$  (b, d, f) films calculated according to initial (curve 1)<sup>8</sup> method, modification 1 (curve 2) and modification 2 (curve 3),  $C_{TBA} = 50$  (a, b), 500 (c, d), 2000 mg/L (e, f).

Results of the modified methods do change depending on whether dissolution of CP film is considered or not. Therefore, processes of CP film dissolution and HSC rate itself do not equally depend on corrosion inhibitor presence in media, in other words inhibitor does not equally slow down steel corrosion rate and dissolution of a polysulfide film.

It is necessary to note that  $Z_{CP}$  and  $Z_{in}$  are not constant (especially in modified methods) and, hence,  $Z_{CP}$  will gradually increase and  $Z_{in}$  will decrease, while steel HSC will not completely stop. Finally the moment of their balance or even  $Z_{CP}$  domination could come even in case of  $C_{TBA} = 2 \text{ g/L}$ .

### Analysis of modification 3

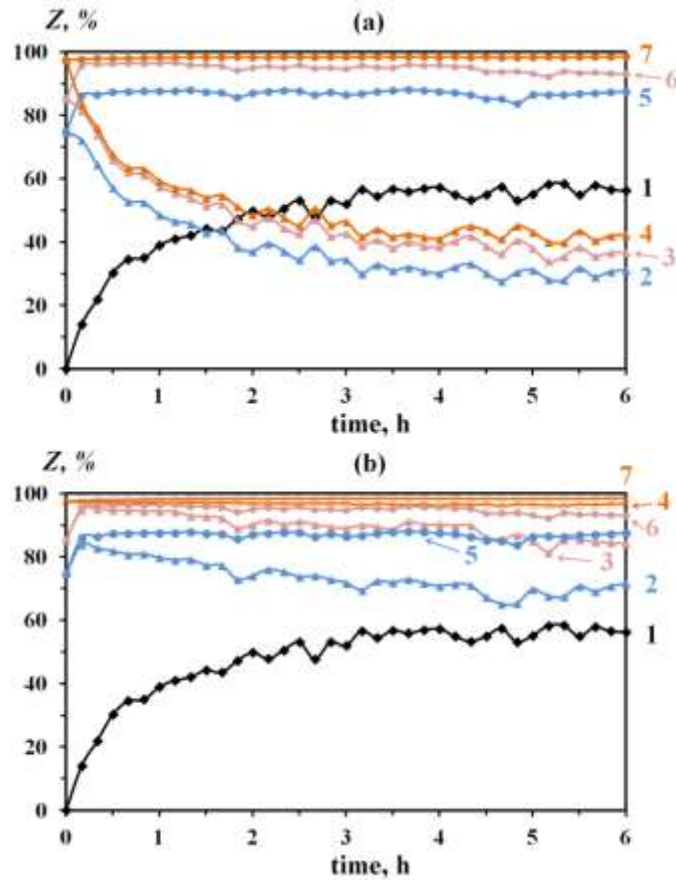
Assumptions on the additivity of protective effects,  $Z$ , and protection coefficients,  $\gamma$ , (modification 3) of superficial film components were considered in this section.

Results, obtained using the initial method<sup>8</sup> and this modification, are presented in Figure 4. As indicated above,  $Z_{CP}$  is, in this case, directly defined from the  $K_{bg}$  kinetics, and therefore does not depend on methods of additivity conception. Findings of this work (curve 1, Figures 4(a) and 4(b)) also confirm this.  $Z_s$ , in its turn, is determined by the  $K_{in}$  kinetics and the  $K$  value at starting point, i.e. it does not depend on methods of additivity expression as well (curves 5–7, Figure 4).

As to Equation (15),  $Z_{in}$  has to be slightly higher in the case of  $\gamma_i$  additivity than that under the assumption of  $Z_i$  additivity, considering that the polysulfide film is capable of retarding HSC ( $Z_{CP} > 0$ ).<sup>1,9</sup> This is proved by the performed estimation results (curves 2–4 on Figures 4(a) and 4(b)). As one would expect  $Z_{in}$  value increases with the growth of  $C_{in}$ .

Thus, the contribution of the inhibitor film is dominant according to the initial method with the  $\gamma_i$  additivity consideration, while CP film has the dominant contribution under  $Z_i$  additivity approach.

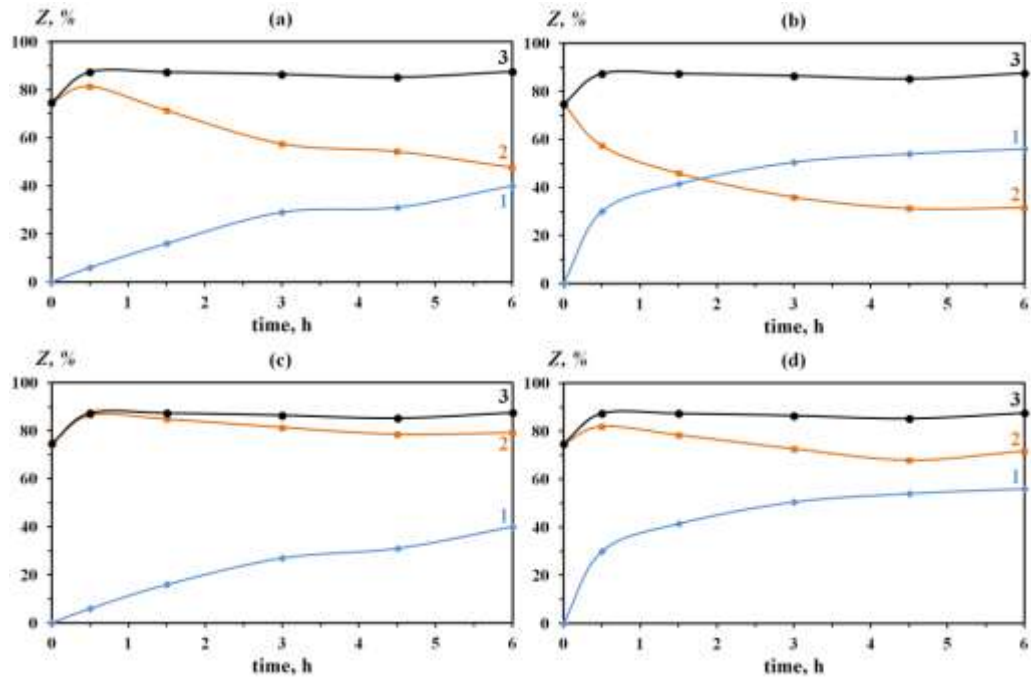
However, it is noted<sup>15</sup> that the initial method is not entirely correct in its estimation of CP film action in an inhibited environment thus equalizing it with  $Z_{CP}$  in a background by their efficiency. Meanwhile, the formed CP film has a smaller thickness in the inhibited environment due to the delayed mechanism of inhibitor action. It is obvious that  $Z_{CP}$  value in the presence of inhibitor has to be reasonably lower than that in the background, allowing for an absence of superficial films interaction. In addition, CP film can be dissolved in a liquid phase and exfoliated from metal on achievement of certain critical film thickness.



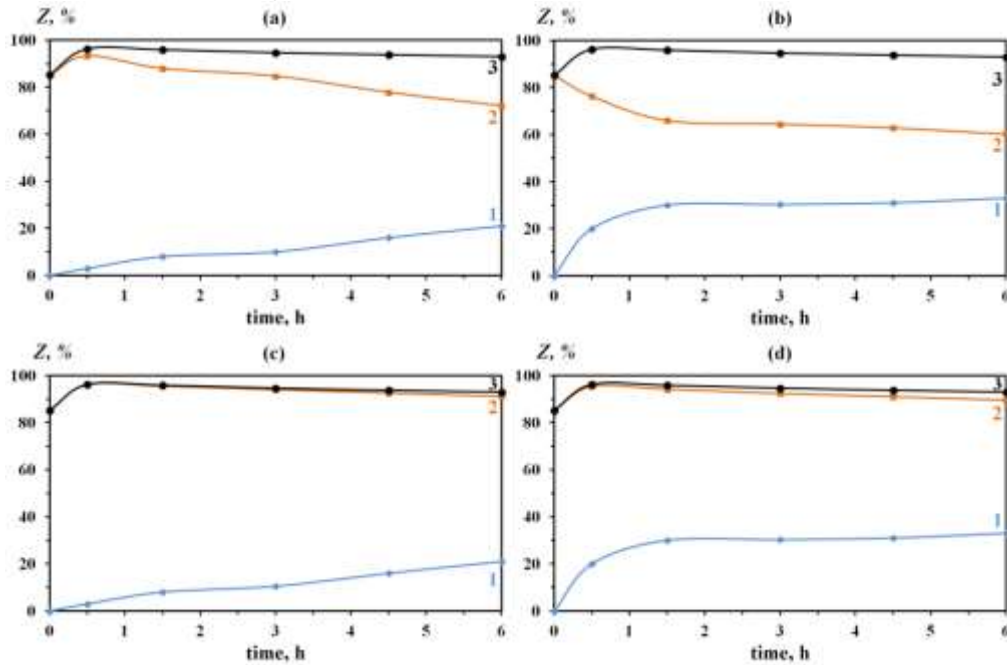
**Figure 4:**  $Z_{CP}$  (1) and  $Z_{in}$  contributions (2–4) to  $Z_s$  (5–7), calculated by means of initial method with assumptions of the additivity of protective effects (a) or protection coefficients (b) of superficial protective film components.  $C_{in} = 50$  (2, 5), 500 (3, 6) and 2000 mg/L (4, 7).

Estimation of  $Z_{CP}$  and  $Z_{in}$  at various  $C_{in}$  using the modified method with consideration of the different approaches to additivity interpretation (modification 3) are given in Figures 5 to 7.

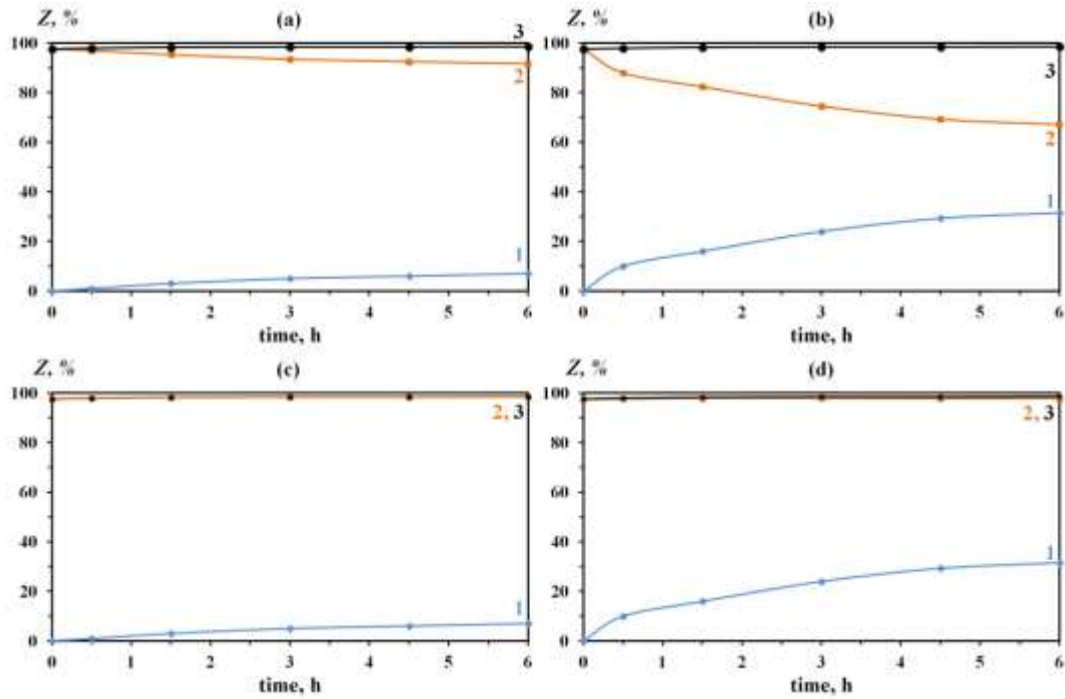
It is expected that, as decrease in the thickness of CP film and dissolution of this film has an opposite impact on the  $Z_{CP}$  value, it will affect the estimation results. Thus, consideration of  $Z_i$  additivity leads to the contrary conclusions on the dominating contribution for 50 mg/L of inhibitor:  $Z_{in}$  dominates in the case of taking into account the decrease of CP film thickness only; on the contrary,  $Z_{CP}$  prevails after 2 hours of exposure under additional control of sulfide film dissolution (Figures 5(a) and 5(b)).



**Figure 5:**  $Z_{CP}$  (1) and  $Z_{in}$  (2) to  $Z_{\Sigma}$  (3), calculated by means of taking into consideration the reduction of CP film thickness (a, c) and its dissolution (b, d) with assumptions of the additivity of protective effects (a, b) or protection coefficients (c, d) of superficial protective film components.  $C_{in} = 50 \text{ mg/L}$ .



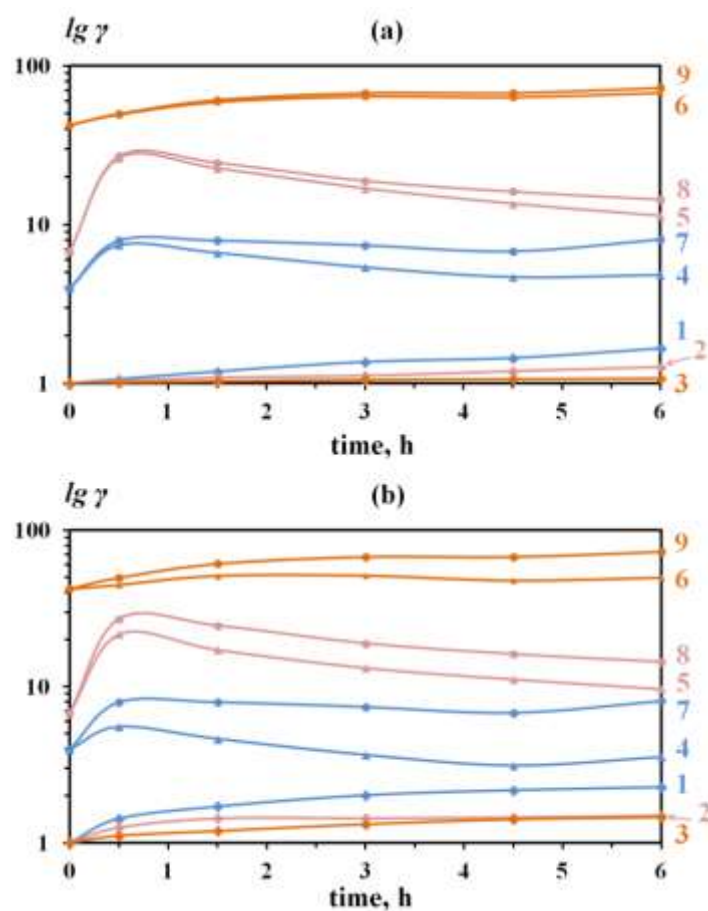
**Figure 6:**  $Z_{CP}$  (1) and  $Z_{in}$  (2) to  $Z_{\Sigma}$  (3), calculated by means of taking into consideration the reduction of CP film thickness (a, c) and its dissolution (b, d) with assumptions of the additivity of protective effects (a, b) or protection coefficients (c, d) of superficial protective film components.  $C_{in} = 500 \text{ mg/L}$ .



**Figure 7:**  $Z_{CP}$  (1) and  $Z_{in}$  (2) to  $Z_S$  (3), calculated by means of taking into consideration the reduction of CP film thickness (a, c) and its dissolution (b, d) with assumption of the additivity of protective effects (a, b) or protection coefficients (c, d) of superficial protective film components.  $C_{in} = 2000$  mg/L.

Another approach ( $\gamma$  additivity) qualitatively changes the situation, but these tendencies for distribution revision remain the same:  $Z_{CP}$  increases and  $Z_{in}$  decreases, both specified factors being put into account. The contribution of  $Z_{in}$  however dominates in each case (Figures 5(c) and 5(d)).

$Z_S$  and  $Z_{in}$  naturally increase with  $C_{in}$  growth to 500 mg/L, and  $Z_{CP}$  on the contrary decreases with respect to the values received at smaller  $C_{in}$ , but the tendencies of contributions change remain the same (Figure 6). It should also be noted that  $Z_{in} \approx Z_S$  in this case, if the results are based on  $\gamma$  additivity approach. Moreover,  $Z_{in}$  continues to grow with the further growth in  $C_{in}$ , and almost completely reaches the  $Z_S$  values illustrated by means of protective effect value (curves 2 and 3 in Figures 7(c) and 7(d)). It is logical when  $Z_{in} \approx Z_S$  it would be more convenient to present the contributions at high inhibitor concentration (2000 mg/L) through  $\log \gamma = f(\tau)$  chart as it is shown in Figure 8.



**Figure 8:**  $Z_{CP}$  (1–3) and  $Z_{in}$  (4–6) to  $Z_s$  (7–9), calculated by means of taking into consideration the reduction of CP film thickness (a) and its dissolution (b) with assumptions of protection coefficients additivity.  $C_{in} = 50$  (1, 4, 7), 500 (2, 5, 8) and 2000 mg/L (3, 6, 9).

Thus, the  $Z_s$  value does not depend on accounting of sulfide film thickness reduction, its dissolution and way of additivity expression as it follows from the above mentioned results.

The  $Z_{CP}$  contribution, in its turn, significantly depends on accounting of CP film thickness (modification 1), its dissolution (modification 2), and to a small extent on the way of additivity expression (modification 3). On the contrary, the  $Z_{in}$  value strongly depends on approach of additivity expression, and more weakly – on CP film thickness change. The approach considering the  $\gamma_i$  additivity leads to increase in the dominating contribution value, and this influence continues to amplify with growth of this value itself.

## Conclusions

1. Some modifications of method for separate estimation of superficial film components contributions to total protective effect are offered in this paper. Comparison of modified methods results is carried out by the example of hydrogen sulfide corrosion inhibition in liquid phase by tributylamine.
2. Modification 1 accounts for thickness change of corrosion products film under inhibitory influence of the amine on corrosion rate. Modification 2 takes into account both dissolution of corrosion product film in liquid and thickness reduction of this film according to modification 1. Modification 3 considers additivity of protection coefficients of superficial films instead of additivity of corrosion protective effects as it is accepted in other methods.
3. Calculation according to modification 1 shows that error in estimation of corrosion products film contribution in initial method raises as protective effect of an inhibitor increases. It is due to parent assumption about equal protection effectiveness of corrosion products film in background and inhibited environments, so it leads to over-estimation of corrosion products film contribution.
4. Analysis of modification 2 indicates that it is necessary for the accounting of corrosion product film dissolution in liquid to get more correct data about films contribution.
5. Data received from modification 3 shows that the account of protection coefficients additivity for system components leads to significant growth in the dominating contribution value, and  $Z_{in}$  is the dominating contribution in the case of hydrogen sulfide corrosion inhibition.
6. The  $Z_x$  value does not depend on account of sulfide film thickness reduction, its dissolution, and way of additivity expression. The  $Z_{CP}$  contribution significantly depends on account of corrosion product film thickness, its dissolution, and it weakly depends on way of additivity expression. The  $Z_{in}$  value strongly depends on approach to additivity expression, and it more weakly depends on account of corrosion product film thickness changes.
7. From the results, this discussion concludes that modification 3 with accounting thickness change of corrosion products film under an inhibitory influence and solution of this film is the most correct method for separate estimation of superficial film components contributions to total protective effect.



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