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Utilization of Adsorption Kinetics Rate Constants to Better Define Corrosion Inhibitor Availability

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ABSTRACT

The Corrosion Inhibitor Availability Model as defined in 2000 (CIAM 2000) presents a simplified binary approach to corrosion inhibitor performance. In particular, the corrosion inhibitor is assumed to be active and fully effective from the instant it is injected to the instant it no longer injected. As a consequence, the CIAM 2000 does not account for the transient performance of the corrosion inhibitor namely, the time required to reach steady state and the time required for the inhibitor to desorb or persistency. In the following paper Langmuir adsorption kinetics are utilized to analyze the corrosion inhibitor performance curve and based on the adsorption and desorption rate constants the CIAM 2000 is updated to better account for the short term/transient response of the corrosion inhibitor. In particular, an attempt is made to better define and quantify “persistency” of the corrosion inhibitor in terms of the desorption rate constant and the surface residence time.

Key words: Corrosion Inhibitor, Performance, Availability Model, Langmuir Kinetics

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INTRODUCTION

The Corrosion Inhibitor Availability Model from 2000 (CIAM 2000) present a rather simple view on the presence or absence of the corrosion inhibitor.¹ In the presence of the corrosion inhibitor i.e. injection is “on,” then the model assumes the inhibited corrosion rate, CR_{In} , and in the absence of the corrosion inhibitor i.e. injection is “off,” the model assumes the uninhibited corrosion rate, CR_{Un} . While this is a valid assumption for extended continuous time-frames on the order of 100's of days the model is questionable for shorter duration loss of corrosion inhibitor injection.

The reason for this doubt is the “persistence” of the corrosion inhibitor such that when corrosion inhibitor injection is off the corrosion inhibitor does not desorb instantly from the surface. However, there is no clear definition or basis for characterizing persistency although Ramachandra has provided some very useful insight.²

In this paper the work from the companion paper is extended to include the adsorption kinetics of the “on” part of the duty-cycle when the corrosion inhibitor is present and the “off” part of the duty-cycle when the corrosion inhibitor is absent.³

As will be seen, for short duration duty-cycles the behavior of the corrosion inhibitor and the resultant corrosion rate can differ substantially from the assumptions in the CIAM 2000 as was demonstrated by Ramachandra in 2018.²

RESULTS AND ANALYSIS

In the companion paper a typical laboratory corrosion inhibitor performance test can be analyzed to yield the necessary parameters to model the kinetics of adsorption (and desorption as will be shown later). The key results are shown in **Error! Reference source not found.** and summarized in Table 1 details of the experimental procedure and the analysis methods are given in the supporting paper.³

It is of particular interest to note the value of the desorption rate constant is comparatively small and as a result the residence time on the surface is large.⁴ For the particular chemistry used in this test work $t_{Res} \approx 10^6$ s, as a consequence the desorption process is comparatively slow, which has a significant impact on the “off” portion of the duty-cycle.

LANGMUIR ADSORPTION KINETICS - MODEL EXTENSION

Basic Langmuir Kinetic Model

The Langmuir model of Karpovich and Blanchard has been used in this investigation and the key equations are summarized in the following.^{3,5,6}

The Langmuir model differential equation,

$$\frac{d\theta}{dt} = k_a(1-\theta)C - k_d\theta \quad (1)$$

The analytical solution of the differential equation with the initial condition at $t = 0$ that $\theta(t) = 0$, then,

$$\theta(t) = \frac{C}{C + (k_d/k_a)} \left[1 - \exp(-(k_a C + k_d)t) \right] \quad (2)$$

Following substitution of $k_{obs} = k_a C + k_d$ and $K' = C/(C + k_d/k_a)$ then the simplified form of the equation is,

$$\theta(t) = K' \left[1 - \exp(-k_{obs}t) \right] \quad (3)$$

Basic Langmuir Kinetic Model Extension^{7,8}

For further analysis it is necessary to extend the basic model presented above with a revised boundary condition that at $t = 0$ the surface coverage can have any arbitrary initial surface value, θ_{init} , between 0 and 1. The result of solving this differential equation with the revised boundary condition at $t = 0$ then $\theta = \theta_{init}$ the result is,

$$\theta(t) = K' \left[1 - \exp(-k_{obs}t) \right] + \theta_{init} \exp(-k_{obs}t) \quad (4)$$

Equation (4) obviously reduces to Equation (2) when $\theta_{init} = 0$.

For the case when the inhibitor injection is “off” after a period “on” then $\theta_{init} > 0$ and $C = 0$, in which case Equation (4) can further reduces given $C = 0$ then $K' = 0$ and $k_{obs} = k_d$, resulting in,

$$\theta(t) = \theta_{init} \exp(-k_d t) \quad (5)$$

The above expression is of the same form as many other physical models namely an exponential decay.

Exponential Decay⁷

A quantity is subject to exponential decline if it decreases at a rate proportional to its value at a given time. The process can be represented by the differential equation,

$$\frac{dN}{dt} = -\lambda N \quad (6)$$

where N is the quantity and λ is a positive rate constant referred to a exponential decay constant. The solution to the equation is given as,

$$N(t) = N_0 \exp(-\lambda t) \quad (7)$$

where $N(t)$ is the quantity at time t and $N_0 = N(0)$ is the initial quantity at $t = 0$.

Also, the rate, λ , is sometimes replaced with the exponential rate constant, τ , however the two are very related as $\tau = 1/\lambda$.

An intuitive (and familiar) characteristic of the exponential decay is the time required for the decaying quantity to fall to one half of the initial value, $t_{1/2}$. In which case $N(t) = \frac{1}{2} N_0$ and following substitution in equation (7) we have,

$$\frac{1}{2} N_0 = N_0 \exp(-\lambda t_{1/2}) \quad (8)$$

$$t_{1/2} = \frac{\ln(2)}{\lambda} = \tau \ln(2) \quad (9)$$

There are a number of examples from physics which follow this pattern, perhaps two of the better known are radioactive decay and the voltage discharge in resistor-capacitor network.^{9,10}

Characteristic Time of Desorption - Definition of “Persistence”

The analysis above suggests that the persistency of corrosion inhibitor can be characterized via a half-life, $t_{1/2}$, (or a time constant) which is the time required for the surface coverage to be reduced by a half under the condition of $C = 0$ and $\theta_{init} > 0$. From equation (5) we have,

$$\frac{1}{2} \theta_{init} = \theta_{init} \exp(-k_d t_{1/2}) \quad (10)$$

$$t_{1/2} = \frac{\ln(2)}{k_d} \quad (11)$$

As was shown elsewhere, k_d can be determined from the basic corrosion inhibitor time performance curve and as a result provides a clear and quantifiable definition of persistency, namely as the time required for the surface coverage to half in the absence of corrosion inhibitor injection.³ This can be readily be quantified as the reciprocal of the desorption rate constant and which in turn can be determined from routine corrosion inhibitor testing such ASTM G 59 and ASTM G 185.^{11,12}

For the particular chemistry tested then the characteristic time for desorption, $t_{d,1/2}$,

$$t_{d,1/2} = \frac{\ln(2)}{k_d} = 418000 \text{ s} \approx 116 \text{ hr} \quad (12)$$

Characteristic Time of Adsorption

A similar approach can be used to determine the characteristic time for the adsorption process. Making the substitutions $k_d = 0$ and $init = 0$ then Equation (4) reduces to,

$$\theta(t) = 1 - \exp(-C k_a t) \quad (13)$$

In the limit $t \rightarrow \infty$ then $\theta(t) \rightarrow 1$ since there is no desorption reaction so the characteristic time to achieve half the final surface coverage is given by,

$$\frac{1}{2} = 1 - \exp(-C k_a t) \quad (14)$$

$$t_{a,1/2} = \frac{\ln(2)}{C k_a} \approx 11600 \text{ s} \approx 3.2 \text{ h} \quad (15)$$

In summary, the characteristic half-time for the desorption reaction, $t_{d,1/2} \approx 116 \text{ hr}$, and the characteristic half-time for the adsorption reaction, $t_{a,1/2} \approx 3.2 \text{ hr}$, so as would be expected, for this system the adsorption reaction proceeds significantly faster than the desorption reaction and hence the equilibrium position is biased toward adsorption rather than desorption as would be expected.

NUMERICAL EXPLORATION

Summary of the CIAM 2000

The CIAM 2000 is essentially a binary function, the inhibitor is either “on” or “off” as can be viewed as a weighted average corrosion rate, $CR_{Wt.Ave}$,¹

$$CR_{Wt.Ave} = CR_{In}A + CR_{Un}(1-A) \quad (16)$$

Where A is the fraction of time that the inhibitor is “on” and clearly $(1-A)$ is the fraction of time the inhibitor is “off.” So A represents the duty-cycle for the corrosion inhibitor injection system.

In this section the general absorption kinetic model will be explored and the effect of duty-cycle on the overall performance curve is examined. Note, while the absolute values are specific to this corrosion inhibitor chemistry tested the overall approach should have broader applicability.

Basic Adsorption and Desorption Profiles in Time

Figure 2 show the basic adsorption and desorption curves using the extended kinetic model including progress of each reaction in terms of the characteristic times for each. As the characteristic half-lives are very different the time scales on the two curves are approximately an order of magnitude different.

The persistency, $t_{d,1/2}$, is clearly shown in Figure 2 (b) with the coverage halving for each step in $t_{d,1/2}$. However the characteristic time for adsorption, $t_{a,1/2}$, is not as readily seen in Figure 2 (a) as at large t there is a significant impact on the surface coverage from the desorption reaction. For the first couple of time steps of $t_{a,1/2}$ it can be seen that the surface coverage is approximately at $t = t_{a,1/2} \rightarrow \theta \approx 0.5$ and at $t = 2 t_{a,1/2} \rightarrow \theta \approx 0.75$ with the effect of desorption being important after this second time step.

Putting the two profiles together gives a surface coverage profile over a duty-cycle of approximately 1:10 and shown Figure (3) (a) in which highlights the very different time scales over which these two processes approach steady state.