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# WHEN IS TOO LATE TO INJECT A BIOCIDE? A SHORTINTRODUCTION TO A LONG STORY

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## ABSTRACT

***In this paper, a mathematical model based on Diffusion laws is presented to describe the dynamism by which biocides can be absorbed underneath biofilms. We will show that to get higher dosage of any biocide under biofilms, more time is needed and this time is a function of biofilm thickness. The practical outcomes of this approach are:***

1) ***Biocide penetration into biofilms can be best explained by Diffusion laws,***
2) ***Biocide type (oxidising or non-oxidising) is not a parameter in biocide penetration time length,***

***The thicker the biofilm becomes, the longer it takes for the biocide to get absorbed. The relationship between biofilm thickness and time to get a certain concentration under the biofilm is non-linear.***

**Keywords:**
*Biofilm, Biocide, Diffusion, Microbiologically Influenced Corrosion (MIC).*

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## 1. INTRODUCTION

### *1.1.FORMATION IS HIGHLY LIKELY*

A biofilm not being a biofilm means that it is quite possible for it to become very corrosive to the metallic substrate. The details if this mechanism has been explained elsewhere [2 It has always been a matter of concern for industries to know, even roughly, how long it takes for a given biocide to penetrate into a biofilm. The practical significance of this matter and its impact on the economy of biocide application is so high.

However in the context of microbiologically influenced corrosion (MIC), the concept of biofilm has been named wrongly. In fact, a biofilm is neither a totally biological matter nor a film: the word "biofilm" was first reportedly introduced Biofilm in 1978 [1]. The importance of a biofilm not actually being a biofilm can be stated in the following three points:

1. In a biofilm, in addition to biological matter such as bacteria, there is non-organic matter that is mainly the debris existing in an industrial system. In other words, if housekeeping is not observed, biofilm],
2. As a biofilm doesn't have a continuous, rigid structure like a coating film, the biocide penetration into the biofilm will be performed via a rather open structure and this phenomenon is governed by laws of diffusion.

## *1.2.BIOFILM FORMATION STAGES*

Biofilm is not a static structure but a dynamic one; this means that a biofilm is formed, matures and then is damaged and re-built again. This "formation cycle" requires that the chemicals to be used to control biofilm, must be so effective that they can intervene into this cycle somewhere, either at the beginning, or during thickening or at the re-building stage. Figure 1 schematically shows the steps involved in biofilm formation procedure:

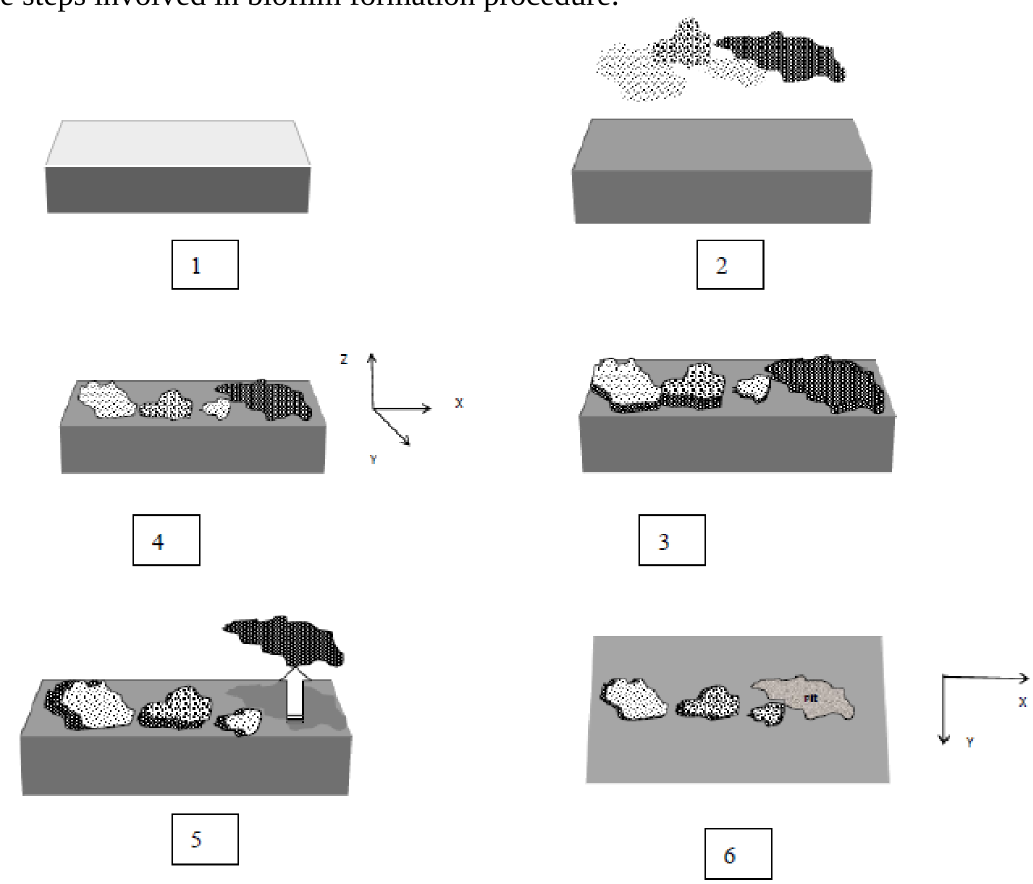


***Figure 1:*** Stages involved in biofilm formation: (1) bare metal, (2) to (4) planktonic bacteria become settled on the surface and will be transferred into sessile bacteria stage, (5) as time goes

by, the diffusion of nutrients and oxygen become harder resulting in bacterial communities die. These dead bacterial cells, however, will stay at their places unless shear forces generated through external conditions in the bulk solution help to slough off the biofilm. (6) Low- and high-oxygen pressure spots thus produced will contribute to the establishment of corrosion cells (e.g. differential aeration Cells) [2].

### *1.3.BIOCIDE DIFFUSION INTO THE BIOFILM*

Biocides will be effective on corrosion only if they penetrate into the biofilms. The reason for such a requirement is that is that biofilms (sessile bacteria) constitute the majority of corrosion [3]. Therefore a very important criterion to select a certain biocide, in addition to being broad-spectrum; economic; non-toxic to the environment and not having antagonistic effects with other chemicals already available in the system, is for it to be able to penetrate into the biofilm. Biocides' penetration into biofilms obeys Diffusion laws. Our approach is to model both the thermodynamics and kinetics of biocide penetration into a biofilm, irrespective of the following factors:

a) Biocide type (oxidising or non-oxidising),
b) Bacteria type (oxygen consumption regime, morphology, energy obtaining method (e.g. anaerobic respiration /fermentation), temperature range of being active,),
c) The type of substrate on which the biofilm has been formed

## 2. METHOD AND DISCUSSION

Let us assume that "z" is the average thickness of a biofilm. If $C_o$ is the concentration of a given biocide out of the biofilm and $C_f$ is the final biocide concentration of the biocide that we want it to penetrate into the biofilm to the depth of "h", the initial and boundary conditions can be shown as (1) to (3):

(Initial Condition) For t=0 & z> h then $C=C_0$ (1)

(Boundary Condition) For t>0 & z=0 then $C=C_s$ (2)

(Boundary Condition) For t>0…& z=h then C=Cs (3)

Solving Fick's second Law for (1) to (3) results in (4):

$$C(h,t)= C_s \left(1-\text{erf}\left(\frac{h}{2\sqrt{Dt}}\right)\right) + C_0 \left(1-\text{erf}\left(\frac{h}{2\sqrt{Dt}}\right)\right) \quad (4)$$

Where ""D is the diffusion coefficient. In equation (4) "erf" is the error function that can be calculated as per given values [4].

Assuming that after time "t", all of the biocide (that is, 100% of it) can penetrate into the depth "h" of the biofilm so that $C_o=0$, then (4) can be simplified as (5):

$$C(h,t)= C_s \left(1-\text{erf}\left(\frac{h}{2\sqrt{Dt}}\right)\right) \quad (5)$$

According to (5), the "biocide penetration time"- C(h,t)- will vary with an error function. In (5) for constant $C_s$ and D values, (5) can be simplified even further to (6) assuming that $t_2 > t_1$:

$$C(h1,t_1) < C(h2,t_2) \tag{6}$$

The practical meaning of (6) is that by increasing the time for penetration (t), biocide can penetrate into deeper depths ($h_2 > h_1$). Figure .2 schematically shows what is expressed in (6):

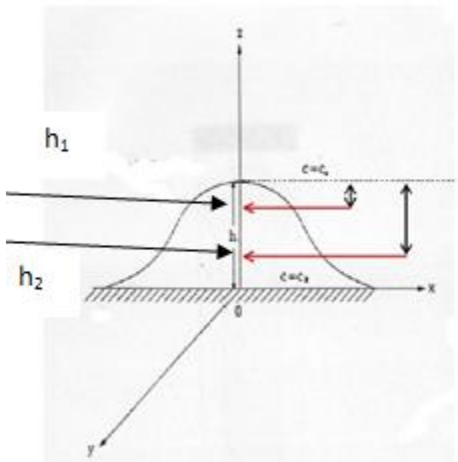


*Figure 2:* Schematic presentation for increasing penetration depth by increasing the time required to let the biocide penetrate.

Equation (5) implies that within the same time interval, more biocide ($C_s$) will enter into the biocide if we increase the initial concentration of the biocide ($C_o$) this is called "Shock Treatment". Also, by letting the biocide penetrate deep enough into the biofilm, one can expect to get more concentration of the biocide within the biofilm Experiences have shown that [5] injection of high dosage of a biocide within a short time has been effective on controlling sessile bacteria, also it has been demonstrated that [6] injection of 2 ppm hypochlorite has had no effects on a biofilm whereas injection of 16 ppm of the same chemical followed by a 2 ppm injection of it has had significant impact on the activity of the sessile bacteria.

However what happens in reality is that a certain percentage of the biocide is accumulated within the biofilm. This percentage can be taken as , practically speaking, 90%. In other words, if $C_s = 0.9\ C_o$. In addition, while in (5) the diffusion coefficient of the biofilm has been taken as the same of that of water, in reality it is not so. Biofilms are watery structures and therefore the diffusion of biocide is not taking place through pure water but a watery structure whose diffusion depends upon factors such as bacteria, extra- cellular polymer substance (EPS), gas bubbles and non-biological debris. In other words, within biofilms one has to correct diffusion coefficient (D) to effective diffusion coefficient($D_e$). For a slab-shaped biofilm with an average depth of "h", the time that it takes for 90% of a given biocide to penetrate underneath the biofilm can be shown as (7) [7].

$$t_{90} = 1.03\,\frac{\boldsymbol{h^3}}{\boldsymbol{D_e}} \tag{7}$$

Equation (7) is very important especially from an industrial-practical point of view. A practical example of this equation can be stated as below [6]:

If at a temperature of 24$^{o}$C and within 6 days, a biofilm is formed with an average thickness of 10 mm, the time required for a given to penetrate into this biofilm and constitute a concentration of 90% of the concentration of that biocide outside the biofilm will be one-hundred times that of the penetration time when the thickness of the biofilm was only 1 mm. In other words, if the penetration time for a biofilm thickness was about 12 minutes, when the thickness of the biofilm increases to 10mm, the time required for the biocide penetration will be 20 hours. This shows that without observing routine monitoring the biofilm formation and

thickening, just applying a biocide will not have its expected detrimental impact on biofilm. Figure 3 shows an example of application of a biocide (Chlorine) on the cooling tower of a power plant without observing biofilm development stages:

***Figure 3:*** Inadequate application of a biocide (residual Chlorine in water= 1 ppm) without a proper biofilm thickening management (Reza Javaherdashti's Personal Collection). Biofilm developed on the concrete wall of the cooling tower (Left) and its magnified view (Right).

The above also shows that no matter the type of the biocide, if a good house-keeping procedure is not in place, application of biocide alone will not have a significant impact. In addition, there is no linear relationship between the thickness of the biofilm and penetration time. The non-linear nature of the relationship that exists between the thickening of the biofilm and the penetration time (as given above in the example) does have practical importance that calls for a much better corrosion management and corrosion knowledge management 8] [procedure in industries.

## 3. CONCLUSIONS & RECOMMENDATIONS

- Biocide penetration underneath a biofilm obeys Diffusion Laws,
- Diffusion Laws governing biocide diffusion are not dependent upon the type of biocide (oxidising or non-oxidising biocide)

- By increase in biofilm thickness, the time required for biocide penetration also increases in a non-liner manner; the practical importance of this is that by a slight increase in the average thickness of a given biofilm, the time required for biocide penetration will increase as a non-linear function.
- Without a proper corrosion management and corrosion knowledge management in place, mere application of biocides wills not manage the problem of biofilm-induced corrosion.

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