

Revisiting exponential stress corrosion model

Isaac Elishakoff* and Yohann Miglis

*Department of Ocean and Mechanical Engineering, Florida Atlantic University, Boca Raton,
FL33431-0991, USA*

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Abstract. One of the prevailing models that describe the stress corrosion is represented by an exponential dependence between rate of corrosion and stress, suggested by Gutman, Zainullin and Zuripov. This study revisits the exponential model and derives analytical expressions for the structures' durability which is postulated as the time for stress level to reach its yield value. Comparison is conducted with other possible models, namely with linear, quadratic or cubic cases.

Keywords: stress corrosion, durability, time to failure, exponential corrosion model.

1. Introduction

The durability of a structure under corrosion is one of the main issues in ocean engineering. The problems remain not well understood, and applied methods used appear to be not on the safe side.

Applying a stress to an element of metal situated in a corrosive environment increases the stress corrosion rate beyond its initial stress-free corrosion rate counterpart. Copson (1983) identifies several factors associated with the stress-corrosion cracking, namely specific alloy composition, unique microstructure resulting from metallurgical processing, a tensile stress at exposed surfaces, a specific environment.

Revie (2007) explains that the multiplicity of the factor leads to a complicated prediction of the mechanism of time to failure. He writes "Depending on the metal – environment combination and the stressing condition, the time to failure can vary from minutes to many years. ... Such failure occurred, for example, in 0.7% C steel cables of the Portsmouth, Ohio, bridge after 12 years in service. The cables cracked at their base where rain water, presumably containing trace amounts of ammonium nitrate from the atmosphere, had accumulated and concentrated".

It is natural to assume that stress-corrosion dependence ought to utilize experimental data pertinent to alloy composition and corrosive environment. Still, analytical approaches to stress corrosion appear the only means of both the reconciling with experimental data and providing prediction of future life of structure. Several models have been proposed in the literature. Dolinskii (1967) studied the case when stress $\sigma(t)$ and corrosion rate $v(t)$ are connected linearly. Miglis and Elishakoff (2011) generalized the Dolinskii's (1967) linear relationship by proposing a n^{th} order polynomial relationship. In their paper, Gutman, Zainullin and Zuripov (1984) and monograph by Gutman (2000) proposed an exponential relationship. In this study, we revisit Gutman's (2000)

*Corresponding author, Professor, E-mail: elishako@fau.edu

exponential model with attendant closed-form expression for the time to failure.

2. Elastic deformation of a bar in a corrosive environment

In this study, we consider a bar subjected to a tensile load P . The cross section area is circular with radius r . The tensile stress equals

$$\sigma(t) = P/\pi r(t)^2 \quad (1)$$

The bar is placed in a corrosive environment that causes radius r to decrease in time. As a result the radius is a time dependent quantity $r(t)$. Consequently, for a given stress, the radius will reach a value such as the bar reaches the yield stress of the metal σ_y .

In the following study, we derive Eq. (1) in order to find analytical expressions for the Time to Failure T_f of a structure under corrosion.

We differentiate stress σ with respect to time t in Eq. (1) to get

$$\frac{d\sigma}{dt} = -\frac{2P}{\pi r^3} \frac{dr}{dt} \quad (2)$$

At the initial time the radius equals r_0 . The stress level at $t = 0$ equals

$$\sigma_0 = P/\pi r_0^2 \quad (3)$$

In view of the fact that $r_0^2 \sigma_0 = P/\pi$, Eq. (2) can be rewritten as

$$\frac{d\sigma}{dt} = \frac{-2r r_0^2 \sigma_0}{r^4} \frac{dr}{dt} \quad (4)$$

From Eq. (1) we express $r^4 = P^2/\pi^2 \sigma^2$. Hence the derivative of stress becomes

$$\frac{d\sigma}{dt} = \frac{-2r \pi^2 r_0^2 \sigma_0 \sigma^2}{P^2} \frac{dr}{dt} \quad (5)$$

Bearing in mind that according to Eq. (1) $r_0^2 \sigma_0 \pi^2 / P^2 = 1/\sigma_0 r_0^2$ and substituting it in Eq. (5) we get

$$\frac{d\sigma}{dt} = -\frac{2\sigma^2 r}{\sigma_0 r_0^2} \frac{dr}{dt} \quad (6)$$

According to Gutman, Zainullin and Zuripov (1983) the variation of the radius can be described as a sum

$$\frac{dr}{dt} = \left(\frac{dr}{dt} \right)_1 + \left(\frac{dr}{dt} \right)_2 \quad (7)$$

The term $(dr/dt)_1$ is associated with the Poisson's effect. Indeed, the deformation in transverse direction equals

$$\varepsilon_y = \frac{r(t) - r_0}{r_0} \quad (8)$$

Then, using Poisson's equation $\varepsilon_y = -\mu\varepsilon_x$ with $\varepsilon_x = \sigma(t)/E$ we get

$$\frac{r(t) - r_0}{r_0} = -\mu \frac{\sigma(t)}{E} \quad (9)$$

Differentiation of this expression with respect to time leads to

$$\left(\frac{dr}{dt} \right)_1 = -\mu \frac{r_0}{E} \frac{d\sigma(t)}{dt} \quad (10)$$

where ν is the Poisson's ratio. The second term is postulated by Gutman, Zainullin and Zuripov (1983) as

$$\left(\frac{dr}{dt} \right)_2 = -v_0 \exp\left(\frac{\sigma V_m}{3RT}\right) \quad (11)$$

where V_m is the molar volume of the metal, $R \approx 8.31 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$ the universal gas constant, T the absolute temperature in K . Introducing Eqs. (10) and (11) in Eq. (6) we obtain

$$\frac{d\sigma}{dt} = \frac{2r\sigma^2 \mu r_0}{r^2 \sigma_0 E} \frac{d\sigma}{dt} + \frac{2r\sigma^2}{r^2 \sigma_0} \exp\left(\frac{\sigma V_m}{3RT}\right) \quad (12)$$

In view of the identity $r_0 \sqrt{\sigma_0} = r \sqrt{\sigma}$ and we get governing differential equation

$$\frac{d\sigma}{dt} = \frac{2\sigma^{\frac{3}{2}}}{r_0 \sqrt{\sigma_0}} \left[\frac{\mu r_0}{E} \frac{d\sigma}{dt} + v_0 \exp\left(\frac{\sigma V_m}{3RT}\right) \right] \quad (13)$$

or, after some algebra

$$\frac{d\sigma}{dt} \left[1 - \frac{2\sigma^{\frac{3}{2}} \mu r_0}{\sqrt{\sigma_0} r_0 E} \right] = \frac{2\sigma^{\frac{3}{2}}}{r_0 \sqrt{\sigma_0}} \left[v_0 \exp\left(\frac{\sigma V_m}{3RT}\right) \right] \quad (14)$$

Eq. (14) is arranged conveniently as

$$\left[\frac{r_0 \sqrt{\sigma_0} \sigma^{-3/2}}{2v_0} \exp\left(-\frac{\sigma V_m}{3RT}\right) - \frac{\mu r_0}{v_0 E} \exp\left(-\frac{\sigma V_m}{3RT}\right) \right] d\sigma = dt \quad (15)$$

We integrate this function between 0 and t for the time variable, and from σ_0 to σ_y for the stress

$$\int_{\sigma_0}^{\sigma} \frac{r_0 \sqrt{\sigma_0} \sigma^{-3/2}}{2v_0} \exp\left(-\frac{\sigma V_m}{3RT}\right) d\sigma - \int_{\sigma_0}^{\sigma} \frac{\mu r_0}{v_0 E} \exp\left(-\frac{\sigma V_m}{3RT}\right) d\sigma = \int_0^t dt \quad (16)$$

We introduce new variables

$$a = \frac{V_m \sigma_y}{3RT}, \quad \chi = \frac{\sigma V_m}{3RT} \quad (17)$$

Differentiation of χ with respect to t yields

$$\frac{d\chi}{dt} = \frac{V_m}{3RT} \frac{d\sigma}{dt} \quad (18)$$

Substitution of Eq. (18) into Eq. (16) leads to

$$\frac{r_0 \sqrt{\sigma_0}}{2\nu_0} \frac{3RT}{V_m} \left(\frac{3RT}{V_m} \right)^{-3/2} \int_{aF_0}^{aF} \frac{\exp(-\chi)}{\sqrt{\chi^3}} d\chi - \frac{\mu r_0}{\nu_0 E} \frac{RT}{V_m} \int_{aF_0}^{aF} \exp(-\chi) d\chi = t \quad (19)$$

In view of the equality

$$\int \frac{\exp(-\chi)}{\sqrt{\chi^3}} d\chi = -\frac{2e^{-\chi}}{\sqrt{\chi}} - 2\sqrt{\pi} \operatorname{erf}(\sqrt{\chi}) \quad (20)$$

with $\operatorname{erf}(\chi)$ denoting the error function defined as

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (21)$$

Eq. (19) is reduced to

$$\frac{r_0}{\nu_0} \left[\frac{\sqrt{\sigma_0}}{2} \sqrt{\frac{V_m}{3RT}} \int_{aF_0}^{aF} \frac{\exp(-\chi)}{\sqrt{\chi^3}} d\chi + \frac{\mu RT}{V_m E} [\exp(-aF) - \exp(-aF_0)] \right] = t \quad (22)$$

with F_0 being the ratio of initial stress to yield stress, and F the ratio of the stress at the time t to the yield stress

$$F_0 = \frac{\sigma_0}{\sigma_y}, \quad F = \frac{\sigma}{\sigma_y} \quad (23)$$

Eq. (22) can be simplified by using Eq. (23)

$$\sqrt{\frac{\sigma_0 V_m}{3RT}} = \sqrt{\frac{(\sigma_0/\sigma_y) \sigma_y V_m}{3RT}} = \sqrt{aF_0} \quad (24)$$

So Eq. (22) becomes

$$\begin{aligned} \frac{r_0}{\nu_0} \left[\frac{\sqrt{aF_0}}{2} \left[-\frac{2 \exp(-aF)}{\sqrt{aF}} - 2\sqrt{\pi} \operatorname{erf}(\sqrt{aF}) + \frac{2 \exp(-aF_0)}{\sqrt{aF_0}} + 2\sqrt{\pi} \operatorname{erf}(\sqrt{aF_0}) \right] \right. \\ \left. + 3 \frac{\mu RT}{VE} [\exp(aF) - \exp(aF_0)] \right] = t \quad (25) \end{aligned}$$

Substituting $\sigma = \sigma_y$, $F = 1$ and replacing t the time to failure T_f results in the expression of the structure's durability

$$\frac{r_0}{v_0} \left[\frac{\sqrt{aF_0}}{2} \left[-\frac{2 \exp(-a)}{\sqrt{a}} - 2\sqrt{\pi} \operatorname{erf}(\sqrt{a}) + \frac{2 \exp(-aF_0)}{\sqrt{aF_0}} + 2\sqrt{\pi} \operatorname{erf}(\sqrt{aF_0}) \right] + 3 \frac{\mu RT}{VE} [\exp(a) - \exp(aF_0)] \right] = T_f \quad (26)$$

In Figs. 1 and 2, the time to failure T_f in Eq. (26) is plotted for different σ_0 . The initial radius of the bar is fixed at $r_0 = 0.1m$. The metals considered are iron and aluminum. The temperature is set at $T = 293$ K. The mechanical and chemical properties of the iron are $\sigma_y = 200MPa$, $V_m = 7.11 \cdot 10^{-6} m \cdot mol^{-1}$, $E = 210MPa$, $\mu = 0.285$. The respective properties of the aluminum are $\sigma_y = 40$ MPa, $V_m = 9.99 \cdot 10^{-6} m^3 \cdot mol^{-1}$, $E = 69$ MPa, $m = 0.34$.

In both cases, the durability T_f decreases when the corrosion rate v_0 increases, as expected. With the increase of σ_0 the durability T_f decreases. For the iron bar (Fig. 1), the durability reduces by 53% when the initial stress increases three times, from 30 to 90 MPa. The durability decreases from 16 years to 8 years for an initial corrosion rate v_0 set at $10^{-10} m \cdot s^{-1}$, when the initial stress increases

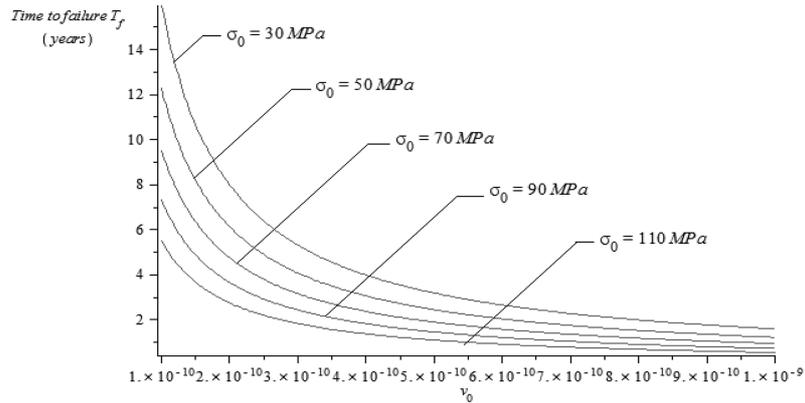


Fig. 1 Time of failure T_f of an iron bar versus the initial corrosion rate v_0

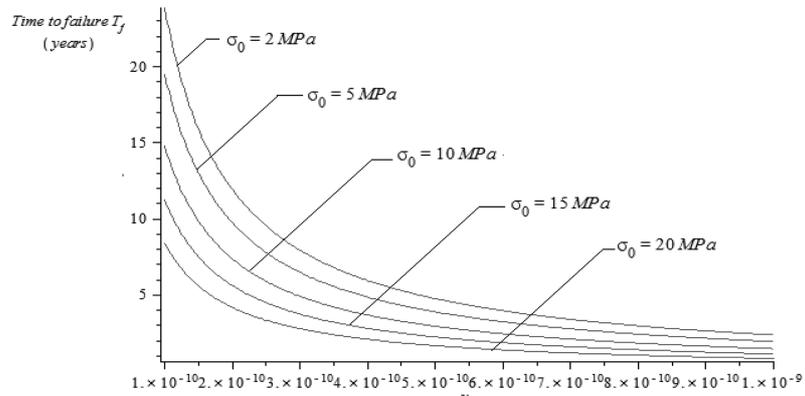


Fig. 2 Time to failure T_f of an aluminum bar versus initial corrosion rate v_0

tenfold for the aluminum bar, from to $\sigma_0 = 2 \text{ MPa}$ (Fig. 2). For the fixed initial corrosion rate v_0 , with increase of the initial stress σ_0 the time to failure T_f decreases, this result is in accordance with our anticipation. For example, for $v_0 = 5 \cdot 10^{-10} \text{ m} \cdot \text{s}^{-1}$, the time to failure T_f for the iron bar with $\sigma_0 = 50 \text{ MPa}$ constitutes 2.42 years whereas for the aluminum bar $T_f = 4.12$ years for $\sigma_0 = 5 \text{ MPa}$.

3. Effect of neglecting the stress dependence

Some authors evaluate the time to failure T_f without taking into account the effect of the stress σ . They are using the so-called uniform corrosion model. We will show hereinafter that this simplification may yield large errors. Within this assumption time to failure is denoted as $T_{f,u}$.

To deal with this case we put formally in Eq. (11) $\sigma = 0$ to get

$$\frac{dr}{dt} = -v_0 \quad (27)$$

tegrating Eq. (27) with respect to time gives

$$r(t) = r_0 - v_0 t \quad (28)$$

Expressing Eq. (28) in terms of time t and radius $r(t)$ yields

$$t = \frac{r_0}{v_0} \left[1 - \frac{r(t)}{r_0} \right] \quad (29)$$

The value of the radius $r(t)$ when the yield stress is reached is denoted as r_y . From Eq. (1) we set

$$r_y / r_0 = \sqrt{\sigma_0 / \sigma_y} = \sqrt{F_0} \quad (30)$$

Durability estimate $T_{f,u}$ becomes

$$T_{f,u} = \frac{r_0}{v_0} (1 - \sqrt{F_0}) \quad (31)$$

Values for the time of failure $T_{f,u}$ for an iron bar with a corrosion rate v_0 set at $10^{-10} \text{ m} \cdot \text{s}^{-1}$ are summarized in Table 1.

As the initial stress increases, the error between the two models becomes larger. For $\sigma_0 = 80 \text{ MPa}$, the percentage-wise difference constitutes 173%. It must be observed that the uniform corrosion model yields an overestimation of the time to failure $T_{f,u}$, and thus is not on the safe side. In Table 2 we study the case of the aluminum.

As we observe, the uniform corrosion rate does not provide a good estimate for the time to failure

Table 1 Comparison of the time to failure for two different corrosion models (iron bar)

$\sigma_0 \text{ (MPa)}$	Time to failure T_f in years with the exponential stress corrosion relationship	Time to failure $T_{f,u}$ in years with the uniform corrosion model
30	15.97	26.92
50	12.26	24.71
70	9.51	23.43
80	8.36	22.86

Table 2 Comparison of the time to failure for two different corrosion models (aluminium bar)

$\sigma_0(MPa)$	Time to failure T_f in years with the exponential stress corrosion relationship	Time to failure $T_{f,u}$ in years with the uniform corrosion model
5	19.50	29.08
10	14.77	28.00
20	8.39	26.46
30	3.75	25.28

in the case of the aluminum bar either. The effect of stress on the corrosion rate is not negligible, overestimation in the case of $\sigma_0 = 30 MPa$ constitutes a factor of over 6.

4. Approximation of the coefficients with a polynomial relationship using Gutman's model

Dolinskii (1967) proposed a linear relationship between stress and corrosion rate. Miglis and Elishakoff (2011) proposed polynomial based relationships between stress and corrosion rate. We first deal with Dolinskii's linear relationship. The value of the radius at the time instant t is

$$r(t) = r_0 - \int_0^t v(x) dx \quad (32)$$

Differentiating Eq. (32) yields the decrease in time of the radius

$$\frac{dr(t)}{dt} = -v(t) \quad (33)$$

$v(x)$ being the corrosion velocity in $m \cdot s^{-1}$, expressed with a polynomial with coefficients that are determined experimentally.

The first case we study is the one when corrosion rate and stress depend linearly upon each other. The decrease in time of the radius can be expressed as

$$\frac{dr}{dt} = -v_0 \left[1 + \frac{m}{v_0} \sigma(t) \right] \quad (34)$$

the coefficient m being a characteristic of the material. In the case $\sigma V/3RT \ll 1$. So it is instructive to expand expression in Eq. (11) as a Taylor series

$$\frac{dr}{dt} = -v_0 \left[1 + \frac{\sigma V_m}{3RT} \right] \quad (35)$$

which leads to the estimate of m as

$$m = \frac{V_m v_0}{3RT} \quad (36)$$

The durability of an elastic bar with a linear relationship between stress and corrosion is (Gutman *et al.* 1984)

$$\left[\frac{mP\sigma(t) \cdot \ln \left(\frac{Pv_0 - Pm\sigma(t) + 2v_0R_0^2\pi\sigma(t) - 2\sqrt{v_0(v_0R_0^2\pi - Pm)}\sqrt{\sigma(t)(P + R_0^2\pi\sigma(t))}}{v_0 + m\sigma} \right)}{2v_0\sqrt{v_0\pi(v_0R_0^2\pi - Pm)}\sqrt{\sigma(P + R_0^2\pi\sigma(t))}} \right]_{\sigma_0}^{\sigma_y} \sqrt{\frac{P + R_0^2\pi\sigma(t)}{\sigma(t)}} = T_f \quad (37)$$

with $R_0 = R$ the inner radius of the bar, in our case $R_0 = 0$. The expression in the parenthesis must be evaluated at $\sigma = \sigma_y$ and $\sigma = \sigma_0$, with subsequent subtraction of results.

In the case of the iron bar, we get $m = 9.72 \cdot 10^{-20}$. For an initial stress of 30 MPa, the durability within Dolinskii (Gutman 2000) model is 18.09 years, whereas it constitutes 15.98 years within exponential model by Gutman, Zainullin and Zuripov (1983). These two results are relatively close. For the aluminum bar, we have $m = 1.36 \cdot 10^{-19}$. The durability within Gutman's model constitutes 14.77 years for an initial stress of 10 MPa, whereas it is 15.43 years within Dolinskii (Gutman 2000) model. This difference is also explained by the fact that the exponential model takes into account the elastic deformations of the bar with the Poisson's ratio.

We now compare Gutman, Zainullin and Zuripov's (1983) model with the quadratic model proposed in (Gutman 2000). In this case the relationship between radius $r(t)$ and stress $\sigma(t)$ is described by the following expression (Gutman 2000)

$$\frac{dr}{dt} = -v_0 \left[1 + \frac{m}{v_0}\sigma(t) + \frac{n}{v_0}\sigma^2(t) \right] \quad (38)$$

In new circumstances the coefficient m is left unchanged in Eq. (37). The coefficient n is evaluated as $n = v_0(V_m/3RT)^2/2$. For the iron we get $n = 9.36 \cdot 10^{-29}$, whereas for the aluminum $n = 4.73 \cdot 10^{-29}$. The durability with a quadratic relationship reads [4]

$$\begin{aligned} T_f = & 2 \sum_{i=1}^2 \frac{1}{PS_i^3 n \pi R \left(\frac{s \omega(i+1)}{s \omega(i)} - 1 \right) \left(1 + \frac{P}{\pi R^2 S_i} \right)} \left[P \pi R^2 \left[\sigma \left(1 + \frac{P}{\pi R^2 \sigma_y} \right)^{3/2} - \sigma_0 \left(1 + \frac{P}{\pi R^2 \sigma_0} \right)^{3/2} \right] \right. \\ & - \pi^2 R^4 s_i \left[\sigma \left(1 + \frac{P}{\pi R^2 \sigma_y} \right)^{3/2} - \sigma_0 \left(1 + \frac{P}{\pi R^2 \sigma_0} \right)^{3/2} \right] + P R^2 \pi \left[\sigma \sqrt{1 + \frac{P}{\pi R^2 \sigma_y}} - \sigma_0 \sqrt{1 + \frac{P}{\pi R^2 \sigma_0}} \right] \\ & \left. + \pi^2 R^4 s_i \left[\sigma_y \sqrt{1 + \frac{P}{\pi R^2 \sigma_y}} - \sigma_0 \sqrt{1 + \frac{P}{\pi R^2 \sigma_0}} \right] + \frac{1}{2} P^2 \sqrt{1 + \frac{P}{s_i \pi R^2}} \right] \\ & \ln \frac{\left(\frac{\sigma_0}{s_i} - 1 \right) \left[1 + \frac{\sigma_y}{s_i} + \frac{2\pi R^2 \sigma_y}{P} + 2\pi R^2 \frac{\sigma_y}{P} \sqrt{1 + \frac{P}{s_i \pi R^2}} \sqrt{1 + \frac{P}{\pi R^2 \sigma_y}} \right]}{\left(\frac{\sigma_y}{s_i} - 1 \right) \left[1 + \frac{\sigma_0}{s_i} + \frac{2\pi R^2 \sigma_0}{P} + 2\pi R^2 \frac{\sigma_0}{P} \sqrt{1 + \frac{P}{s_i \pi R^2}} \sqrt{1 + \frac{P}{\pi R^2 \sigma_0}} \right]} \quad (39) \end{aligned}$$

with s_1 and s_2 being defined as

$$s_1 = \frac{-m + \sqrt{m^2 - 4v_0 n}}{2n}, \quad s_2 = \frac{-m - \sqrt{m^2 - 4v_0 n}}{2n} \quad (40)$$

introduced as roots of quadratic equation $v_0 + m\sigma(t) + n\sigma^2(t) = 0$. In Eq. (40), the permutation function ω_i is defined as

$$\omega = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 1 \end{pmatrix}$$

The permutation function ω is function which associates the value of the front row line to his image in the second row line, so that we have, $s_{\omega(1)} = s_1$, $s_{\omega(2)} = s_2$, $s_{\omega(3)} = s_1$.

As a result, for the iron bar we get a durability of 18.03 years, and 15.43 years for the aluminum bar. Since Dolinskii's linear relationship yielded respectively 18.09 years and 15.43 years we see that there is an extremely small difference yielded between linear and quadratic relationships.

For a cubic case the relationship between corrosion and stress reads

$$\frac{dr}{dt} = -v_0 \left[1 + \frac{m}{v_0} \sigma(t) + 1 + \frac{n}{v_0} \sigma^2(t) + 1 + \frac{q}{v_0} \sigma^3(t) \right] \quad (41)$$

The coefficient q must be evaluated as $q = v_0(V_m / 3RT)^3 / 3!$ using the Taylor's series expansion of the Gutman, Zainullin and Zuripov (1983) formula in Eq. (11). For the iron its value is $q = 1.53 \cdot 10^{-38}$, and $q = 4.27 \cdot 10^{-38}$ for the aluminum. Its order of magnitude being small, we derive the same results for the durability as the ones found within the quadratic case.

In Fig. 3, we show the differences of the decreasing rate of the radius $|dr/dt|$ in Eq. (11) as a function of $\sigma(t)$ for the different types of dependence for the iron bar. As is seen, Gutman's model can be accurately approximated by a quadratic relationship.

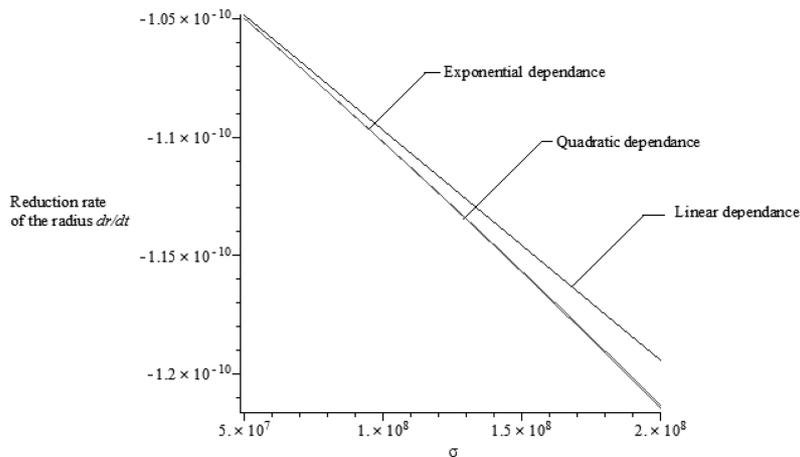


Fig. 3 Rate of decrease of the radius versus the stress σ

5. Conclusions

In this study we extend Gutman's model for the durability of tensed bar under corrosion. For the first time in the literature, the exact expression for the durability are derived and compared with results furnished by linear, quadratic and cubic approximations.

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