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Cathodic control using cellular automata approach

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Abstract

We present a stochastic three dimensional cellular automata model of aqueous corrosion. We consider the cathodic reaction with dissolved oxygen and different concentrations of the oxidizer. We study the role and the stability of the passive layer and its effect on the kinetics, surface morphology and roughness of the metallic surface. The model considers balanced spatially separated anodic and cathodic reactions and is capable of illustrating the cathodic control of the corrosion rate. Besides the electrochemical reactions, we take into account ionic diffusion, acido/basic neutralization. Results are compared to aqueous corrosion of Fe in near neutral solution.

Keywords: corrosion, cathodic control, dissolved oxygen, cellular automata, passivation

1. Introduction

2 The evaluation of the damage of a material, due to the action of corrosion, represents an
3 important challenge on both economic and scientific levels, [1, 2]. Limiting the degradation of
4 metals will enhance their durability leading to financial gain and avoiding costs which can reach
5 4% of international GDP [1, 3]. Corrosion Engineering is mainly focused on practical advances
6 and relies on collecting existing data about corrosion in view of improving corrosion protection [4].
7 In contrast, experimental or theoretical scientific studies aim at modelling for understanding and
8 predicting corrosion rates in order to adjust and optimize materials composition and resistance.

9 In this article, we focus on aqueous corrosion. Aqueous corrosion occurs as a result of a
10 combination of chemical and electrochemical reactions on a metal surface including electronic
11 transfer between two regions associated to the anodic and cathodic reaction, plus an ionic diffu-
12 sion between the different species in the solution surrounding the metal.

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13 Anodic reactions are generally related to metal oxidation. Cathodic reactions depend on
14 the type of the oxidant present in the solution. For aqueous corrosion and anaerobic systems,
15 only a reduction of H^+ or the reduction of the water molecules takes place. In the case of
16 aerobic systems, called also aerated systems, the reduction reaction is set by the amount of
17 dissolved oxygen (DO) present in the electrolyte. As shown in many works, DO in solution has
18 an important effect on the corrosion rate. For an example, in the case of carbon steel, it has been
19 reported that the corrosion rates of the material are higher in solutions with the presence of DO
20 independently of the type of the solution like hydrolic acid, sulphyric acid or sodium chloride
21 (3.5% NaCl) [5] .

22 During corrosion, the metal can be covered by an oxide layer formed by the metal itself as
23 a consequence of the anodic reaction [6]. The formation of the passive layer or its dissolution
24 taking place at random locations over the surface leads to an heterogeneous morphology of the
25 surface and the appearance of surface roughness. This roughness is considered often to have
26 as a major influence on the kinetics of the deterioration of a metal. Many studies have been
27 completed to evaluate the relationship between the surface roughness and the kinetics of the
28 corrosion process using several methods. For magnesium alloy AZ91 [7], stainless steels [8, 9],
29 copper [10], aluminum or titanium-based alloys [11] an increase in the surface roughness, increases
30 the susceptibility to localized corrosion. Typically, the general and localized corrosion behaviour
31 of alloys would depend on their passivation properties. Hence, it is important to know the
32 passivation behaviour of alloys with different surface finish to correlate the surface roughness to
33 their general corrosion and pitting tendency [12, 7]. For metals with the ability to form a passive
34 layer, a decrease in surface roughness increases the corrosion resistance but for the ones with no
35 passive film, the opposite trend has been observed e.g. mild steel [13] and AE44 magnesium alloy
36 [12]. In fact, the surface roughness increases the specific area of the metal surface in contact
37 with the electrolyte.

38 In this work, we have considered cellular automata modelling. The cellular automata mod-
39 elling is a powerful and successful method in modelling the evolution of a system modelled by a
40 discrete lattice decomposed into cells which evolve according to a set of rules and depending on
41 the cells' neighborhood. This type of modelling is based on a discretization in both space, time
42 and consideration of physical states and chemical species as different states of the cell. Cellular
43 automata modelling of corrosion started with P. Meakin et al. in 1993, [14] and after that,
44 different algorithms have been developed using cellular automata in the framework of corrosion
45 processes studies. An overview of cellular automata modelling of the corrosion processes can be

46 found in [15, 16]. In the present work, we use a three dimensional corrosion model with spa-
 47 tially separate anodic and cathodic reactions and accounting of acido-basic species in solution
 48 [17, 18, 19]. A new feature is introduced with accounting for cathodic reaction taking place with
 49 dissolved oxygen DO .

50 The paper is organised as follows. We first present the model and its cellular automata im-
 51 plementation, in particular concerning the representation of small oxygen concentrations. Then
 52 we present the different results concerning the corrosion rate and the roughness as a function of
 53 different effects like passivation or oxygen concentration. Then a small section compares model
 54 results to experimental values for the corrosion rate. Finally, summary and conclusions are given.

55 2. Model

56 2.1. Cellular automata model

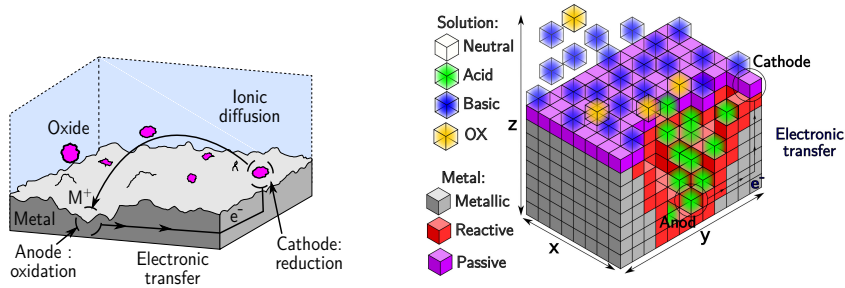


Figure 1: Cellular automata model (right) based on the corrosion scenario (left)

57 Cellular automata (CA) modelling is based on a simplified reality where the system is mod-
 58 elled on a lattice by regular cells which can take a finite number of states representing in our
 59 case chemical species in possibly different physical states, see figure 1. In the present model we
 60 take for simplicity a cubic lattice. The states in this model are the following. For solid sites, we
 61 have metal sites which are subdivided into reactive sites of the metallic surface R and bulk metal
 62 M and also oxide or passive sites P . Metallic R sites can host anodic and cathodic reactions,
 63 whereas oxide sites can only host cathodic reactions. The solid material is immersed in an elec-
 64 trolyte. For the solution states, we distinguish acid A (i.e. H^+), basic B (i.e. OH^-), neutral N
 65 solution sites and for this aerated system we also take into account dissolved oxygen sites DO .

66 In the CA, the evolution of the cells is given by rules in relation with the neighbourhood
 67 of the evolving cell. In this work, Moore neighbourhood is taken with 26 neighbours in the

68 three dimensional space. This extended neighbourhood allows for detailed accounting of a cell's
69 neighbourhood. Here, the evolution rules for the cells account for two processes: diffusion and
70 chemical/electrochemical reactions. In particular, we will consider the possibility of having
71 anodic and cathodic electrochemical half-reactions in spatially separated sites. We make sure
72 when executing a pair of half-reactions, that they are paired i.e. the anodic and cathodic sites
73 are connected by metal to ensure the electronic connectivity between those sites. This is achieved
74 by using the burning algorithm detailed in [20].

75 For comparison with the literature, we will now consider experimental systems and results
76 taken from [21, 22].

77 2.2. Diffusion

We first express diffusion in terms of the CA. The diffusion of species in solution follows a random walk which verifies [23]:

$$\langle r^2 \rangle = 2 d D \Delta t_{\text{diff}} \quad (1)$$

$\langle r^2 \rangle$ is the average of the square of the distance traveled in a time Δt_{diff} , $d = 3$ is the space dimension and D is the diffusion coefficient. In the CA, a site in solution site diffuses by swapping content with an other solution type cell in it's neighbourhood, this rules has an exception detailed below in the case an acidic and basic cell are adjacent, in this case a reaction takes place. In the Moore neighborhood, the average distance of an elementary displacement in all possible directions gives [17]

$$\langle r^2 \rangle = 2.0769 a^2 \quad (2)$$

78 where a is the characteristic length of a cell, we will hereafter take $a = 10 \mu m$.

79 For comparison with results in [22], we consider systems at 50°C . In these conditions, diffusion
80 coefficient for DO is $4.50 \cdot 10^{-5} \text{cm}^2 \text{s}^{-1}$ [24]. For H^+ , OH^- we have diffusion coefficients of the
81 order $7.3 \cdot 10^{-5} \text{cm}^2 \text{s}^{-1}$ [17, 25]. To simplify the simulation and keep the same diffusion algorithm
82 for all the species in solution, we will take the identical value for corresponding to the diffusion
83 of DO . In this paper, we will focus on the effect of DO . With the above diffusion coefficient
84 and a characteristic size of a cell of $10 \mu m$, and according to equation (1), we have the value
85 of a single diffusion time step $\Delta t_{\text{diff}} = 1.54 \cdot 10^{-2} \text{s}$. Relation with the corrosion time step, is set
86 by the parameter N_{diff} as $\Delta t_{\text{corr}} = N_{\text{diff}} \Delta t_{\text{diff}}$. We considered simulations with typically $2 \cdot 10^5$
87 corrosion time steps, and study the cases with $N_{\text{diff}} = 100, 250, 500$ and 1000 . This corresponds,

88 respectively to 85.3, 212, 427, 853 hours of a macroscopic real simulated time. In the following,
 89 we choose to represent time in number of corrosion time steps units. From a computational point
 90 of view, the size of the cellular automata being of the order $\approx 10^8$ sites, simulations can take
 91 from several days to several weeks with parallel algorithms in CUDA environment on NVIDIA
 92 TESLA K80 cards.

93 2.3. Chemical, electrochemical reactions

94 As mentionned above, a reaction occurs when diffusing acidic A (H^+) and basic B (OH^-)
 95 sites meet in solution and react by annihilating and are replaced by a neutral sites. Note that
 96 in the initial state, at time $t = 0$, the metal is immersed into a neutral solution, when corrosion
 97 takes, acidic and basic sites can be produced as detail in the following.

98 Besides diffusion, sites can react and change chemical or electrochemical state depending
 99 on the neighbourhood. In table 1, we present the possible electrochemical reactions which we
 consider to contribute to the corrosion process. They occur on the metallic surface. The elec-

Table 1: Electrochemical reactions

Chemical reactions	Cellular automata rules	Environnement	Probabilities
Anodic			
$M + H_2O \rightarrow MOH_{aq} + H^+ + e^-$	Metal \rightarrow Acid	Acid, Neutral	P_{sse}
$M + OH^- \rightarrow MOH_{solid} + e^-$	Metal + Basic \rightarrow Passif + Neutral	Basic	P_{sse}
Cathodic			
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	Surf + DO + Acid \rightarrow Surf + Neutral	Acid, Neutral	P_{sse}
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	Surf + DO + Neutral \rightarrow Surf + Basic	Basic	P_{sse}
Spatially Joint (SJ) reactions			
$M + \frac{1}{2} H_2O + \frac{1}{4} O_2 \rightarrow MOH_{aq}$	Metal + DO \rightarrow Neutral	Acid ou Neutral	P'_{oxi}, P_{oxi}
$M + \frac{1}{2} H_2O + \frac{1}{4} O_2 \rightarrow MOH_{solid}$	Metal + DO \rightarrow Passive	Basic	1
$MOH_{solid} \rightarrow MOH_{aq}$	Passif \rightarrow Neutral	Acid ou Neutral	P'_{oxi}, P_{oxi}

Surf = **Metal** or **Oxide** (passive metal)

100

101 trochemical reactions for the metal involve a single electron, however the model can easily be
 102 generalized to any number of electrons.

103 The program accounts for cathodic reaction with oxygen in different environments depending
 104 on the presence and number of a H^+ sites in the neighbourhood.

105 • Anodic reactions:

106 For Acidic and neutral environment, we have metal oxidation and cation hydrolysis. In basic
 107 environment, an insoluble hydroxide is formed and precipitates on the surface. In both environ-
 108 nments, we have either a production of H^+ or a consumption of OH^- which corresponds to a
 109 decrease of the value of the pH thus acidification of the solution.

110 • Cathodic reactions:

111 We have reduction of DO presented differently according to the environment: acidic, neutral or
112 basic. We have respectively either a consumption of H^+ ions or a production of OH^- ions. In
113 both cases there is an increase in pH i.e. basification of the solution locally.

114 2.4. Representing DO concentration in the CA

In oxygenated water, hematite (Fe_2O_3) or ferric hydroxydes ($Fe(OH)_3$ or $FeOOH$) are the main corrosion products. But in water without dissolved oxygen or low oxygen concentration, magnetite (Fe_3O_4) or ferrous hydroxydes ($Fe(OH)_2$) are the corrosion products. To simplify the modelling, we choose to form the same oxide, magnetite Fe_3O_4 whatever is the oxygen concentration and compare with experimental results in [22] and consider the following chemical reaction:



115 In this article $50^\circ C$ systems are considered. The observed oxygen concentrations are approxi-
116 mately from 1 to 8 *ppm* (*ppm* = *mg/kg*). In the following, we will take a typical value of 6 *ppm*
117 of DO in solution. We present hereafter how to represent this small concentration within the
118 cellular automata.

119 For quantitative evaluation in the CA, two steps have to be considered. First we need to
120 evaluate the quantity of DO in a site considering that in the CA there is stoichiometric reaction
121 of a single DO site with a single metal site according to the cellular automata rules in table 1.
122 Second given the quantity of DO in a single site, we have to estimate the number of DO sites to
123 represent on average the 6 *ppm* concentration of DO in solution.

124 To evaluate the first step, we use the molar volume of iron at room temperature is $v_m^{Fe} =$
125 $7.09 \cdot 10^{-6} m^3 mol^{-1}$. The numbers of moles of iron in a cell is then $n_{Fe} = \frac{a^3}{v_m^{Fe}}$ which reacts with
126 $n_{O_2} = \frac{2}{3} n_{Fe}$ of DO according to equation (3). This gives us the DO content of a cell.

We now consider the second step, to estimate the concentration of DO sites to represent the 6 *ppm* = 6 *mg/kg* concentration. Considering the molar mass of dissolved oxygen is $32 gmol^{-1}$, a site in these conditions will hold $n_{DO} = 6 \times \frac{(10^{-4})^3}{32 \cdot 10^3}$ moles. The dilution rate of 6 *ppm* corresponds to a dilution in number of sites of

$$\frac{n_{DO}}{n_{O_2}} = 1.987 \cdot 10^{-6} \approx 2 \cdot 10^{-6} \quad (4)$$

127 In the simulation, the DO concentration is fixed by imposing a fixed concentration on the last top
128 plane of the simulation box which is parallel to the metallic surface, figure 2. Systems simulated

129 have lattice size (1024, 1024, 128) sites along x , y , z directions. The last top plane has dimensions
 130 1024×1024 sites, therefore the dilution rate corresponds to approximately keeping two sites in
 131 the last top plane as shown in figure 2 at each simulation step. This plane is furthest from the
 132 reacting surface and allows to simulate the diffusive layer effect. By diffusion i.e. random walk,
 133 the oxygen sites are then free to leave this plane and diffuse in the rest of the volume to reach the
 134 reactive surface and a cathodic reaction can take place. Being consumed at the metallic surface
 135 there concentration is not fixed in the volume, there is profile.

136 Note that the above representation of a low DO concentration from few highly concentrated
 137 DO cells may appear unusual. We recall this is the consequence of the CA representation with
 138 a one to one cell reaction between metal and DO . It must be emphasized that only the average
 139 collective effect of the DO sites over a large number of time steps has a meaning. The small
 140 number of events due to the low DO concentration is compensated by a large simulation time
 141 for which the accumulation of corrosion events spread over the entire surface leads to an average
 142 effect which is representative.

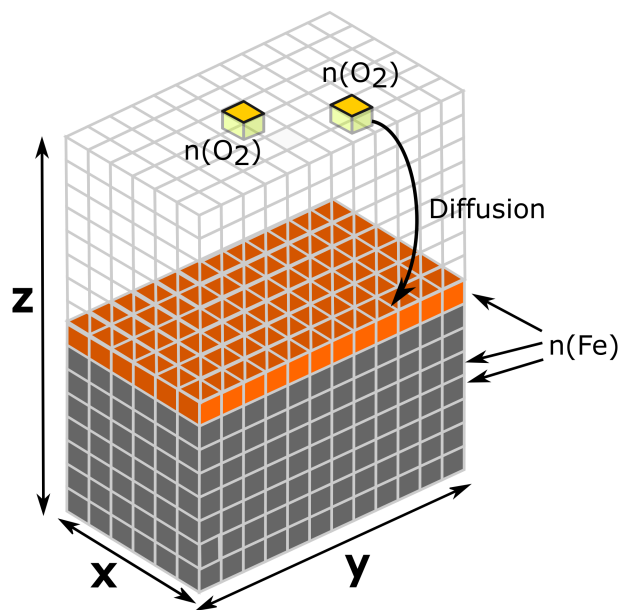


Figure 2: Cellular automata with fixing a density of two sites of oxygen in the last plane $n(O_2)$ and $n(Fe)$ refers to, respectively, the number of moles of oxygen and iron in one site.

143 Finally, also note that due to the low ppm concentration of DO , anodic corrosion half-reactions

144 occur very seldom, we are in a cathodic controlled corrosion. In this case, no accumulation of
 145 acidic and basic sites is expected. Indeed, after having been produced by the anodic or cathodic
 146 reactions, acidic and basic sites have sufficient time to diffuse away from the metallic surface
 147 where they are produced. This is contrast with conditions investigated in previous papers,
 148 where the absence of cathodic control allowed for much faster corrosion rates [17, 18, 19]. Thus
 149 with a small amount of *DO* the transition to the localized corrosion regime presented in these
 150 papers is more difficult to occur. We therefore focus on studying the corrosion and passivation
 151 phenomena only in neutral medium with a probability P_{oxi} which controls the dissolution of
 152 oxides in this environment.

153 2.5. Studied quantities

154 In what follows, we will calculate different quantities:

- The corrosion rate v_{corr} : equal to the derivative of the corrosion height loss Δh_{loss} in a units divided by the corrosion elementary time Δt_{corr} , quantity of interests for engineers. As for each corrosion step, we execute a number N_{diff} of diffusion steps, the corrosion rate is calculated using :

$$v_{\text{corr}} = \frac{a\Delta h_{\text{loss}}}{\Delta t_{\text{corr}}} = \frac{a\Delta h_{\text{loss}}}{N_{\text{diff}}\Delta t_{\text{diff}}} \quad (5)$$

155 where a is the lattice site characteristic size.

- The chemical roughness σ_{chem} : equal to the number of surface reactive R and P sites, which represent also the number of cathodic sites N_c , divided by the surface sites in a plane [17, 26, 27]

$$\sigma_{\text{chem}} = \frac{N_c}{N_x \times N_y} \quad (6)$$

156 For a rough surface, this quantity becomes larger than one and being related to the number of
 157 reactive sites, as it is the interface between the metal and the solution, it is directly related to
 158 the kinetics of corrosion.

159 For both quantities, we will study the effect of the parameter N_{diff} given in the equation (5).
 160 We will also study the effect of the dissolution probability in neutral environment: P_{oxi} on the
 161 corrosion regime.

162 **3. Results**

163 *3.1. Oxide stability and corrosion rate*

164 In this section we investigate the relationship between the oxide stability and the corrosion
165 kinetics by varying the dissolution probability: P_{oxi} .

166 In figure 3, we present the evolution of the corrosion rate for different values of the dissolution
167 probability and for given values of diffusion step N_{diff} . We observe that the corrosion rate
168 increases at the beginning of the process, until it reaches a stable state (stationary regime) for all
169 given values of N_{diff} : 100, 250, 500 and 1000. This can be understood if account for the increase
170 of chemical roughness which is presented below and reflects the increase in the available number
171 of reacting sites. Also, the higher the value of P_{oxi} the more we dissolve oxide sites on the surface
172 limiting the passivation effect of the oxide leading to a faster corrosion rate. For $P_{\text{oxi}} = 0.01$ and
173 0.1, the difference is insignificant the dissolution of the oxide being for both values quantitative,
174 there is no passivation. The system reaches a limiting corrosion rate fixed only by the cathodic
175 reaction controled by the diffusion of DO.

176 *3.2. Stationary corrosion rate and diffusion*

177 In the previous paragraph, we have seen that the kinetic of the corrosion process varies with
178 the dissolution rate of the oxide P_{oxi} in a similar way for all values of the diffusion rate N_{diff} . In
179 the differents plots, it appears that the value of the corrosion rate decreases with increasing the
180 value of N_{diff} as expected as the diffusion time is constant and N_{diff} sets the corrosion time which
181 increases linearly with this parameter. In other words the corrosion rate is inversely proportional
182 to N_{diff} . This is verified in figure 4 where we plot for different values of P_{oxi} , the corrosion rate of
183 the stationary regime as a function of $\frac{1}{N_{\text{diff}}}$ where we observe a linear behavior for all values of
184 P_{oxi} . But we also note that the linear behaviour corresponds to different slopes, showing the effect
185 of P_{oxi} on the corrosion kinetics. This is also expected as low values of P_{oxi} imply passivation
186 therefore lower corrosion kinetics. Again, the cases $P_{\text{oxi}} = 0.01$ and 0.1 corresponding to high
187 oxide dissolution exhibit no passivation and cathodic control from *DO* diffusion.

188 *3.3. Chemical roughness*

189 During the corrosion process, the reactive surface in contact with the solution evolves with
190 the surface roughness. This roughness is due to both: corroded sites and sites protected by
191 passivation preventing corrosion. Both type of sites being stochastically distributed on the
192 surface contribute to an inhomogeneous corrosion of the surface. In figure 5, we note that

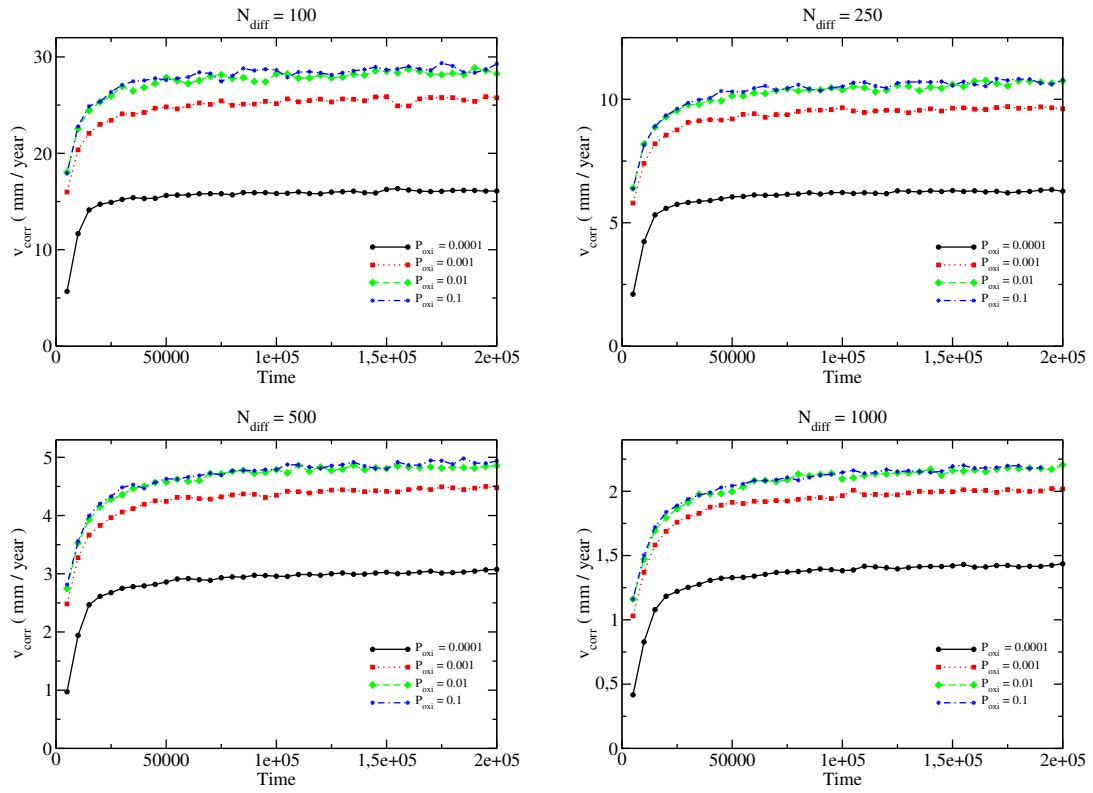


Figure 3: Corrosion rate for $N_{\text{diff}} = 100, 250, 500$ and 1000 and different values of P_{oxi} .

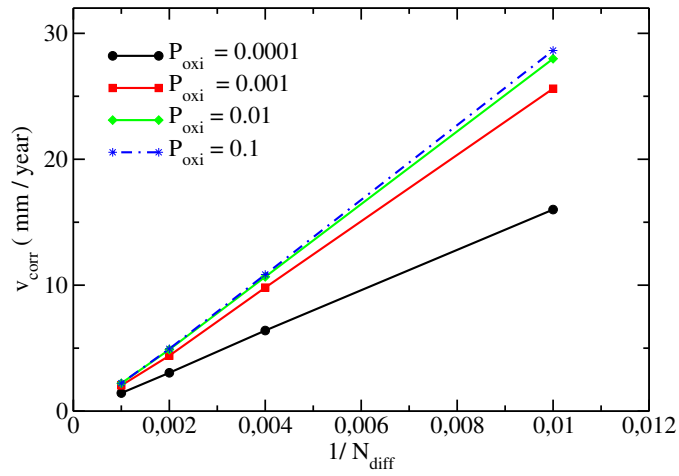


Figure 4: Corrosion rate as a function of $1/N_{\text{diff}}$ and different values of P_{oxi} .

193 this roughness σ_{chem} follows the same evolution than the corrosion rate as a function of time
 194 although the magnitude of the change is different. There is a transition to a steady state for
 times comparable to those of the corrosion rate. Note that the stationary value of the roughness

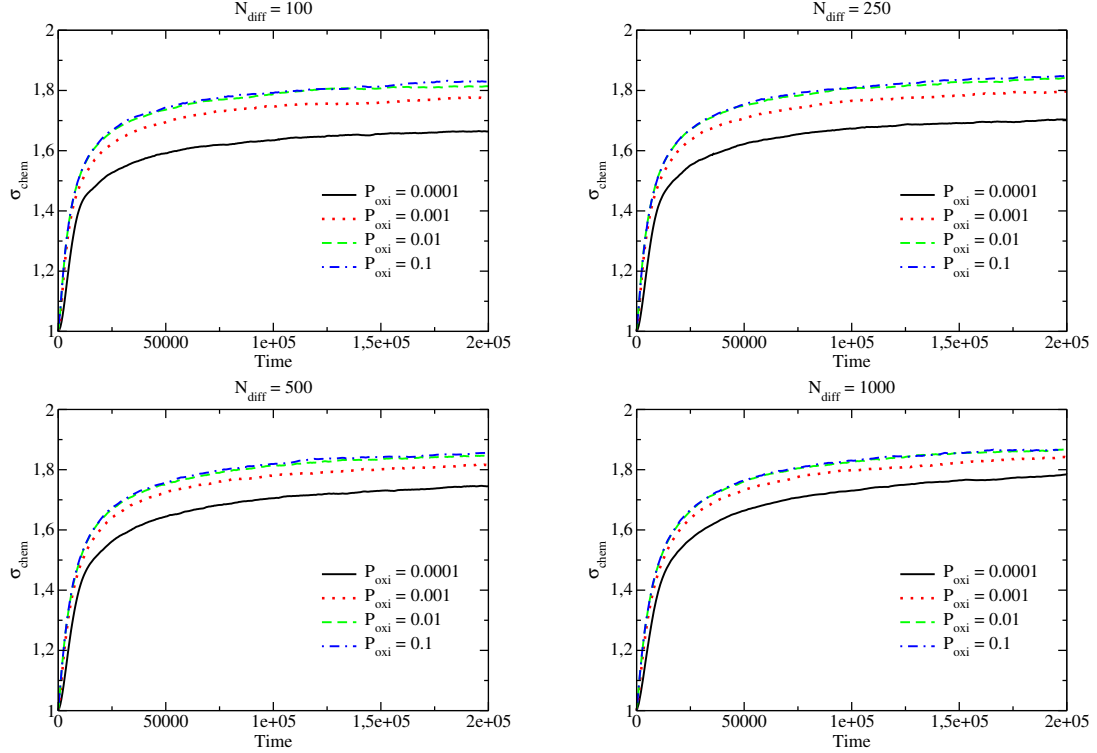


Figure 5: Chemical surface roughness σ_{chem} with $N_{diff} = 100, 250, 500$ and 1000 and different values de P_{oxi} .

195
 196 is weakly influenced by the diffusion time step N_{diff} , so it has a small dependence to the corrosion
 197 rate. Whereas increasing the probability of dissolution of the oxide P_{oxi} , the chemical roughness
 198 is slightly increased. Nonetheless, both effects remain relatively weak and in all cases there is an
 199 increase in number of reacting sites which can be correlated to an increase in corrosion. In the
 200 absence of passivation $P_{oxi} = 0.01$ and 0.1 , the roughness reaches a limit as shown before for the
 201 corrosion rate.

202 3.4. Passivation

203 During the simulation, at each time step the number of anodic and cathodic sites are recorded.
 204 From Table 1, we recall that anodic reactions can occur only on the metal sites whereas cathodic
 205 reactions can take place on both the metal and the oxide sites. The difference between cathodic

206 and anodic sites is then equal to n_{ox} the number of oxide sites on the surface and provides
 207 information on the passivation state of the surface.

208 The evolution of n_{ox} is presented first in plots at fixed N_{diff} and different values of P_{oxi} , then
 at fixed P_{oxi} for different values of N_{diff} . Figure 6 shows the evolution of the number of oxide

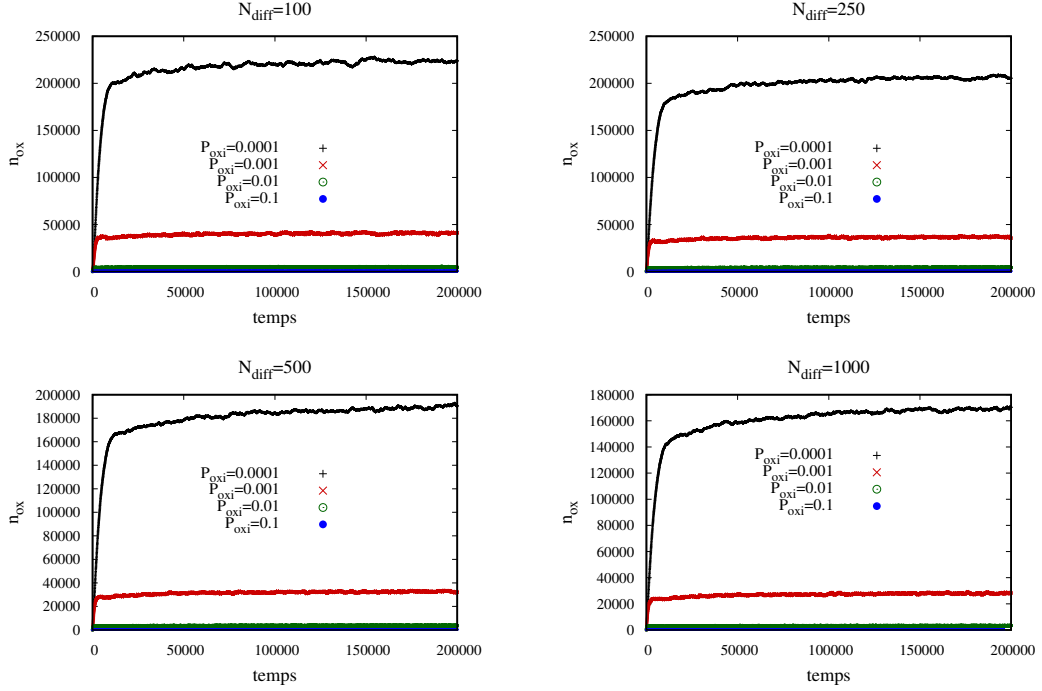


Figure 6: Evolution of oxide number for $N_{\text{diff}} = 100, 250, 500$ and 1000 and different values of P_{oxi} indicated at each plot

209

210 sites for fixed values of N_{diff} and different values $P_{\text{oxi}} = 0.0001, 0.001, 0.01$ and 0.1 . As expected
 211 the dissolution probability P_{oxi} of the oxide has a direct strong effect on n_{ox} . The higher the
 212 dissolution rate, the fewer the number of oxides on the surface. Figure 7 shows the evolution of
 213 the number of oxide sites for fixed values of P_{oxi} and different values of $N_{\text{diff}} = 100, 250, 500$ and
 214 1000 . For instance for $P_{\text{oxi}} = 0.0001$ and $N_{\text{diff}} = 100$, there are $\approx 2.25 \cdot 10^5$ oxide sites formed on
 215 the metal which represents a coverage ratio of about 22% with respect the planar surface. For
 216 a variation of an order of magnitude of $N_{\text{diff}} = 1000$, the number of oxides in stationary regime
 217 varies only of 25%, the effect is more limited. For all values of P_{oxi} presented, the variation is
 218 less than 50%. For $P_{\text{oxi}} = 0.01$ and 0.1 , when dissolution is quantitative, there are respectively
 219 only a few thousand and a few hundred sites of oxides negligible compared to the 10^6 sites on the

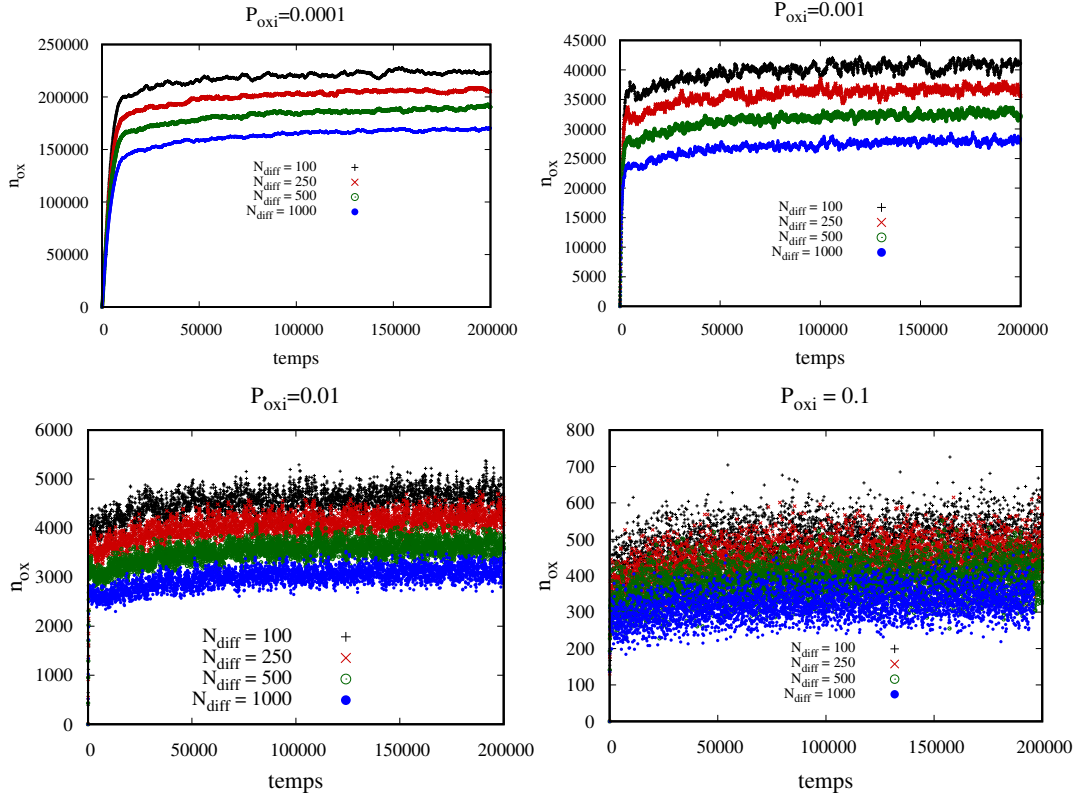


Figure 7: Number of oxide sites for $P_{\text{oxi}} = 0.0001, 0.001, 0.01$ and 0.1 and different values of N_{diff} indicated at each plot

220 surface. Typically 500 sites correspond to a coverage rate of 0.05 %, so the surface can hardly be
 221 considered passivated. The fluctuation of this number are in this case large.

Second, we present the stationary values of n_{ox} as a function of the parameters N_{diff} and P_{oxi} . Figure 8, we plot the stationary value of n_{ox} as a function of N_{diff} for different values P_{oxi} . A low dependence of the number of oxides with N_{diff} is noted in contrast to the effect of P_{oxi} which is clearly visible in figure 9. We consider on the plots that a coverage of less than 1 % corresponds to a no passivation regime. Figure 9 shows in a log – log scale, the P_{oxi} dependence for different N_{diff} values. In this representation, we observe an almost a linear behavior with P_{oxi} . The linear fit of $\log(n_{\text{ox}})$ with the function $f(x) = a_1 x + a_2$ is shown in Table 2. The standard error on the coefficients is around 3 – 4 % for a_1 and 5 % for a_2 . As a first approximation, we observe that a_1 is close to -1 , which corresponds to a behavior in inverse of the value of P_{oxi} . This behavior can be understood from a simple model. In the stationary state, we have a balance between production of oxide sites that we note δn_{ox} and their dissolution with a kinetic proportional to

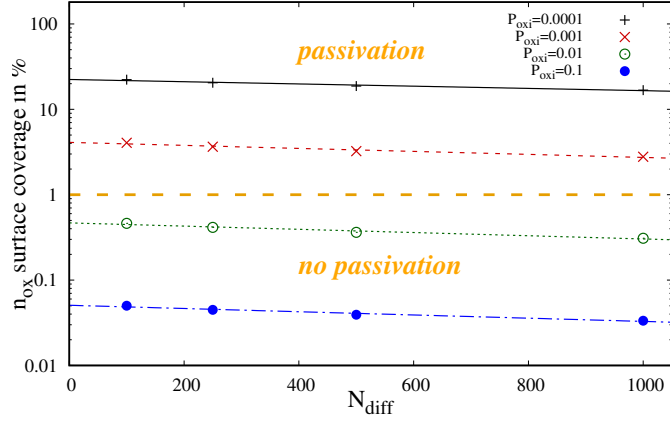


Figure 8: Coverage of the surface with oxide sites in % in stationary regime as a function of N_{diff} for different values of P_{oxi} . Orange dotted line separates passivated (above) and non passivated regimes (below).

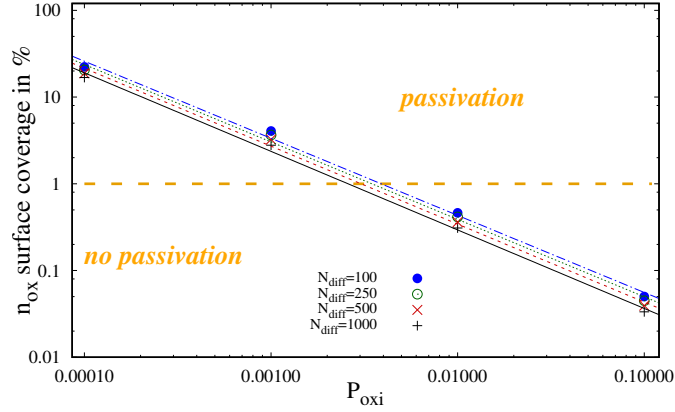


Figure 9: Coverage of the surface with oxide sites in % in stationary regime in a function of P_{oxi} for different values of N_{diff} . Orange dotted line separates passivated (above) and non passivated regimes (below).

their number n_{ox} and their probability of dissolution P_{oxi} . We recall that we study the effect of the dissolution parameter only in neutral medium due to slow corrosion. Always as a first approximation, we can assume that P_{oxi} parameter does not directly affect the corrosion thus δn_{ox} is independent of this parameter in this approximation. So, in the stationary state, we have an equilibrium between production δn_{ox} and dissolution $n_{\text{ox}}P_{\text{oxi}}$ of oxide sites which gives the relation

$$n_{\text{ox}} \approx \frac{\delta n_{\text{ox}}}{P_{\text{oxi}}} \quad (7)$$

222 This justifies the inverse dependence of n_{ox} with P_{oxi} . In reality, for the different values of N_{diff} , on

Table 2: Fits for the function $f(x)$ function corresponding to figure 9.

N_{diff}	a_1	error	a_2	error
1000	-0.90575	3.4%	1.6566	5.2%
500	-0.89865	3.8%	1.7377	5.4%
250	-0.89260	4.1%	1.8046	5.5%
100	-0.88875	4.3%	1.8584	5.6%

223 average coefficient a_1 is closer to -0.89 . This is so because the amount of oxide sites produced
 224 in the stationary state is not independent of P_{oxi} . Oxide sites are produced at metal reactive
 225 sites, the number of these sites depends on chemical roughness, on the dissolution rate of oxide
 226 sites therefore depends partly on the parameters P_{oxi} and N_{diff} . For small P_{oxi} , the number of
 227 oxide sites is larger on the surface, therefore the number of reactive sites is lower, which produce
 228 a smaller number of oxide sites δn_{ox} . In contrast, in the case of a fast dissolution, δn_{ox} increases
 229 as a function of P_{oxi} . Assuming that it can be written as a law of power, by putting such an
 230 expression in equation 7, we would obtain a lower exponent in absolute value of -1 .

231 3.5. Oxygen concentration Effect

232 Previous studies on the corrosion of iron showed that corrosion is faster with increasing
 233 DO concentration [28]. However, the iron release in solution decreases with increasing the DO
 234 concentration [29]. The combined effects of corrosion, oxide production and dissolution and
 235 roughness may lead to complicated effects. In this part, we study the effect of the oxygen
 236 concentration on the kinetics of the corrosion process. An important point, in this paper, is to
 237 show that the limited flux of DO reaching the metal surface induces a slow corrosion rate due
 238 to a cathodic control of the corrosion. Corrosion rates for three oxygen concentrations will be
 239 presented. They do not correspond precisely to real systems because in normal pressure and
 240 temperature DO is already saturated for a few ppm . Such concentrations could be reached at
 241 higher pressures and temperatures like supercritical systems. The solubility of oxygen changes by
 242 4 orders of magnitude in supercritical water at $500^\circ C$ in [30, 31]. But we should also reconsider
 243 the values of other parameters such as diffusion coefficients. In [32], Xiao Ji et al., using molecular
 244 dynamic simulation, calculated the diffusion coefficient of oxygen, nitrogen and sodium chloride
 245 in supercritical water. They demonstrated that the diffusion coefficient of oxygen increases
 246 with the temperature. X. Zhao et al. used molecular dynamic simulation to calculate diffusion
 247 coefficient of O_2 [33] and water [34], at $300 K$, $1 atm$ and in supercritical conditions. Respectively

248 their diffusion coefficients at normal conditions are equal to $2.0 \cdot 10^{-5} \text{cm}^2/\text{s}$ and $2.1 \cdot 10^{-5} \text{cm}^2/\text{s}$.
 249 Whereas in supercritical conditions, they predict $811.2 \cdot 10^{-5} \text{cm}^2/\text{s}$ at 973K and 250atm for
 250 oxygen and $741.9 \cdot 10^{-5} \text{m}^2/\text{s}$ for water.

251 However a comparison with such systems is made difficult by the fact that besides *DO* con-
 252 centration other parameters like diffusion coefficients also change. In the following, we consider
 253 three different *DO* concentrations assuming to simplify that all other parameters, like diffusion
 254 coefficients, remain identical. The aim is to focus on *DO* effects on corrosion only.

255 We present in figure 10, snapshots of the surface for $P_{\text{oxi}} = 0.0001$ and we choose the value
 of $N_{\text{diff}} = 250$. Snapshots for other values of N_{diff} are qualitatively similar. We see that with

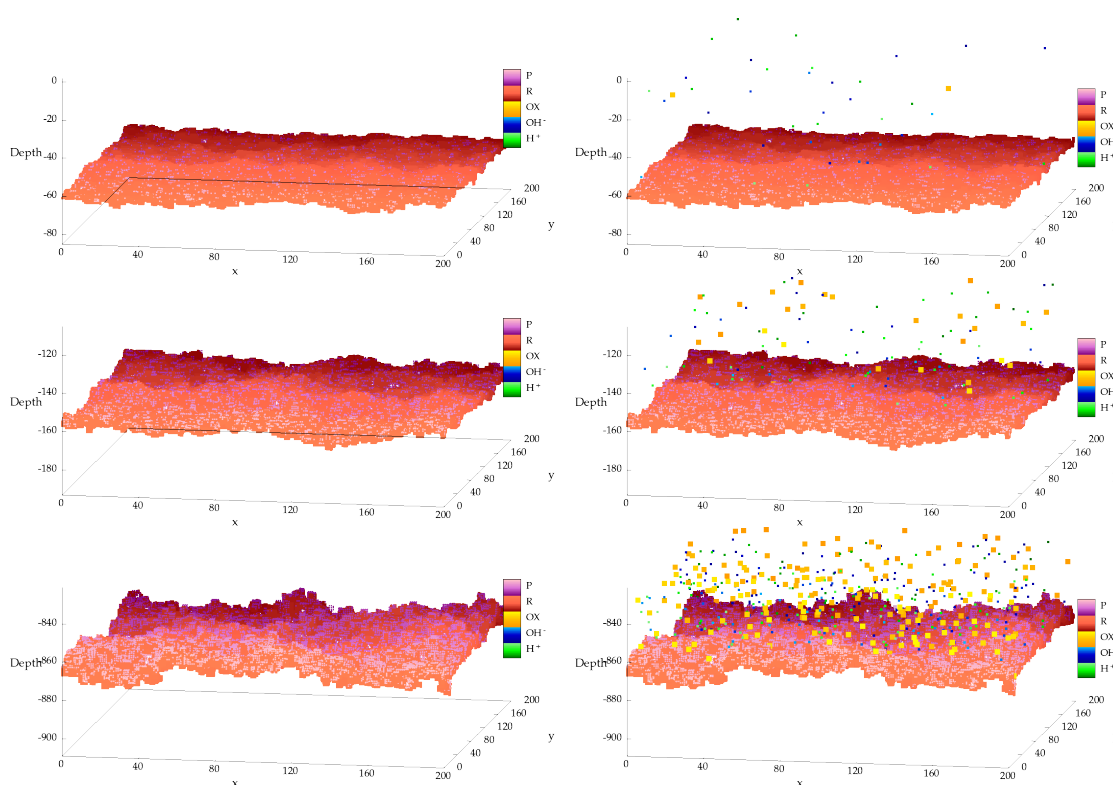


Figure 10: Corroded metallic surface, lines correspond to different *DO* concentration, from the top to the bottom: $c_{\text{O}_2} = 2 \cdot 10^{-6}, 2 \cdot 10^{-5}, 2 \cdot 10^{-4}$ number of sites of the last plan that remain constant ($2 \cdot 10^{-6}$ sites corresponds to 6ppm of *DO* (*OX* on the figure)). The left column only shows the metallic surface with *R* and *P* sites, the right column also *DO*, H^+ and OH^- sites.

256

257 the increase in the number of *DO* in solution, there is also an increase in the number of H^+
 258 and OH^- sites and an increase in the surface roughness. This relates to the fact that when

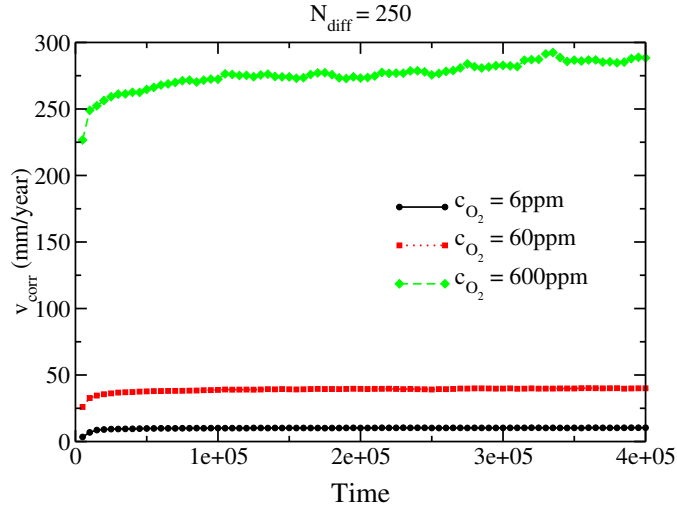


Figure 11: Corrosion rate for $N_{\text{diff}} = 250$, $P_{\text{oxi}} = 0.0001$ and different concentrations of oxygen.

259 we increase the oxygen concentration, we increase the number of electrochemical reactions with
 260 production of H^+ and OH^- ions. Also, with fixed P_{oxi} parameter, the number of oxide sites
 261 on the surface increases with DO in solution. Since the process is stochastic the formed oxide
 262 number are randomly distributed on the metallic surface, corrosion can occur only between the
 263 passivated sites contributing to an increase in surface roughness.

264 Figure 11 shows the evolution of the corrosion rate for given values $N_{\text{diff}} = 250$ and $P_{\text{oxi}} =$
 265 0.0001 and different values of the oxygen concentration. We notice that the kinetic of the
 266 stationary state varies significantly with the oxygen concentration. For instance for c_{O_2} from
 267 6ppm to 60ppm the corrosion rate is multiplied by 5. The precise dependence will be detailed
 268 below.

269 Figure 12 shows the corrosion rate of the stationary regime for $N_{\text{diff}} = 250$ and for the values
 270 $P_{\text{oxi}} = 0.0001, 0.001, 0.01$ and 0.1 as a function of the oxygen concentration in log – log scale. We
 271 can see that we have approximately a scaling law with the concentration of oxygen, especially
 272 for large values of P_{oxi} . If we adjust the log – log scale with the linear function $f(x) = b_1 x + b_2$
 273 we obtain results in table 3 for the coefficients b_1 and b_2 for the different values of P_{oxi} . We can
 274 see that the regression is better for large values of P_{oxi} when the dissolution of the oxide leads
 275 to a few passivated regions of the metallic surface.

276 For small dissolution rate (small P_{oxi}), the oxide remains stable on the surface and thus
 277 protects the metal and slows its corrosion rate, which is visible of the corrosion rate figure 12. As

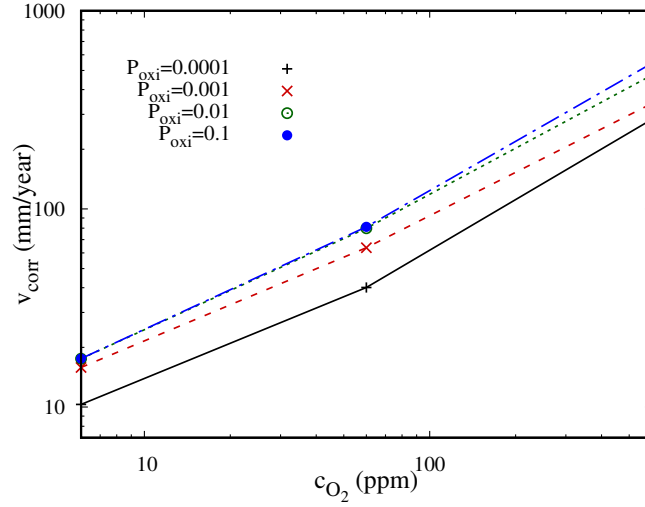


Figure 12: Corrosion rate in stationary regime for different values of $P_{\text{oxi}} = 0.0001, 0.001, 0.01$ and 0.1 in a function of oxygen concentration. Points corresponds to the adjustment of straight lines in log – log scale.

Table 3: Parameters b_1 and b_2 for $f(x)$ to fit the corrosion rates of 12.

P_{oxi}	b_1	error	b_2	error
0.0001	0.71926	10%	5.069	7%
0.001	0.66584	5.4%	4,974	3.4%
0.01	0.71560	4.6%	5,303	3.0%
0.1	0.74529	6.2%	5.465	4.0%

278 mentionned earlier, the effect is negligible in the case of $P_{\text{oxi}} = 0.01$ and 0.1 , for which there is a
 279 strong dissolution, the behavior is almost identical for small concentrations $c[\text{O}_2] = 2.10^{-6}$ and
 280 2.10^{-5} . Since the amount of DO is low, few oxide sites are produced and for these two values of
 281 P_{oxi} , they are immediately dissolved. In the case of $c[\text{O}_2] = 2.10^{-4}$, there is a slight difference
 282 because the oxide production starts to be quantitative.

283 It can be seen that the corrosion rate depends on the concentration of oxygen. But the
 284 behavior is not linear with the oxygen concentration, it increases more slowly with a weaker
 285 exponent between 0.66 and 0.74 . The corrosion rate with cathodic control from DO is modified
 286 due to the formation of the oxide. The corrosion rate is slowed down due to passivation. This
 287 effect increases with the concentration of DO . For a given P_{oxi} , the dissolution rate is fixed, but
 288 at the same time a larger DO concentration increases the production rate of oxides.

289 4. Comparison with experimental kinetics

290 In this Section, we compare the results of the model to experimentally measured weight loss
291 of Fe_3O_4 in water in 50°C in experiences performed by D.C. Smith and B. McEnaney in [22].
292 For the weight loss and 4 ppm of DO at 50°C , they found a corrosion rate around $1.1\text{mm}/\text{year}$.
293 In previous sections, we have shown how it is possible to model small oxygen concentrations like
294 6 ppm and at the same time account for stoichiometric reactions. Here we aim for approximate
295 comparison with experimental results. For computational reasons, to avoid fractional number of
296 lattice sites in the last plane, we have made the calculations with a DO concentration of 6 ppm.
297 In the future a fractional number of sites can be considered by introducing a probability of
298 having 1 or 2 DO sites on the last plane. However, this solution has been ruled out here because
299 of lengthy simulation times. With 6 ppm of DO , diffusion step $N_{\text{diff}} = 1000$ and a dissolution
300 probability in neutral solution $P_{\text{oxi}} = 0.001$ our simulations predicts a corrosion rate around
301 $2.04\text{mm}/\text{year}$. For this value of $P_{\text{oxi}} = 0.001$, the coverage corresponds approximately to 2.6%,
302 this value is consistent with the fact that iron does not strongly passivate. If we linearly rescale
303 the 6 ppm concentration results for 4 ppm concentration, we would obtain a $1.36\text{mm}/\text{year}$ which
304 is comparable to the $1.1\text{mm}/\text{year}$ value measured experimentally although higher. A lower value
305 of current could mean a lower value of P_{oxi} . Another hypothesis is that we have neglected the
306 Pilling Bedworth factor [35, 36] accounting for the fact that the oxide has a larger molar volume
307 than the metal. The efficiency of the oxide to passivate the surface would then be greater. This
308 effect is similar to a smaller value of P_{oxi} which also leads to a smaller current. For simplicity,
309 this correction has not been accounted for in this work as simulation for one set of parameters are
310 already long but will be considered in the future. Finally, note that in the absence of roughness
311 the corrosion rate would be $0.75\text{mm}/\text{year}$ for a flat surface. This is smaller than the experimental
312 value, which seems to confirm the role of roughness.

313 **5. Conclusion**

314 In this paper, we investigate a cellular automata model for aqueous corrosion accounting for
315 spatially separate and balanced anodic and cathodic half reactions. In comparison to previous
316 similar models, we account here for a cathodic reaction with dissolved oxygen. Cathodic control
317 of corrosion is shown in relation with the flux of dissolved oxygen reaching the metallic surface.
318 To our knowledge this is the first model providing an explicit mechanism accounting for this
319 process. For low DO concentration, whether there is or not passivation, we remain in cathodic
320 control regime determined by DO diffusion. On the contrary, for higher DO concentration there
321 is a stronger effect of the passive layer on the kinetics.

322 To reach quantitative results, we have shown how to compel both stoichiometric corrosion
323 reactions and small dissolved oxygen concentrations as those found in aqueous solutions within
324 in the framework of a cellular automata approach. The scarcity of corrosion events requires long
325 simulation times and intensive use of computational resources which have been implemented
326 in parallel GPU simulations. Results of the model are comparable to experimental results and
327 can be improved in the future by avoiding some approximations introduced for computational
328 reasons.

329 The study shows the important role of the surface roughness, in relation to stochastic pas-
330 sivation on the metallic surface, on corrosion kinetics. This justifies the choice for stochastic
331 cellular automata modelling in contrast to continuous deterministic models like finite element
332 approaches [37, 38, 39, 40]. Different scaling laws have been obtained demonstrating the role of
333 passivation on corrosion kinetics, both from a direct passivation effect of the surface or through
334 a modification of the surface roughness.

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340 **Data availability statement**

341 The data that support the findings of this study are available from the corresponding author
342 upon reasonable request

343 **References**

- 344 [1] G. Jacobson. International measures of prevention, application, and economics of corrosion
345 technologies study. <http://impact.nace.org/economic-impact.aspx>, 2016.
- 346 [2] Iso 8044:2015, corrosion des mtaux et alliages. [https://www.iso.org/obp/ui/#iso:std:iso:8044:ed-](https://www.iso.org/obp/ui/#iso:std:iso:8044:ed-4:v1:en)
347 [4:v1:en](https://www.iso.org/obp/ui/#iso:std:iso:8044:ed-4:v1:en), 2015.
- 348 [3] F. Moulinier. Combien coûte la corrosion ? *TSM*, 7/8:26–38, 2010.
- 349 [4] ASM International. Handbook Committee. *ASM Handbook*. Number v. 13, pt. 2 in ASM
350 Handbook. ASM International, 1990.
- 351 [5] A. Ismail and NH. Adan. Effect of oxygen concentration on corrosion rate of carbon steel
352 in seawater. *American Journal of Engineering Research*, 3(1):64–67, 2014.
- 353 [6] N. Sato. Some concepts of corrosion fundamentals. *Corrosion science*, 27(5):421–433, 1987.
- 354 [7] R. Walter, M. Bobby Kannan, and M Bobby. Influence of surface roughness on the corrosion
355 behaviour of magnesium alloy. *Materials & Design*, 32(4):2350–2354, 2011.
- 356 [8] T. Hong and M. Nagumo. Effect of surface roughness on early stages of pitting corrosion of
357 type 301 stainless steel. *Corrosion science*, 39(9):1665–1672, 1997.
- 358 [9] Y. Zuo, H. Wang, and J. Xiong. The aspect ratio of surface grooves and metastable pitting
359 of stainless steel. *Corrosion Science*, 44(1):25–35, 2002.
- 360 [10] W. Li and DY. Li. Influence of surface morphology on corrosion and electronic behavior.
361 *Acta materialia*, 54(2):445–452, 2006.
- 362 [11] M. Cabrini, A. Cigada, G. Rondell, and B. Vicentini. Effect of different surface finishing and
363 of hydroxyapatite coatings on passive and corrosion current of Ti6Al4V alloy in simulated
364 physiological solution. *Biomaterials*, 18(11):783–787, 1997.
- 365 [12] R. B. Alvarez, Holly J. Martin, MF. Horstemeyer, Mei.Q. Chandler, N. Williams, Paul T.
366 Wang, and A. Ruiz. Corrosion relationships as a function of time and surface roughness on
367 a structural AE44 magnesium alloy. *Corrosion Science*, 52(5):1635–1648, 2010.
- 368 [13] L. Abosrra, Ashraf Ashour, S. Mitchell, and Mansour Youseffi. Corrosion of mild steel and
369 316L austenitic stainless steel with different surface roughness in sodium chloride saline
370 solutions. In *EUROCORR 2009*, volume 65, pages 161–172, 06 2009.

- 371 [14] P. Meakin, T. Jøssang, and J. Feder. Simple passivation and depassivation model for pitting
372 corrosion. *Physical Review E*, 48(4):2906, 1993.
- 373 [15] C. F. Pérez-Brokate, D. Di Caprio, D. Féron, J. de Lamare, and A. Chaussé. Overview of
374 Cellular Automaton Models for Corrosion. In *Cellular Automata*, number 8751 in Lecture
375 Notes in Computer Science, pages 187–196. Springer International Publishing, January 2014.
- 376 [16] M. Zenkri, D. Di Caprio, C. F. Pérez-Brokate, D. Féron, J. de Lamare, A. Chaussé, ,
377 F. Larbi, and F. Raouafi. Contribution of cellular automata to the understanding of corrosion
378 phenomena. *Condens. Matt. Phys.*, 20:33802:1–13, 2017.
- 379 [17] C.F. Pérez-Brokate, D. di Caprio, D. Féron, J. de Lamare, and A. Chaussé. Three dimen-
380 sional discrete stochastic model of occluded corrosion cell. *Corrosion Science*, 111:230 – 241,
381 2016.
- 382 [18] C.F. Pérez-Brokate, D. di Caprio, D. Féron, J. de Lamare, and A. Chaussé. Probabilistic
383 cellular automata model of generalized corrosion, transition to localized corrosion. *Corrosion*
384 *Engineering, Science and Technology*, 52–51:186–193, 2017.
- 385 [19] C.F. Pérez-Brokate, D. di Caprio, D. Féron, J. de Lamare, and A. Chaussé. Pitting corrosion
386 modelling by means of a stochastic cellular automata-based model. *Corrosion Engineering,*
387 *Science and Technology*, 52(8):605–610, 2017.
- 388 [20] D. Stauffer and A. Aharony. *Introduction to percolation theory*. Taylor & Francis, London,
389 2nd edition, 1994.
- 390 [21] E. Schaschl and G.A. Marsh. The effect of dissolved oxygen on corrosion steel and on
391 current required for cathodic protection. *Corrosion*, 13(4):35–43, 1957.
- 392 [22] D.C. Smith and B. McEnaney. The influence of dissolved oxygen concentration in the
393 corrosion of grey cast iron in water at 50° C. *Corrosion Science*, 19:379–394, 1979.
- 394 [23] C.F. Pérez-Brokate, D. di Caprio, E. Mahé, D. Féron, and J. de Lamare. Cyclic voltam-
395 metry simulations with cellular automata. *Journal of Computational Science*, 11:269–278,
396 November 2015.
- 397 [24] R. T. Ferrell and D. M. Himmelblau. Diffusion coefficients of nitrogen and oxygen in water.
398 *Journal of Chemical & Engineering Data*, 12(1):111–115, 1967.

- 399 [25] G. Engelhardt, M. Urquidi-Macdonald, and D. D. Macdonald. A simplified method for
400 estimating corrosion cavity growth rates. *Corrosion Science*, 39(3):419–441, March 1997.
- 401 [26] D. di Caprio and J. Stafiej. Effect of low oxygen concentration on the oxidation behavior
402 of Ni-based alloys 625 and 825 in supercritical water. *Electrochimica Acta*, 54:3884–3890,
403 2010.
- 404 [27] D. di Caprio and J. Stafiej. Effect of low oxygen concentration on the oxidation behavior
405 of Ni-based alloys 625 and 825 in supercritical water. *Electrochimica Acta*, 56:3963–3968,
406 2011.
- 407 [28] G. Gedge. Corrosion of cast iron in potable water service. In *Proc. corrosion and related*
408 *aspects of materials for potable water supplies, proceedings of the institute of materials con-*
409 *ference*. London, UK, 1992.
- 410 [29] Laurie S McNeill and Marc Edwards. Iron pipe corrosion in distribution systems. *Journal-*
411 *American Water Works Association*, 93(7):88–100, 2001.
- 412 [30] X. Tang, S. Wang, L. Qian, Y. Li, Z. Lin, D. Xu, and Y Zhang. Corrosion behavior of nickel
413 base alloys, stainless steel and titanium alloy in supercritical water containing chloride,
414 phosphate and oxygen. *Chemical Engineering Research and Design*, 100:530–541, 2015.
- 415 [31] J. Yang, S. Wang, X. Tang, Y. Wang, and Y. Li. Effect of low oxygen concentration on the
416 oxidation behavior of Ni-based alloys 625 and 825 in supercritical water. *The Journal of*
417 *Supercritical Fluids*, 131:1–10, 2018.
- 418 [32] Xiao Ji, Lu Jiu-Fang, Chen Jian, and Li Yi-Gui. Molecular dynamics simulation of diffusion
419 coefficients of oxygen, nitrogen and sodium chloride in supercritical water. *Chinese Physics*
420 *Letters*, 18(7):847, 2001.
- 421 [33] Xiao Zhao, Yuanxue Liu, Jian Zou, Qiuxia Wang, Hao Liu, Hua Zhang, and Hui Jin.
422 Determining diffusion coefficients of oxygen in supercritical water with molecular dynamics.
423 *Thermal Science*, 23:781–787, 2019.
- 424 [34] Xiao Zhao and Hui Jin. Investigation of hydrogen diffusion in supercritical water: A molec-
425 ular dynamics simulation study. *International Journal of Heat and Mass Transfer*, 133:718–
426 728, 2019.

- 427 [35] D. Di Caprio, C. Vautrin-Ul, J. Stafiej, J. Saunier, A. Chaussé, D. Féron, and J.P. Badiali.
428 Morphology of corroded surfaces: Contribution of cellular automaton modelling. *Corrosion*
429 *Science*, 53(1):418–425, 2011.
- 430 [36] C. Xu and W. Gao. Pilling-bedworth ratio for oxidation of alloys. *Material Research*
431 *Innovations*, 3(4):231–235, 2000.
- 432 [37] D. R. Gunasegaram, M. S. Venkatraman, and I. S. Cole. Towards multiscale modelling of
433 localised corrosion. *International Materials Reviews*, 59(2):84–114, 2014.
- 434 [38] Digby D. Macdonald. The history of the Point Defect Model for the passive state: A brief
435 review of film growth aspects. *Electrochimica Acta*, 56(4):1761–1772, January 2011.
- 436 [39] F. Thébault, B. Vuillemin, R. Oltra, C. Allely, and K. Ogle. Modeling bimetallic corrosion
437 under thin electrolyte films. *Corrosion Science*, 53(1):201 – 207, 2011.
- 438 [40] F. Thébault, B. Vuillemin, R. Oltra, C. Allely, and K. Ogle. Reliability of numerical models
439 for simulating galvanic corrosion processes. *Electrochimica Acta*, 82(Supplement C):349 –
440 355, 2012. Electrochemical frontiers in global environment and energy.