Polish J. Chem., **78**, 1795–1810 (2004)

Simulations of Corrosion Processes with Spontaneous Separation of Cathodic and Anodic Reaction Zones*

by C. Vautrin-Ul[1], A. Chaussé[1], J. Stafiej[2] and J.P. Badiali[3]**

[1]*Laboratoire Analyse et Environnement, UMR 8587, Université d'Evry Val d'Essonne, Bd F. Mitterrand, 91025 Evry, France*
[2]*Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland*
[3]*Laboratoire d'Electrochimie et de Chimie Analytique, ENSCP et l'Université P. et M. Curie, UMR 7575, 4. Place Jussieu, 75005 Paris, France*

(Received March 10th, 2004; revised manuscript July 15th, 2004)

We present a simple cellular automata model for mimicking corrosion processes of corrodable materials covered by an ideal insulating and protective layer. A small defect in this layer brings the corrodable material into the contact with the outer environment and initiates the formation of a cavity. We study the evolution of the cavity in terms of time dependence of its size, morphology and chemical composition as determined by the corrosion-passivation phenomena at the corrosion front and diffusion within the cavity. We mimic the diffusion of reaction products as a random walk and we can control the diffusion rate with respect to that of corrosion. If the diffusion is very fast the cavity can be assimilated to a half-circle filled up by a neutral solution. When the diffusion rate decreases the cavity shape becomes more and more irregular and the solution contains large domains essentially acidic or basic comparable to cavity size. A quantitative analysis of simulations also reveals the existence of an incubation time during which the corrosion is not clearly visible. If the diffusion rate is low, the stochastic processes that we have considered lead to an unpredictable shape for the cavity and to a large dispersion of the incubation times. Then we clearly observe spontaneous formation of the cathodic and anodic reaction zones at the corrosion front. We discuss these results in a simple case.

Key words: corrosion modeling, stochastic lattice gas automata, diffusion-reaction systems

Corrosion processes are of considerable practical and economical interest due to the widespread use of metallic materials [1]. In contact with a given environment most of these materials are highly unstable. They may reach a relative stability due to the formation of a kinetic barrier of passivation at their surface. Passivation is a complicated interfacial phenomenon and progresses in corrosion science have to combine the investigations obtained in several research domains such as, for instance, electrochemistry and material engineering. In parallel to the need of multidisciplinary grounds corrosion processes deal with wide ranges of time and length scales [2]. An-

---

* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.
** To whom correspondence should be directed.

other difficulty comes from the fact that corrosion often takes place in a natural environment which is ill defined with respect to crucial physicochemical characteristics such as chemical composition and physical state of the constituents.

Modeling of corrosion phenomena is of particular interest for the problem of containers to store nuclear waste or hardly degradeable toxic substances when long term predictions and high reliability are needed [3]. Then we cannot rely on simplified extrapolations of the experimental data measured in a limited time scale. Such extrapolations should take into account the nonlinearity and stochastic character of the corrosion processes. In this paper we intend to get some insights concerning the effects of diffusion and spontaneous separation of anodic and cathodic reaction zones on the development of the corrosion front in the cavity initiated by a small defect of the ideal protective layer.

At a mesoscopic scale on which we focus here one of the major difficulties concerns the role and the description of stochastic processes involved in corrosion mechanisms. These processes originate the roughness of the material-environment interface and, more dramatically, they may initiate a pitting corrosion [4]. Keeping in mind these phenomena, the use of deterministic partial differential equations seems difficult or even hopeless. However this stochastic character enters naturally in the framework of the lattice gas cellular automata models [5,6] – noted as CA models hereafter. There have already been several attempts to employ CA models in the domain of corrosion [5–8]. We have used such models for describing the growth and morphology of layers formed on corroding surfaces [9,10].

In this paper we introduce a simple CA model to describe what happens when anodic and cathodic reactions may occur at spatially separated locations of the corrosion front. The implicit role of the insulating layer is to force electroneutrality. It follows that cathodic and anodic reaction events have to occur at the same time. In addition to these reaction processes, this model takes into account diffusion and recombination of the corrosion products. Note that simple basic facts associated for instance with diffusion-reactions processes as those considered here, may generate very complicated behaviors [11–13]. In some cases it has been checked that CA models work quite well [12].

In what follows, we do not consider a specific system *e.g.* a given type of steel in contact with a particular electrolyte solution. Rather than that we try to analyze the consequences on the structure of the metal/environment interface of a few number of basic processes which are general and common to a wide class of interfaces. In other words, we hope that the processes that we have retained in the model are sufficient to reproduce the gross features of general observed behaviors. In order to do that we start on common experimental observations performed on iron, steel, aluminum and other materials [6,14–18]. These observations can be summarized as follows. Once depassivated at a spot on its surface the material can be subject to anodic dissolution. Metal cations produced in this process undergo hydrolysis leading to acidification and anions from the electrolyte of the outer environment migrate close to the dissolving surface to compensate the charge of dissolved cations. Thus the solution produced by the anodic dissolution of the metal is characterized by a low pH and enriched in aggressive anions. Such a composition enhances depassivation and prevents repassivation promoting a further dissolution of the anodic material. In contrast, the water decomposition in the cathodic process leads to a basification of the solution next to the material surface. This is generally beneficial for the passive state of the surface.

In this paper we try to construct a very simple and general model based on these observations and investigate the consequences of this model for the development of the corrosion front initiated by a local damage of a protective layer. The layer is insulating and, in contrast to the pitting corrosion, both anodic and cathodic reactions must occur at the corrosion front delimiting the cavity and developed from a single damage of the insulating protective layer. However, the observed spontaneous spatial separation of anodic and cathodic reaction zones may be important for the pit nucleation mechanism on passivating metal surfaces in the closed circuit conditions. In the following Section we describe the model and then we present some first simulation results that are discussed in the last Section.

THE MODEL

In this Section we first present the model in terms of electrochemical and chemical reactions. Then we explain how we realize the model on a lattice and finally we give the rules of transformation introduced in the cellular automaton model.

2.1 Electrochemical and chemical reactions at the corroding surface. Let us put the phenomenology of the corrosion as briefly outlined in the Introduction in a form of chemical and electrochemical reactions. In acidic or neutral medium the depassivation of a metal surface permits its anodic dissolution. Associated with the hydrolysis of the cation we may describe this process by:

$$Me + H_2O + \ldots \rightarrow MeX_{aqu} + e^- + H^+ \qquad (1)$$

What we denote by MeX_{aqu} is a corrosion product the precise chemical nature of which is beyond the scope of our onsiderations. We assume that MeX_{aqu} is detached from the surface and therefore becomes a part of external environment. In contrast, in a basic environment, we have to consider that the following reaction path is likely to occur:

$$Me + OH^- \rightarrow MeOH_{solid} + e^- \qquad (2)$$

and yields a corrosion product $MeOH_{solid}$ which is adherent to the surface. To the anodic processes (1) and (2) we must associate a cathodic reaction. In acidic solution without oxygen the cathodic reaction can be written:

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2 \qquad (3)$$

while in a basic environment we have:

$$H_2O + e^- \rightarrow \tfrac{1}{2}H_2 + OH^- \qquad (4)$$

The two electrochemical reactions, anodic and cathodic, may occur in a close proximity or be spatially separated. In the first case, they are produced in the same chemical environment and we can combine the two electrochemical reactions to obtain the global reaction. Thus, in an acidic medium, from (1) and (3) we expect the global reaction:

$$Me + H_2O + \ldots \rightarrow MeX_{aqu} + \tfrac{1}{2}H_2 \tag{5}$$

while in a basic medium the combination of (2) and (4) leads to:

$$Me + H_2O \rightarrow MeOH_{solid} + \tfrac{1}{2}H_2 \tag{6}$$

The global reactions (5) and (6) do not change the acid or basic character of the solution in their vicinity.

In the second case, when the electrochemical reactions are spatially separated, oxidation and reduction can take place *a priori* in regions having a different acidity or basicity. However, in contrast with the reactions described by (5) and (6), spatially separated electrochemical reactions – noted hereafter as SSE reactions – change the acidity or the basicity of their environment. The cathodic reactions always increase the basicity of the medium; when (3) takes place we have a consumption of a proton and when (4) is realized the water decomposition leaves the hydroxyl ion in the solution. Obviously the anodic reactions always increase the acidity of their local environment by producing an H^+ as shown by (1) or by consuming an OH^- *via* (2).

In addition to electrochemical reactions we assume that the detachment of the corrosion product, $MeOH_{solid}$ from the metal surface is possible because it is well known that aggressive anions in the solution may destabilize the passive layer. The hydrolysis reaction catalyzed by these anions may be written in acidic medium as:

$$MeOH_{solid} + H^+ \rightarrow Me^+ + H_2O \tag{7}$$

To keep the model as simple as possible, we will not consider later these anions explicitly.

However, not only the SSE reactions change the acidic or basic character of the medium. The ions H^+ and OH^- injected into the solution move and we assume that the neutralizing process:

$$H^+ + OH^- \rightarrow H_2O \tag{8}$$

is possible when H^+ and OH^- happen to meet at the same position in space.

2.2 Lattice representation of the corroding system. To introduce a CA model representing the corrosion process considered above we have first to introduce a lattice. The state of the lattice is defined by the state of each lattice site and it is often convenient to speak about states of a lattice site as about chemical species occupying this site. At a mesoscopic scale the lattice sites do not have necessarily a unique chemical composition. To reduce a complicated system to a small number of most essential ingredients we take the number of different kind of sites as small as possible.

The lattice sites which represent the bulk corroding material are denoted M and we call them metal sites or M sites shortly. A metal site is never in contact with the corrosive environment. Located on the surface of the corroding material and exposed to this environment we define two types of metallic sites, R and P that mean reactive and passive sites respectively. Three types of sites denoted A, C and E exist in the environment. The site A (C) indicates that the environment at the position occupied by this site is more acid (basic) than in the original solution and E means that at this site position we have the composition of original solution.

2.3 Transformation rules for the system evolution. The evolution of sites on the lattice is given by a set of rules indicating how we transform the lattice configuration during one time step. However, due to the stochastic aspects of our CA model, the new configuration is not uniquely determined by the preceding one. Basing on the reactions described in Section 2.1 we construct our CA model as a combination of several stochastic processes.

The first one mimics the existence of SSE reactions represented by the equations (1)–(4). It consists of two sub-processes associated with the anodic (1), (2) and cathodic (3), (4) reactions. We have assumed that the two sub-processes are correlated in time – anodic dissolution of a piece of metal is necessarily accompanied by a simultaneous cathodic reaction and the sites where the two reactions occur have to belong to a surface of a single connected piece of material. The connectivity in terms of our lattice model means that there is a suite of nearest neighbor (nn) sites of the types M, P or R linking the sites where the anodic and cathodic reactions take place. Since the transformation of an R site *via* (1) or (2) depends on the state of the solution in its environment with a site R we associate the quantity, N_{nn}^{exc}, that determines the algebraic excess of A over C sites nearest neighbors of R. We may consider N_{nn}^{exc} as a rough estimation of the pH in the vicinity of the reactive site. If $N_{nn}^{exc} \geq 0$ we mimic (1) by:

$$R \rightarrow A \tag{9}$$

otherwise we write

$$R + C(nn) \rightarrow P + E(nn) \tag{10}$$

that represents (2). This last reaction appears when the R site selected at random for anodic reaction is in contact with a net basic solution ($N_{nn}^{exc} < 0$). Then the reactive site turns into a passive one and one C nearest neighbor of R is consumed.

In the present model we adopted the rule that any surface site, R or P, can mediate the cathodic processes with *a priori* equal probabilities. This is an oversimplification as this probability may depend on the state of the surface represented here by active (R) and passive (P) sites and their environment. Also the reaction mechanism may change accordingly. However, as marked in the Introduction we are interested in general features of the corrosion process rather than in a particular system and for this reason we adopt simplifications which facilitate the computations and reduce the number of parameters involved in the model. We represent (3) and (4) by:

$$S + A(nn) \rightarrow S + E(nn) \tag{11}$$

and

$$S + E(nn) \rightarrow S + C(nn) \tag{12}$$

respectively. Here S denotes a surface site (R or P) chosen at random and A(nn) or E(nn) are solution sites among the nearest neighbors of S. We adopt a simple exclusion rule. If the nearest neighbors of the surface site are neither E nor A it follows that the S site is blocked by nearest neighbors of C type and such an S site cannot mediate the cathodic process. Then we repeat the selection from among the remaining sites until a free site is found or until the list of connected surface sites is exhausted. If the cathodic reaction is impossible, the spatially separated anodic and cathodic reactions cannot be realized.

The second stochastic process appears when the two electrochemical reactions occur in a close vicinity. In acidic medium ($N_{nn}^{exc} > 0$) we replace (5) by:

$$R \rightarrow E \tag{13}$$

while for basic medium (6) becomes

$$R \rightarrow P \qquad (14)$$

The third stochastic process mimics the role of aggressive anions taken into account implicitly *via* (7). Here it is represented by:

$$P \rightarrow E \qquad (15)$$

that is only possible in an acidic medium.

Note that a surface site (R or P) is most often attached to M sites. Therefore the dissolution of a surface site puts these M sites in contact with the solution. We adopt the rule that they become R sites. Thus, the dissolution of a P site *via* (15) may create new R sites.

In addition to the previous three stochastic processes located at the surface we take into account stochastic processes related to the motion of C and A species and their possible neutralization (8). The C and A species perform a random walk over E sites according to the following rules. At a given time step each C and A try to jump from their initial position to a nearest neighbor position. These attempts are done in a random order and amount to a random selection of one of the nearest neighbors of the selected walker. The result of the attempted random step depends on the nearest neighbor. If it is an E site the walker is moved to it according to:

$$A_1 + E_2 \rightarrow E_1 + A_2 \qquad (16)$$

and

$$C_1 + E_2 \rightarrow E_1 + C_2 \qquad (17)$$

where subscripts “1" and ”2" denote the source and the target site for the random step. If the walker is an A site and it attempts to step on a C site both annihilate according to:

$$A_1 + C_2 \rightarrow E_1 + E_2 \qquad (18)$$

and *vice versa*:

$$C_1 + A_2 \rightarrow E_1 + E_2 \qquad (19)$$

In the other cases the configuration remains unchanged:

$$A_1 + X_2 \rightarrow A_1 + X_2 \qquad (20)$$

where $X \neq$ E nor C and:

$$C_1 + X_2 \rightarrow C_1 + X_2 \qquad (21)$$

where $X \neq$ E nor A.

2.4 Simulations. With the definitions of lattice states and transformation rules described above we can perform the simulations on a given type of lattice. Because of convenience and practical limitations with respect to simulation time and the size of the system we work on a two dimensional square lattice. The connectivity for the nearest neighbors and random walk is the Von Neumann or 4 – connectivity [12]. We have adopted a slightly different rule for the front connectivity. Two neighboring front sites are connected if they are both von Neumann nearest neighbors or they have an M site as a common von Neumann neighbor. This prevents the inconvenience of the von Neumann neighborhood that a connected M area could have a surface composed of disconnected pieces.

First considering the SSE reactions, we assume that they have an *a priori* probability, p_{sse}, to be realized. However, as we have already pointed out the *a posteriori* probability of this reaction may depend on the blocking of its cathodic part by the presence of C sites. Now we focus on the other kinds of site transformation introduced in Section 2.3. Thus, a P site can be only dissolved *via* (15). The probability of this process depends on the value of N_{nn}^{exc} in its neighborhood. Accordingly we introduce the following probability of dissolution P_{PE}

$$P_{PE} = 0 \ \text{ if } \ N_{nn}^{exc} < 0 \tag{22}$$

$$P_{PE} = p_{oxi} \text{ if } N_{nn}^{exc} = 0 \tag{23}$$

$$P_{PE} = 0.25\, N_{nn}^{exc} \text{ if } \ N_{nn}^{exc} > 0 \tag{24}$$

It follows that a P site is stable in a net basic solution while in a neutral environment there is a certain probability p_{oxi} that the P site gets dissolved. As we should like to imitate the functioning of the passive layer the value of p_{oxi} should be rather small but in actual simulations very low values are impractical because of long times before triggering of the corrosion process, slow evolution and handling the large number of small P islands detached from the corroding material. In an acidic medium we consider that P_{PE} can be large, at least 0.25 and enhanced linearly with N_{nn}^{exc}. For the R site we adopt a similar set of rules but an R site can be transformed into an E or a P site *via* (13) and (14):

$$P_{RE} = p_{cor2} N_{nn}^{exc} \ \text{ and } \ P_{RP} = 0 \ \text{ if } \ N_{nn}^{exc} > 0 \tag{25}$$

$$P_{RP} = p_{cor1} \qquad \text{and } \ P_{RE} = 0 \ \text{ if } \ N_{nn}^{exc} = 0 \tag{26}$$

$$P_{RP} = 1 \qquad \text{and } \ P_{RE} = 0 \ \text{ if } \ N_{nn}^{exc} < 0 \tag{27}$$

It follows that, in a net acidic solution, an R site cannot be converted into a P site but it may turn to an E site with a probability P_{RE} increasing with the strength of the acidity that we write: $P_{RE} = p_{cor2} N_{nn}^{exc}$. In a net basic solutions the probability P_{RP} to change a R into a P site is assumed to be 1, with this choice we mimic the fact that in contact with a basic environment a reactive site gets immediately passivated. In a neutral environment we assume that the passivation is less efficient and give to p_{cor1} a value a little bit smaller than 1.

Finally to regulate the diffusion rate with respect to corrosion rate in a simple way we introduce an integer number N_{diff}. It means that for each time step related to corrosion we perform N_{diff} steps of random walk assuming that the diffusion processes are faster than the corrosion ones.

Clearly, the above schemes and the values that we use for the set of probabilities are only qualitative and conceived on what is generally known or accepted about corrosion processes in some class of materials. The generic features of the corrosion process should not depend, however, on the detailed form of our assumptions.

The results presented in this paper have been obtained in a simulation box of size 1000×1000 sites. The initial configuration is a block of 998×998 M sites bordered by a frame of inert wall sites imitating a non-conductive protective layer. Two M sites at the positions (500, 999) and (501, 999) are then turned into R sites imitating a local damage of the protective layer and putting the M sites in contact with the environment. Then the rules of transformation that we have described determine the front evolution.

RESULTS AND DISCUSSION

In this paper we concentrate on the effects of diffusion and spatially separated anodic and cathodic reactions on the shape and composition of the cavity resulting from the corrosion processes. Therefore for all the simulations reported we select: $p_{oxi} = 0.001$, $p_{cor1} = 0.9$, $p_{cor2} = 0.02$. Concerning p_{sse}, we have retained two values $p_{sse} = 0.1$ or 0.2 and for each of them we increase the rate of diffusion by varying N_{diff} from 1 to 10^4.

Let us start to analyze the case $N_{diff} = 10^4$. In Figure 1a and 1b we have reported the snapshots corresponding to $p_{sse} = 0.1$ and 0.2 respectively. They are obtained at the final moment when the corrosion front reaches the boundary of the simulation box. Roughly the corrosion front appears as a half-circle. A more precise description reveals the existence of a roughness, which is more pronounced in Figure 1b than in Figure 1a. The snapshots also show that the corrosion front is almost totally covered with P sites and the number of R sites is restricted to a few units. The inspection of snapshots does not show the presence of A or C species, thus the solution is neutral. The diffusion appears as very fast in comparison with others processes and the mutual neutralization of A and C is very efficient. In a neutral medium, the SSE reaction is never blocked but effectively realized with the probability p_{sse}. Due to other processes an R site can be changed only into a P site with the probability p_{cor1} and a passive site can be changed into an E site with the probability p_{oxi}.

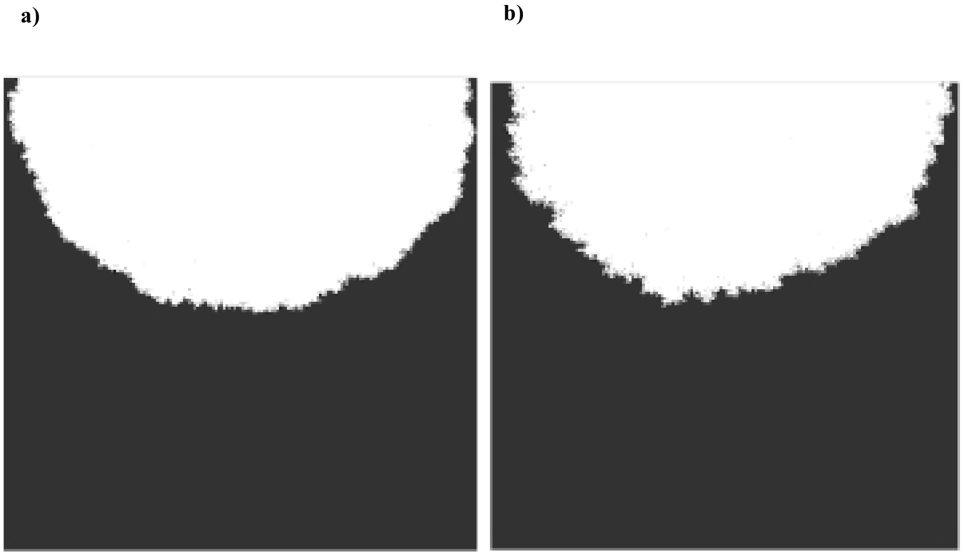

Figure 1. Snapshots obtained when the corrosion front reaches the border of the simulation box. The simulation parameters are: $p_{oxi} = 0.001$, $p_{cor1} = 0.9$, $p_{cor2} = 0.02$, $N_{diff} = 10^4$. In a) $p_{sse} = 0.1$ and the time step of the snapshot is $N_t = 154976$ while in b) $p_{sse} = 0.2$ and the time step is $N_t = 81044$. The gray scale is ascribed to the sites in the order of increasing brightness: P (black), M , R, C , A and E (white).

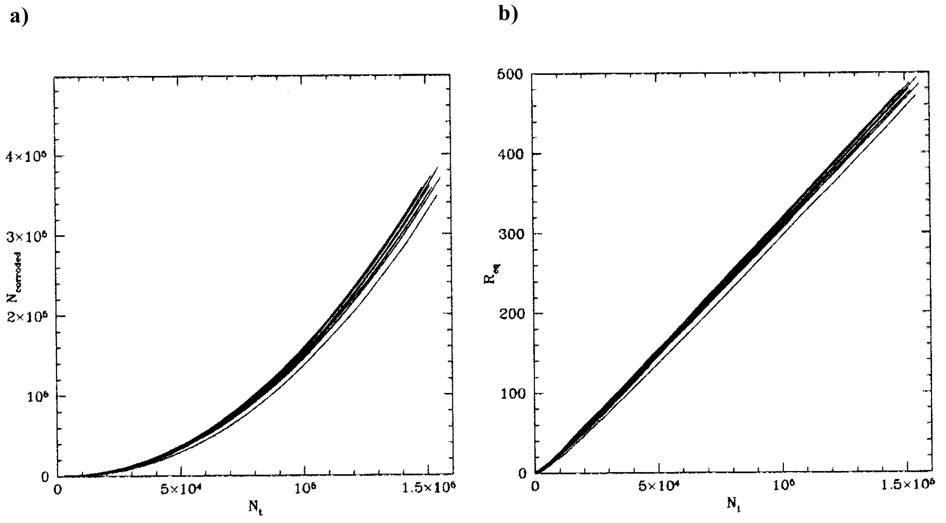

Figure 2. a) Number of corroded metal sites N_{corroded} and b) the equivalent radius of a half-circle $R_{eq} = (2N_{\text{corroded}}/\pi)^{1/2}$ *versus* N_t for 10 independent simulation runs with parameters corresponding to Figure 1a.

We have performed 10 independent simulations corresponding to the parameters of Figure 1a. In order to characterize the time evolution of the corrosion we present the number of destroyed sites, N_{corroded} as a function of the simulation time step N_t (Figure 2a). To N_{corroded} we associate the radius, R_{eq}, of the equivalent half-circle defined according to $R_{eq} = (2N_{\text{corroded}}/\pi\}^{1/2}$. In Figure 2b we see that R_{eq} increases linearly with N_t. Since the R sites are dissolved with p_{sse} but more probably passivated with p_{cor1} we may understand that the surface is essentially covered by passive sites and that the evolution of the corrosion front is determined by p_{oxi}. We may establish this result more precisely by writing the equations of evolution for the number of passive and reactive sites. It is easy to show that the slope of R_{eq} *versus* N_t must be proportional to the product of p_{oxi} by the surface roughness [19]. This reproduces the correct order of magnitude of dR_{eq}/dN_t that we can extract from Figure 2b.

Very similar results have been obtained if we reduce N_{diff} from 10^4 to 10^3. We have still a neutral solution and we observe that the value of dR_{eq}/dN_t is unchanged. A totally different behavior appears for $N_{diff} = 10^2$ as we can see on the snapshots given in Figure 3a and 3b corresponding to $p_{sse} = 0.1$ and 0.2 respectively. The diffusion is not fast enough to produce neutralization of the solution. We clearly observe a coexistence of two domains, one rich in A and the other rich in C. As expected, they are separated by a neutral region. The comparison of Figures 3a and 3b shows the random character of the corrosion evolution. However, the number of corroded sites N_{corroded} and the equivalent radius R_{eq} determined as previously exhibit a rather regular behavior as shown in Figures 4a and 4b. The mean value of dR_{eq}/dN_t is increased as expected since now much more processes are involved in the metal corrosion.

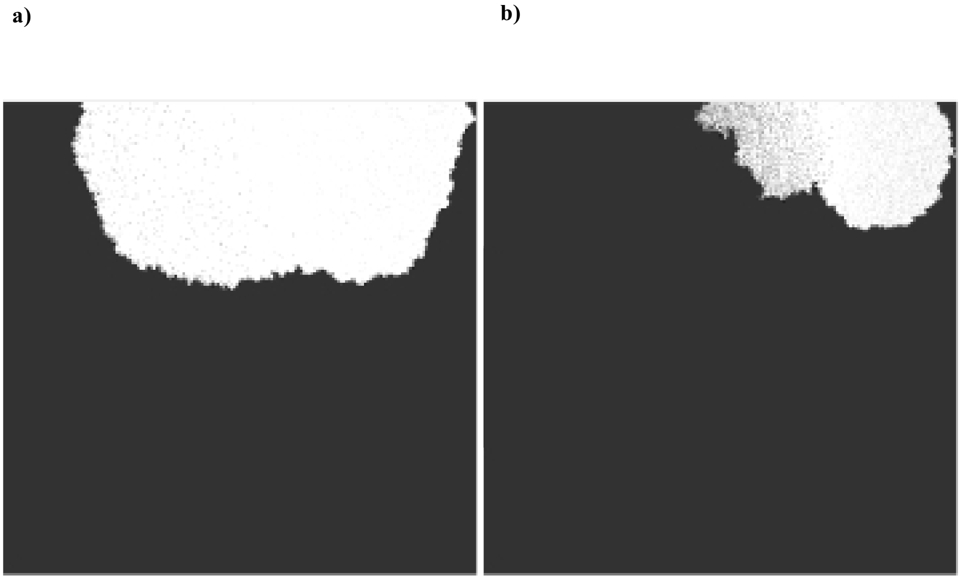

Figure 3. Snapshots obtained as in Figure 1 for $N_{\mathrm{diff}} = 100$. In a) $p_{\mathrm{sse}} = 0.1$ and $N_t = 94672$ while in b) $p_{\mathrm{sse}} = 0.2$ and $N_t = 9704$. The other parameters have the same value as in Figure 1.

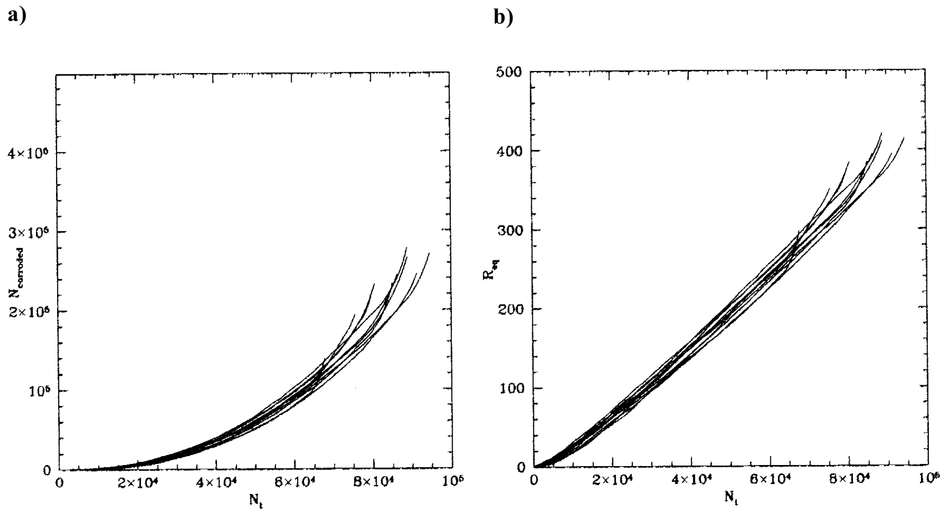

Figure 4. a) Number of corroded metal sites N_{corroded} and b) the equivalent radius of a half-circle $R_{eq} = (2N_{\mathrm{corroded}}/\pi)^{1/2}$ *versus* N_t for 10 independent simulation runs with parameters corresponding to Figure 3a.

In Figures 5 to 8 we present the cases $N_{diff} = 10$ and 1. For $N_{diff} = 10$ (Figures 5a and 5b) we see that the front is far from a half-circle. It is highly irregular and the shape is not well reproducible. A comparison with Figures 3a and 3b shows now several domains where one of the species A or C dominates. The number of such domains seems to increase with the value of p_{sse}. In Figure 5a we observe a single cavity developed with mainly two regions of different acidity. For the higher value of p_{sse} (Figure 5b) we see more irregular coliflower like cavities popping from the corrosion front. At this scale we can observe well the phenomenon of detachment of large pieces of uncorroded material from the corrosion front. The pieces form islands behind the main front and disappear gradually due to the same rules of corrosion processes as for the main front. It follows that depassivation at this length scale can proceed by a sort of excision of the passivated areas by the developing corrosion front. What is observed in Figure 5 is enhanced in Figure 7 for which $N_{diff} = 1$. Now the interior of the cavity is a patchwork of zones where either C or A are present. The zones corresponding to the lower p_{sse} value are larger but less intensely populated as there has been more time for diffusion to spread the inhomogeneous areas formed by the anodic and cathodic reactions.

The results concerning $N_{corroded}$ and R_{eq} are given in Figures 6 and 8. They show the existence of two regimes of corrosion. In the first regime corrosion is practically invisible. It is characterized by an incubation time. The comparison of several simulations performed with the same parameters shows that we have a random distribution

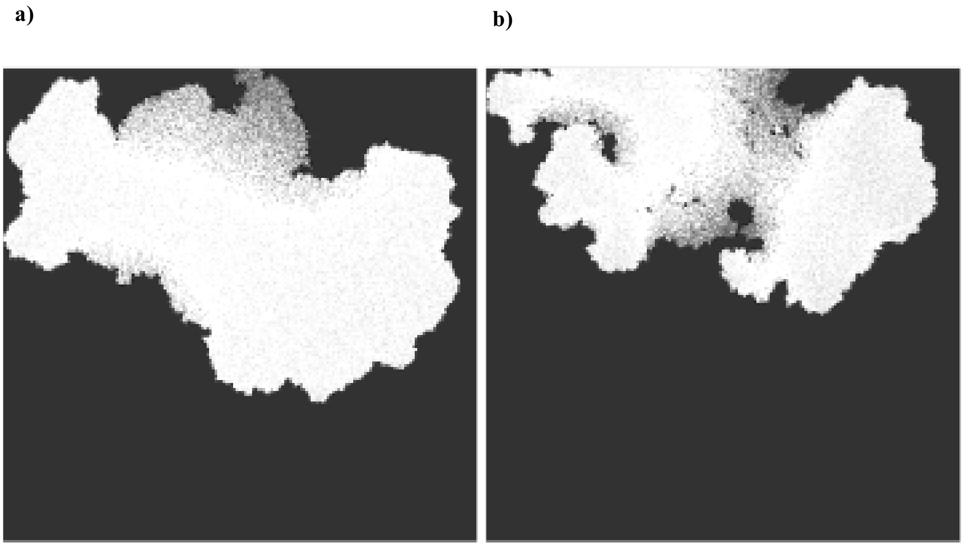

Figure 5. Snapshots obtained as in Figure 1 for $N_{diff} = 10$. In a) $p_{sse} = 0.1$ and $N_t = 9008$ while in b) $p_{sse} = 0.2$ and $N_t = 3569$. The other parameters have the same value as in Figure 1.

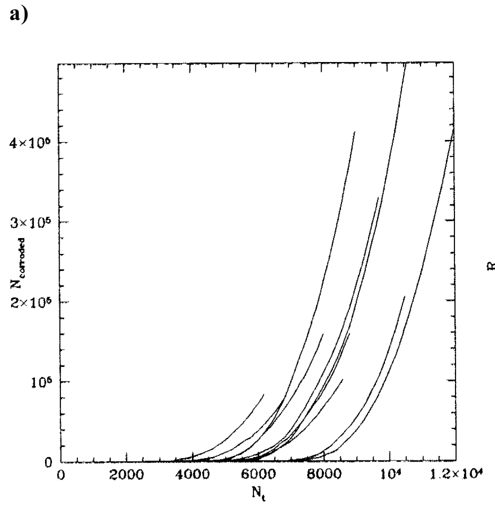

Figure 6. a) Number of corroded metal sites $N_{corroded}$ and b) the equivalent radius of a half-circle $R_{eq} = (2N_{corroded}/\pi)^{1/2}$ *versus* N_t for 10 independent simulation runs with parameters corresponding to Figure 5a.

of these incubation times. After this time we have the second regime in which the equivalent radius R_{eq} increases in the same way independent of the simulation run and dR_{eq}/dN_t has a common value that increases when N_{diff} decreases.

The simulations clearly show how the diffusion rate, *via* N_{diff}, determines the shape of the cavity and its content. Starting from a homogeneous neutral solution located inside a semi-circle we arrive progressively to a cavity having a very irregular and unpredictable shape and filled with domains in which one species, A or C, strongly dominates. We have translated these results in a quantitative way by associating to the snapshots an equivalent radius R_{eq}. For the lower values of N_{diff} an incubation time appears markedly and it is followed by a regime in which R_{eq} increases linearly with N_t. When we focus on this linear regime – the lower N_{diff} the higher dR_{eq}/dN_t is. From among these results we retain two essential points: dispersed incubation times and the formation of large domains in which we have mainly one of the two entities A or C.

Incubation time. The origin of the incubation time is related to the choice of probability, to the value of N_{diff} and to the way by which the initial damage is created. As explained at the end of Section 2.4, two M sites are turned into R sites, which are in a neutral medium. With our choice of probabilities these sites are practically certain to turn to two P sites in next time steps. To change the nature of these sites we have to wait, on the average, a time $1/p_{oxi}$. Then the two sites can be dissolved and two R sites are created in their neighborhood. They have a probability p_{sse} to enter in an SSE reaction and a larger probability p_{cor1} to be passivated. However, on the average, after several attempts an SSE reaction can be realized. The net result is an increasing of the

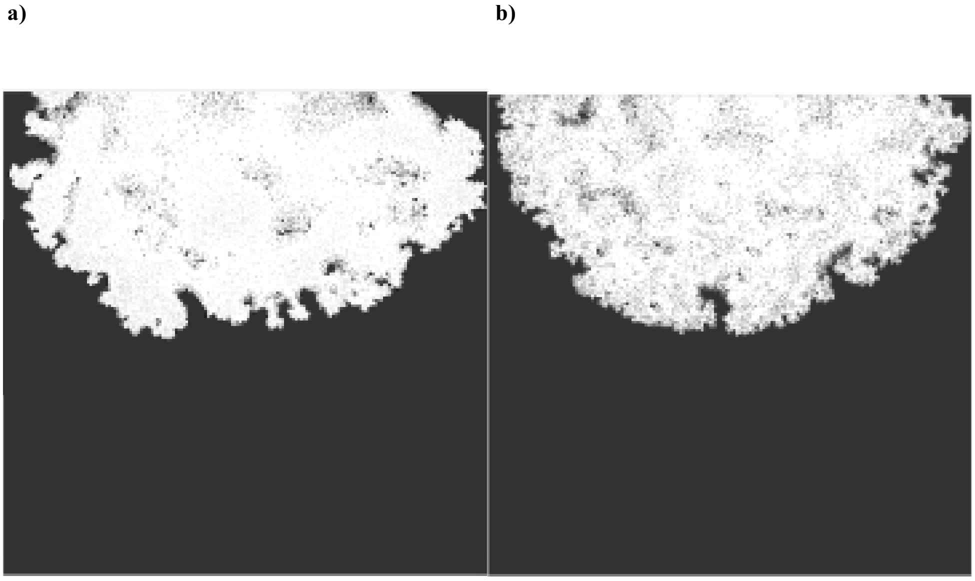

Figure 7. Snapshots obtained as in Figure 1 for $N_{diff} = 1$. In a) $p_{sse} = 0.1$ and $N_t = 4978$ while in b) $p_{sse} = 0.2$ and $N_t = 2716$. The other parameters have the same value as in Figure 1.

number of R sites and the introduction of A and C entities. Accordingly a new stage in the corrosion processes can start. Thus we may expect that the order of magnitude of the incubation time might be several times $1/p_{oxi}$. If the diffusion is very fast the next transformation of the surface sites will be done in a neutral medium and the next evolution is still determined by the set of probabilities p_{sse}, p_{oxi}, p_{cor1}. In contrast, if we assume that diffusion is extremely low other probabilities have to be introduced and the number of stochastic processes that determine the beginning of a regime of corrosion is increased. We expect that this may induce a large dispersion of the incubation time when we repeat a simulation with the same set of probabilities. Thus, the simple arguments presented above may give an insight concerning both the order of magnitude of the incubation time and the origin of its dispersion observed for the smaller values of N_{diff} (Figures 6 and 8).

Formation of domains. To describe the formation of domains of the species A or C we have to go back to the transformation rules introduced in our CA model to see how they create spatial correlations. Let us consider a simple limiting case in which the diffusion rate is very low and the probabilities p_{oxi}, p_{cor1} and p_{cor2} take the values: $p_{oxi} = 0$, $p_{cor1} = 1$ and $p_{cor2} = 0$. The precise value of $p_{sse} > 0$ is irrelevant. With these probabilities the only way to transform a P site is a dissolution in a net acidic medium with a probability $P_{PE} = 0.25\, N_{nn}^{exc}$. An R site can be dissolved or passivated when involved in an SSE reaction. Otherwise dissolution of an R site is impossible while its transformation into a P site is certain in a neutral or basic environment and impossible in an acidic one (*i.e.* if $N_{nn}^{exc} > 0$).

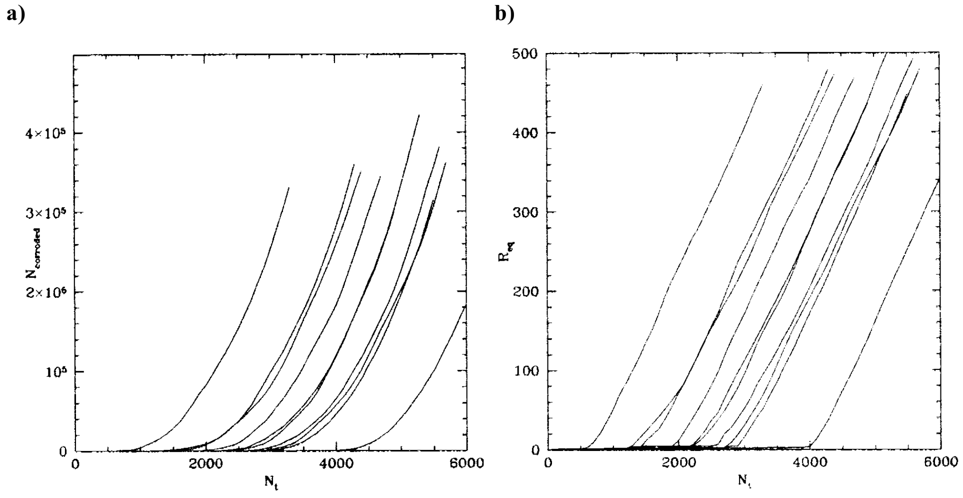

Figure 8. a) Number of corroded metal sites $N_{corroded}$ and b) the equivalent radius of a half-circle $R_{eq} = (2N_{corroded}/\pi)^{1/2}$ *versus* N_t for 10 independent simulation runs with parameters corresponding to Figure 7a.

Let us start with an anodic reaction in an acidic medium. We can imagine the neighborhood of the R site to contain one M, one A and two others sites, noted X_1 and X_2 selected such that the environment of R remains acidic. After the anodic reaction we have two A sites and at least one new R site descendant of the M site. If X_1 and/or X_2 are M sites they will also become R sites. Thus the tendency is to restore or to enhance the initial state in which an R site is in contact with an acidic medium. In next steps, the reactive sites involved in this configuration cannot be changed by a transformation other than anodic dissolution since, in acidic medium, P_{RP} and P_{RE} vanish. Thus, the most probable evolution is to change the configuration by a new anodic dissolution in an acidic medium and then we extend the domain of A species. This acidification can be reduced if the cathodic part of an SSE reaction happens to take place in this domain. In spite of the decrease in the acidity the domain will remain acidic. To summarize, when the anodic part of an SSE reaction is realized in an acidic medium, it is most probably followed by another reaction of the same type in its vicinity leading to the formation of a domain where species A dominate. Let us consider now a configuration in which the anodic part of an SSE reaction takes place in a basic medium. Then a new P site is created in a basic or neutral environment. In a further step, the P site cannot be transformed *via* an SSE reaction and since $P_{PE} = 0$ there is no other way to transform it. However, this P site can participate in the cathodic part of an SSE reaction leading to an increase of the basicity of this region.

Thus, on this extremely simple example we may understand that initially acidic or basic regions tend to persist and even extend. Of course the number of such regions may depend on the rate of neutralization *via* the diffusion process. The results presented in Figures 5 and 7 show that the number of domains increases when we decrease the value of N_{diff} or conversely the size of the domains increases on the average with N_{diff}.

CONCLUSIONS

The model presented in this paper belongs perhaps to the simplest possible descriptions of corrosion processes taking into account stochastic character of diffusion and spatial separation of electrochemical reactions. It cannot cover all the complexity of these processes. It gives however a very clear indication on the conditions when the competition between diffusion and electrochemical reaction may lead to highly irreproducible and irregular cavity shapes on length scales much larger than the lattice constant. Then the irregularities can be observed on a macroscopic scale. In the model we can recognize and classify such behaviors as incubation time, formation of cathodic and anodic reaction zones, roughly regular or irregular front development and associate these behaviors with the relation between the diffusion and corrosion rates.

The model can be readily extended and applied to such issues as the role of the heterogeneity of the corroding material, memory effects with respect to initial conditions as well as pit initiation at heterogeneities and healing.

Acknowledgment

The collaboration of our laboratories takes place in the framework of the PAN-CNRS agreement within the project no. 14470. On the Polish side this work received financing from the Ministry of Science and Informatization for the years 2004–2005, grant no. 3 T08A 010 26.

REFERENCES

1. Landoldt D., Corrosion et Chimie de Surfaces des Métaux, Traité de Matériaux, 12, Presses Universitaires et Polytechniques Romandes, Lausanne 1997.
2. Alkire R. and Verthoff M., *Electrochim. Acta*, **43**, 2733 (1998).
3. Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, Proceedings of the International Workshop, Cadarache, France, European Federation of Corrosion Publications, 36, Féron D. and MacDonald D.D. eds., Maney Publishing 2002.
4. Laycock N.J. and White S.P., *J. Electrochem. Soc.*, **148**, B264 (2001).
5. Meakin P., Jøssang T. and Feder J., *Phys. Rev. E*, **48**, 2906 (1993).
6. Johnsen T., Jøssang A., Jøssang T. and Meakin P., *Physica A*, **242**, 356 (1997).
7. Córdoba-Torres P., Nogueira R.P., de Miranda L., Brenig L., Wallenborn J. and Fairén V., *Electrochim. Acta*, **46**, 2975 (2001).
8. Córdoba-Torres P., Nogueira R.P. and Fairén V., *J. Electroanal. Chem.*, **529**, 109 (2002).
9. Taleb A., Chaussé A., Dymitrowska M., Stafiej J. and Badiali J.P., *J. Phys. Chem. B*, **108**, 952 (2004).
10. Saunier J., Chaussé A., Stafiej J. and Badiali J.P., *J. Electroanal. Chem.*, **563**, 239 (2004).

11. von Neumann J., Theory of Self Reproducing Automata, University of Illinois Press, Campain IL 1966.
12. Chopard B. and Droz M., Cellular Automata Modeling of Physical Systems, Cambridge University ress, 1998.
13. Wolfram S., *Physica D*, **10**, 1 (1984).
14. Frankel G.S., *J. Electrochem. Soc.*, **145**, 2186 (1998).
15. Advances in Localized Corrosion, NACE 9, Isaacs H., Bertocci U., Kruger J. and Śmialowska S. eds., NACE, Houston, TX, 1990.
16. Janik-Czachor M., *J. Electrochem. Soc.*, **128**, 513 (1981).
17. Mańkowski J. and Szklarska-Śmiałowska Z., *Corros. Sci.*, **15**, 493 (1975).
18. Szklarska-Śmiałowska Z. and Mańkowski J., *Corros. Sci.*, **12**, 925 (1972).
19. Vautrin-Ul C., Chaussé A., Stafiej J. and Badiali J.P. (to be published).