Pitting Corrosion of Metals

by Roger Newman

Pitting corrosion of metals is one of the most important electrochemical corrosion phenomena. Corrosion of steel reinforcement in concrete is always in the news, and it starts off as pitting, caused by chloride ions—so it is feasible that pitting is the most costly form of corrosion. Such an assessment might not be the same in every decade, and it is hard to measure the cost of corrosion potentials, and although a "rare event" and empirically a stochastic process,[1] can be considered to nucleate above a critical potential, or pitting potential (E_{pit}), for which one can legitimately seek a deterministic explanation.

This article is about the pitting-potential model of José R. Galvele, introduced in 1976,[2] and its influence on the subsequent development of necessary but not a sufficient condition for pitting. Rapid film-free dissolution creates a special local solution, acidified by hydrolysis of the dissolving metal cations, in which pit growth can proceed. Such an acidification process can overcome strong alkalinity, as in the concrete example given earlier (concrete pore-water has a pH of ~13, which can be reduced to ~5 at a corrosion site).

Transport Processes and the Mechanism of Pitting of Metals

Jose R. Galvele*,[1]

The Ohio State University, Corrosion Center, Columbus, Ohio 43210

ABSTRACT

A pit model was developed on the assumption that the metal ions hydrolyze inside the pits and that the corrosion products are transported by diffusion. Concentrations of Me^{2+}, $Me(OH)^+$, and H^+ ions, as a function of pit depth and current density, for Zn, Fe, Ni, Co, Al, and Cr were calculated. The main reason for passivity breakdown at the initial stages of pit growth, was found to be the localized acidification due to metal ions hydrolysis. Assuming a critical pH value for pit initiation, the following experimental facts could be explained: (i) the effect of the external pH on the pitting potential of Fe and stainless steel; (ii) the effect of sodium borate concentration on the pitting potential of Zn; (iii) the effect of weak acid salts on the pitting potential of Al; (iv) the oscillations of the electrode potential of stainless steel and nickel in solutions of $Cl^- + SO_4^=$ ions; (v) the existence of a pitting inhibition potential; and (vi) the existence of a pitting protection potential. Through analysis of the transport processes inside a pit it was also concluded that the pitting potential of a metal should change with the Cl^- ion concentration according to the equation

$$E_p = E_p^* - B \cdot \log [Cl^-]$$

$B = 0.059V$ being the slope of the curve at room temperature.

control in steel structures and piping, which is also enormous, but would not usually be attributed to "pitting." Pitting is hard to predict or monitor, and propagates rapidly (large unattacked cathode…small pit anode), with no respect for costly materials like stainless steels, nickel alloys, and aluminum alloys. It often grows under the surface of a component, as shown in Fig. 1, and notoriously tends to trigger mechanical failures by fatigue or stress corrosion cracking. It is favored by oxidizing corrosion science. A brief commentary will be given on Galvele's subsequent refinements and clarifications of the model.[3-5]

In the early 1970s, Galvele developed the idea that the nucleation of pitting corrosion of metals in aqueous halide solutions has little to do with the quality of their passivating oxide films ("passive films"), but rather depends on the rate at which the metal can dissolve where the passive film has failed locally for some reason. In other words, penetration of the passive film by the electrolyte is a In the following discussion we do not consider the cathodic reaction (oxygen reduction, chlorine reduction, etc.) that supports the pit anode; all the results are discussed in the context of potentiostatic conditions. The evolution of localized corrosion under natural immersion conditions has its own distinct features, including a kind of "natural selection" wherein corrosion sites of slightly differing geometry compete for the available cathodic current.[6]
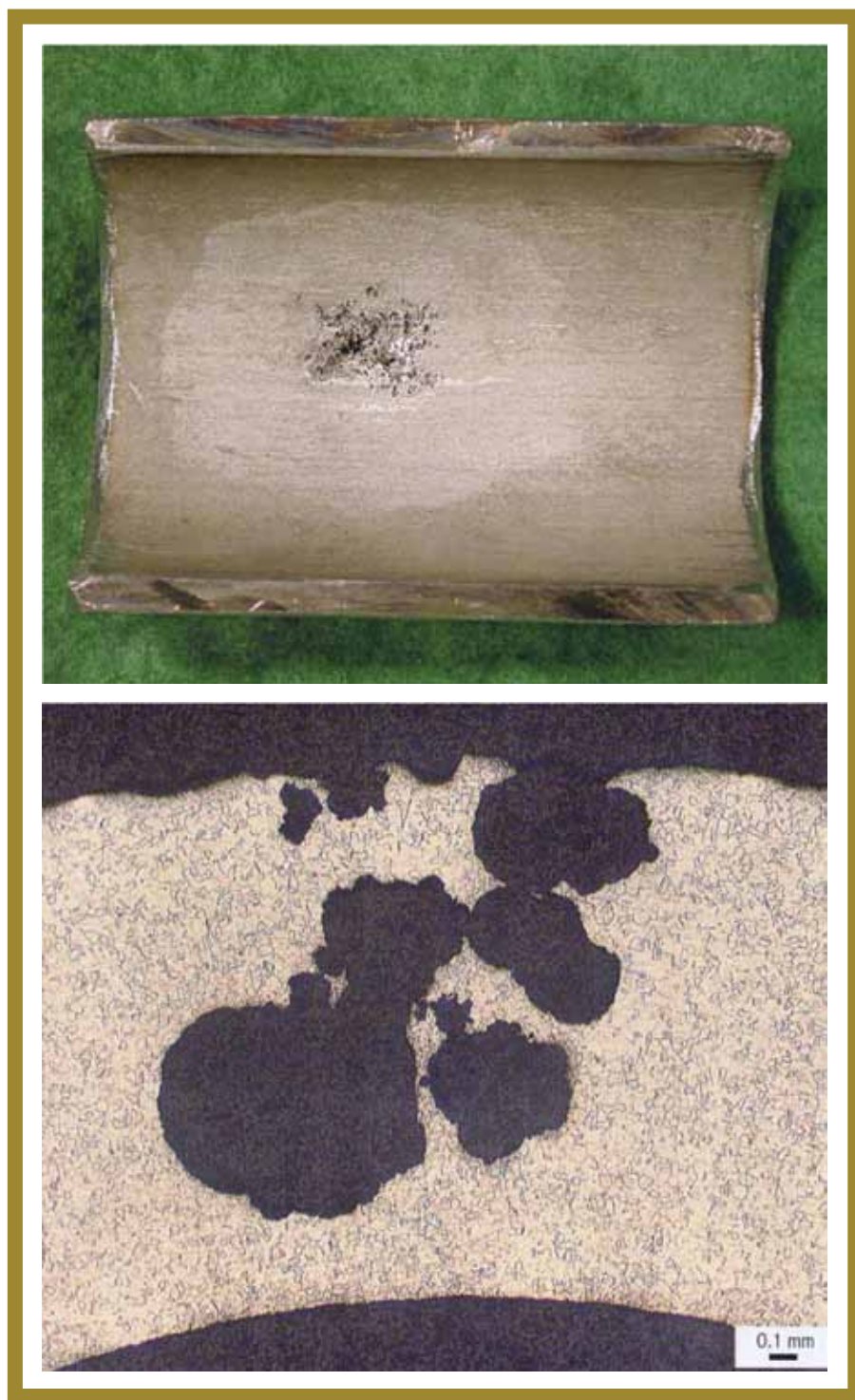
Fig. 1. *Pitting corrosion of a stainless steel pipe, showing growth of pits under the metal surface.* Courtesy of Intertek-CAPCIS

One factor that may have influenced Galvele in developing his pitting model was his experience of the role of plastic strain in stress corrosion cracking, which led him to study the pitting of plastically straining metals.[7-9] The reasoning is simple—if pits prefer to nucleate at sites of passive-film rupture, yet still respect the pitting potential, the role of the passive film in setting E_{pit} has to be questioned. The passive film, according to this argument, merely affects the pit nucleation rate.

In his 1976 paper,[2] Galvele refers to earlier work by Hoar, Kaesche, Freiman, Hisamatsu, and others, in which the authors argued for the importance of local acidification, though not necessarily for the very first stages of pit nucleation (Hoar was happy to deal with both stages separately—he liked to refer to a kind of surface complexation by chloride, leading to thinning of the passive film, and believed that certain alloys like Ni-Sn had very special passive films). Galvele attributes to Vetter and Strehblow the opinion that to talk of solution composition changes controlling the initial stages of pitting is "meaningless." He cites prior work of Pickering and Frankenthal, in which a one-dimensional pit model appeared for the first time, although he points out that those authors started with an acidic solution in which only increases of pH were possible locally.

The Approach in the 1976 Paper

The 1976 paper begins by presenting a simple one-dimensional, local-acidification model, based on metal dissolution, metal cation diffusion, and hydrolysis of these cations. Galvele postulates that pit nucleation requires a critical chemistry to develop at the dissolving metal surface in a one-dimensional cavity whose depth, he believed, could be as small as the thickness of the passive film (2 or 3 nm)—Fig. 2. With today's knowledge we can be fairly sure that the depth of the nucleating cavity (or rather the effective diffusion length in what must be a highly confined geometry), and the concentration of the critical metal salt solution, were both underestimated in Galvele's treatment. Most authorities now refer to critical concentrations of order 1M or higher in Me^{n+}, which for believable anodic current densities (say, less than 100 A cm^{-2} in the most extreme case[10]), entails an effective diffusion length of at least 0.1-1 μm. For "perfectly" flat surfaces, this leads to the speculation that a slow blistering type of corrosion occurs under the passive film, with only molecular-sized channels for communication with the bulk solution; then this structure pops open, leading to pit growth—similar to a proposal of Mattin and Burstein,[11] and recalling earlier work by authors who referred to "salt islands" or "blisters." This critical chemistry is postulated to correspond to a thermodynamic criterion : a critical solubility of metal cations in equilibrium with the relevant oxide or hydroxide. Ion migration is introduced later in the paper, and leads to some of the most impressive predictions of the model.

Metal dissolution occurs at the bottom of the cavity

$$Me \rightarrow Me^{n+} + ne^- \qquad (1)$$
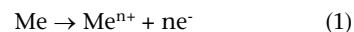
and instantaneous cation hydrolysis occurs by the following.

$$Me^{n+} + H_2O = MeOH^{(n-1)+} + H^+ \qquad (2)$$
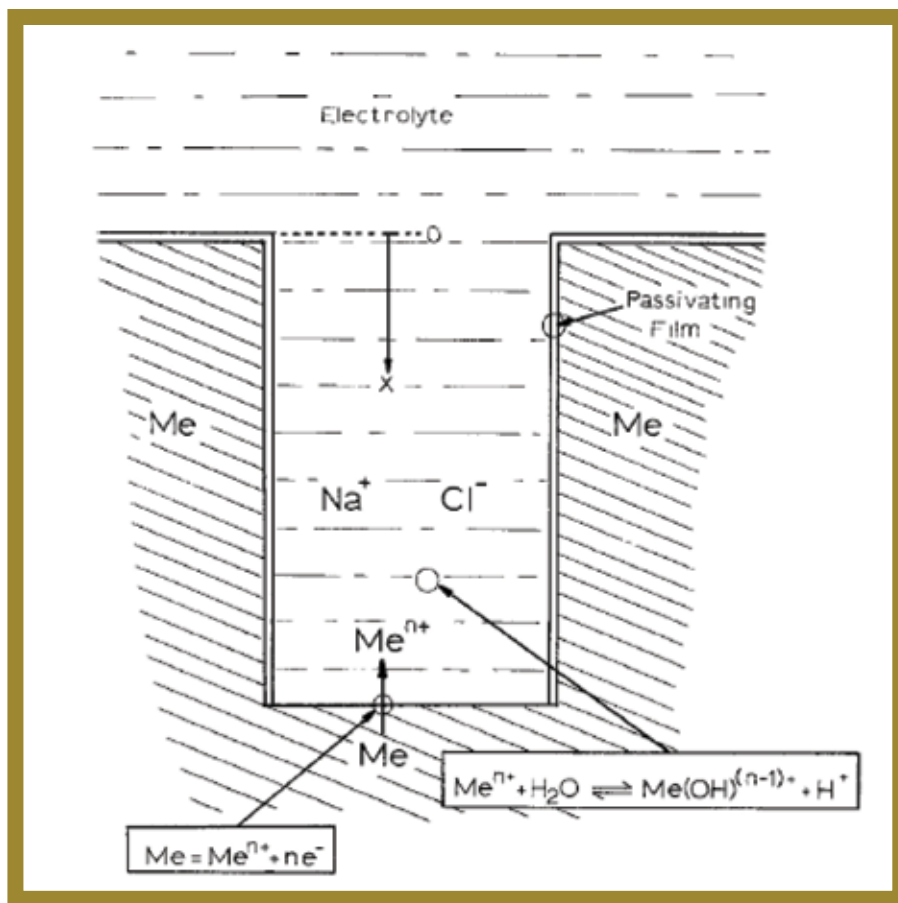
Fig. 2. *Galvele's model pit geometry.[2]*

Then, rewriting the hydrolysis equilibrium as:

$$2Me^{n+} + H_2O + OH^-$$
$$= 2MeOH^{(n-1)+} + H^+ \qquad (3)$$
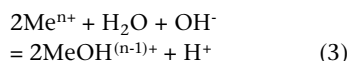
allows the pH of the external solution to be varied in a nicely transparent way. For pitting to be possible in practice, this external pH must lie within the region of stability of an oxide or hydroxide, otherwise the metal just dissolves actively, so many metals only pit in basic halide solutions.

The above reasoning leads to a set of five equations that can be solved for the steady-state concentrations of all species as a function of the anodic current density at the bottom of the "pit" (i) and the depth of the pit (x), provided that the bulk solution is assumed to act as supporting electrolyte, that diffusivities have their dilute-solution values, and that mixing beyond the pit mouth is instantaneous. The five equations are constructed on the following basis:

1. Sum of fluxes of Me^{n+} and $MeOH^{(n-1)+}$ = i/nF (with diffusivities from literature)
2. Net flux of O in O-containing species = 0 (with diffusivities from literature)
3. Net flux of H in H-containing species = 0 (with diffusivities from literature)
4. Hydrolysis equilibrium constant for eq 2 = K_1 (from literature)
5. Ionic product of water = K_w (from literature)

For many conditions of interest, the product of the depth (x) and the current density (i) essentially determines the concentration (c_{Me}^{n+}) of Me^{n+}, because H^+ and $MeOH^{(n-1)+}$ are present at much lower concentration than Me^{n+}. Galvele did not give the ($x.i$) product any particular name, but later ($x.i$), or alternatively the critical value of ($x.i$) to stabilize a pit, became known as the "stability product" (but note that the critical value of ($x.i$) should depend on pH, except near pH 7; researchers who have used the term stability product generally used only one pH, either acidic or neutral).

By solving the five equations with appropriate boundary conditions, diagrams are generated, showing the concentrations of Me^{n+}, $MeOH^{(n-1)+}$, and H^+ as a function of ($x.i$). Then, by referring to the equilibrium between metal oxide (or hydroxide) and Me^{n+}, a critical value of ($x.i$) giving sufficient acidification can be calculated for any assumed (that is, sufficient) equilibrium concentration of Me^{n+}. The problem is—what is this sufficient concentration? Galvele starts by assuming that it is 10^{-6} mol dm^{-3}, and states that conclusions drawn using this assumption could be in error by one pH unit either way. But some of his critical pH values (9.5 for Fe or Ni; 5.0 for Al) appear very high by modern

standards. The likely reason for this is that his proposed level of acidification is too mild to sustain the required anodic current density. Nowadays pitting (and this may be this author's bias drawn from the preponderance of studies of stainless steel and aluminum) is generally considered to require molar, not micromolar levels of Me^{n+} at the bottom of the pit. Importantly, a particular effect sets in when the solution becomes very concentrated, as explained first by Mankowski and Smialowska,[13] and later by Edwards[14]—the extreme anodic current densities required for pitting, at least of stainless steel or aluminum, only become possible when the concentration of the metal salt solution in the pit gets to the point (several molar) that the mean ionic activity coefficient rises steeply above 1, reaching as high as 50 in the FeCr system. This leads to extremely low pH values, not to mention any aggressive effect of the accompanying high chloride concentration.

What Galvele did, in effect, was to equate the critical chemistry for depassivation, which does not correspond to any particular high current density, and is more appropriate for the initiation of crevice corrosion, to the critical chemistry for pit nucleation, which has to permit anodic current densities in the A cm^{-2} range. The corresponding stability products estimated by Galvele were about 10^{-6} A cm^{-1}, whereas modern values range up to 10^{-4} A cm^{-1}. But this subtlety did not become clear until the 1990s, and still could be wrong for particular metals such as zinc. Also, Galvele was well aware that some metals might meet the provisional pit-stability criterion but be unable to generate the current densities required for pit nucleation, and referred to this possibility in the context of pure chromium, which is extremely resistant if not immune to pitting.

Clearly the necessity of having a highly concentrated metal salt solution in the pit nucleus necessitates revision of some details of Galvele's model, without detracting from its remarkable power to explain a wide range of observations. Progress in understanding the effects of concentrated pit chemistries has been slow, but until recently was actively advancing under the auspices of the U.S. Department of Energy and others, in relation to the Yucca Mountain Project.

Effects of pH or Secondary Anions

One of the themes of Galvele's pitting program (the 1976 paper and those following) was the progressive rationalization of the pH and buffer-anion dependence of the pitting potential. In 1976, the absence of migration in the initial model made it difficult to obtain a full range of predictions, but some features were successfully reproduced. For iron, and assuming Tafel kinetics within the pit nucleus (this is a simplification of

course), Galvele found that E_{pit} should be constant between pH 7 and about pH 10, but should then increase as follows:

$$E_{pit} = a + b \log c_{OH^-} \qquad (4)$$

(in this equation b is a coefficient, not a Tafel coefficient).

In 1981, by considering further hydrolysis steps than Eq. 2,[3] Galvele was able to rationalize the pH-independence of the pitting potential of aluminum—a really important result. (Which is not to say that the tendency for pitting is pH-independent—the corrosion potential falls at high pH, and pitting thus ceases under open-circuit conditions.) Similarly, by considering the buffering effect of anions of weak acids, he successfully rationalized the beneficial effect of moderate additions of such ions,[2-4] but noted that when their concentration approaches that of chloride, the assumption of a supporting NaCl electrolyte in the pit must break down. So it was not until his later work that he tackled the fact that pitting vanishes completely above a certain concentration ratio of inhibiting to aggressive anions— where the former include OH⁻. This is of huge importance in concrete technology, where a critical ratio of OH⁻ to free Cl⁻ exists, below which corrosion of the steel reinforcement is inevitable.[15] In the 1976 paper there is a section dealing with the inhibiting effect of sulfate ions on pitting of stainless steel, where Galvele shows that in a reaction/diffusion/migration model, the double charge on the sulfate leads to a spectacular enrichment, relative to chloride, at the bottom of a pit, consistent with complete inhibition. Probably he considered this as a special case, and his hesitation to generalize such an inhibition model in the 1976 paper may be another consequence of his view that critical pit chemistries were not, in general, especially concentrated in Me^{n+}.

Effect of Ionic Strength of the Bulk Solution

A striking feature of pitting in pure NaCl solution is the dependence of the pitting potential (E_{pit}) on the external NaCl concentration, c_∞. Many authors have confirmed that this dependence is of the form:

$$E_{pit} = A - B \log c_\infty \qquad (5)$$

with B generally falling in the range 60-90 mV. Galvele brilliantly adapted a scheme of Vetter to show that this could be rationalized as the variation of the *IR* potential drop in the pit nucleus (at its critical chemistry) with the external NaCl concentration c_∞. Galvele had to assume that the critical chemistry could be either dilute or concentrated in Me^{n+},

so he had to solve the complete set of reaction-transport equations, but now that we know the critical pit chemistry is always concentrated, we can make the simplifying assumption that at the dissolving pit surface ($x = 0$, $c = c_0$):

$$c_0^{Me^{n+}} = \frac{1}{n} \, c_0^{Cl^-} = c^* \qquad (6)$$

where c^* is a convenient symbol for the critical pit chemistry, expressed as $c_{Me^{n+}}$ at the dissolving surface ($x = 0$).

That being the case, all we have to do is to treat Cl⁻ as a non-reacting species, for which:

$$c_0^{Cl^-} = c_\infty \, exp\left(\frac{F.\Delta\phi}{RT}\right) \qquad (7)$$

This equation comes from the consideration that the diffusion and migration fluxes of a non-reacting ion are equal and opposite at steady-state; $\Delta\phi$ is the IR drop in the pit nucleus. Since $c_0^{Cl^-}$ is always the same ($n.c^*$) at the pitting potential, this reduces to:

$$\Delta\phi = Q - \frac{2.3RT}{F} \log c_\infty \qquad (8)$$

where

$$Q = \frac{2.3RT}{F} \log n.c^* \qquad (9)$$

so that

$$E_{pit} = P + Q - \frac{2.3RT}{F} \log c_\infty \qquad (10)$$

where P will depend on the anodic dissolution kinetics of the metal in the local environment. Thus P incorporates the dissolution kinetics, Q the passivation tendency, and the last term the chloride concentration dependence. This extension of Galvele's analysis is previously unpublished in this explicit form, but is obvious enough from published literature.

Solid-Solution Alloying

A natural consequence of Galvele's pitting model is that solid-solution alloying effects on the pitting potential are due to differences in anodic kinetics in the local environment of a pit nucleus (*i.e.*, differences in P, and perhaps, though not necessarily, differences in Q). Muller and Galvele showed that this was consistent with the behavior of Al-Cu, Al-Zn, and Al-Mg alloys,[16-17] and commented on the feasibility of a similar interpretation for stainless steels, although they referred to a sparingly soluble Mo salt in that case—not a fashionable view nowadays. The present author has spent a large part of his career arguing for the dissolution-kinetics argument for Mo alloying,[18-22] and has also published similar arguments related to the Al-Zn system.[23]

Finally, Galvele discusses the relationship between the pitting potential and the protection or repassivation potential. He notes the obvious conclusion that the latter is lower than the former because the pit depth x, in his model, is larger.

Related Advances

The influence of the 1976 paper has been enormous, although some researchers find its conclusions distasteful, because the importance of the passive film *per se* is eliminated, or at least reduced to the mundane task of reducing the number of pits. If funding agencies had believed in Galvele's model, fewer funds might have been available for corrosion research using ultra-high vacuum equipment over the past 30 years. As Galvele says in his conclusions:

> *All the observations reported so far in the literature on the pitting potential can be explained by transport phenomena. Processes like competitive adsorption, salt formation, film contamination, etc., even though present during the pitting process, do not play a major role in fixing the pitting potential.*

The 1976 paper has been cited in over 250 journal publications. T. R. Beck was already applying reaction-transport models to stress corrosion cracking, and later used some of Galvele's insights in his work on pitting,[24] although Beck's work, and that of R. C. Alkire (many publications, of which Ref. 25 is given as an example), tended to focus on diffusion-controlled conditions—that is, the presence of a metal chloride salt film on the dissolving surface—which is far removed from Galvele's relatively dilute local chemistries. Others were attracted by the idea of pit nucleation at a mechanical or otherwise-formed flaw that could be imaged directly[26]—such efforts continue today, with evidence for pores under passive films on aluminum[27] (these authors, however, do not discuss the consequences of exposing the pore in detail, regarding this exposure as the essential event in pit nucleation). Many publications dealt with the dissolution of stainless steels in pits or pit-like geometries,[28] including the requirement that a certain fraction of saturation in metal chloride salt must be achieved.[29] Others dealt with aluminum pitting, the critical chemistry requirement in that case,[30] and the distinction between pits and tunnels.[31] A persistent theme was the initiation of crevice corrosion, which according to most authors occurs by a slow process of passive dissolution, gradually building up the necessary chemistry,[32,33] but according to others, is due to pitting that would be metastable if it were to occur on a free surface, but is stabilized by the crevice (higher 'x' in Galvele's model).[34]

The peak of the influence of the stability product was around 1990, when Pistorius and Burstein, building on an approach of Frankel, et al.,[28] applied the stability constant concept to metastable pits in stainless steel, by carrying out exhaustive analyses of small current transients that occur below the usually-defined pitting potential.[12] By integrating such transients and assuming a hemispherical geometry, they were able to determine the anodic current density in the pit as a function of its radius. Various analyses and conclusions flowed from the work, including the belief that pits were always covered by an anodic salt film from the earliest instant of their nucleation (this remains somewhat controversial; Frankel, et al.[28] believed that the salt film was required for pit stability, but not for the initial growth of metastable pits). An important finding was that the milder the conditions, the more occluded were the detected pits (i.e., the current density was lower than expected for an open cavity). Pits have an ability to self-select for survival, and even more so under open-circuit rather than potentiostatic conditions. Subsequent studies of surface-roughness effects tended to confirm the general validity of such a simple analytical approach.[35,36]

There appears to be a large gulf between the artificial pit or "lead-in-pencil" electrode, with its dimensions of tens to hundreds of microns, and the tiny fissure envisaged by Galvele as the pit nucleus. But in 1997, Laycock and Newman[20] showed that a simple measurement of the transition potential between the bare and salt-covered states for artificial pits in stainless steel, as a function of the prevailing anodic limiting current density, enabled an extrapolation to very small length scales that could predict the pitting potential accurately, including its variation with chloride concentration, Mo alloying, etc. The substitution of bromide for chloride, which tends to eliminate the beneficial effect of alloyed Mo, was shown to obey the same kind of rules[22] (see Fig. 3).

More recently, the "x.i" concept has been incorporated into models of crevice or thin-film corrosion, and combined with scaling laws for crevice corrosion, to make important rationalizations and predictions.[37] Bulk Al-based metallic glasses provide another new type of material where the size-scale of pit nuclei is critical.[38]

It is fundamental to Galvele's model, and necessary for clarity, that there is a clear-cut boundary condition at the mouth of the pit. Yet authors who discuss phenomena involving electrolyte flow, and/or effects of enrichment or depletion of ions outside the pit, including communication between nearby pits,[39-41] find Galvele's basic framework useful, and indeed indispensable for their analysis.

Since the late 1990s, the shape evolution of pits has come to the fore, with electrochemical measurements of single pit growth,[42] video microscopy of foils in cross-section,[42] and a numerical model that reproduces the lacy metal covers observed over pits in stainless steel.[43] These are necessarily mature pits, but similar issues arise in considering the behavior of very small pit nuclei. The point is that any open cavity must split into active and passive areas, because there is a dilution of the acidic solution near the pit rim—at least for stainless steels. All these studies take the Galvele type of criterion as their starting point. So do recent refinements of computational methods for pitting.[44] All improved schemes for simulation of pit growth (e.g., Ref. 45) must draw inspiration, in various ways, from Galvele's pioneering research.

Acknowledgments

About the Author

ROGER NEWMAN is a professor in the Department of Chemical Engineering and Applied Chemistry at the University of Toronto. By training he is a materials scientist. He spent 20 years as an academic in the Corrosion and Protection Centre, University of Manchester Institute of Science and Technology (UMIST), Manchester, UK. His research specialties are localized corrosion and stress corrosion cracking of metals. He has received a number of awards for corrosion research, including the Fischer Medal of DECHEMA, the U. R. Evans Award of the Institute of Corrosion, the W. R. Whitney Award of NACE International, and the H. H. Uhlig Award of the ECS Corrosion Division. He may be reached at roger.newman@utoronto.ca.

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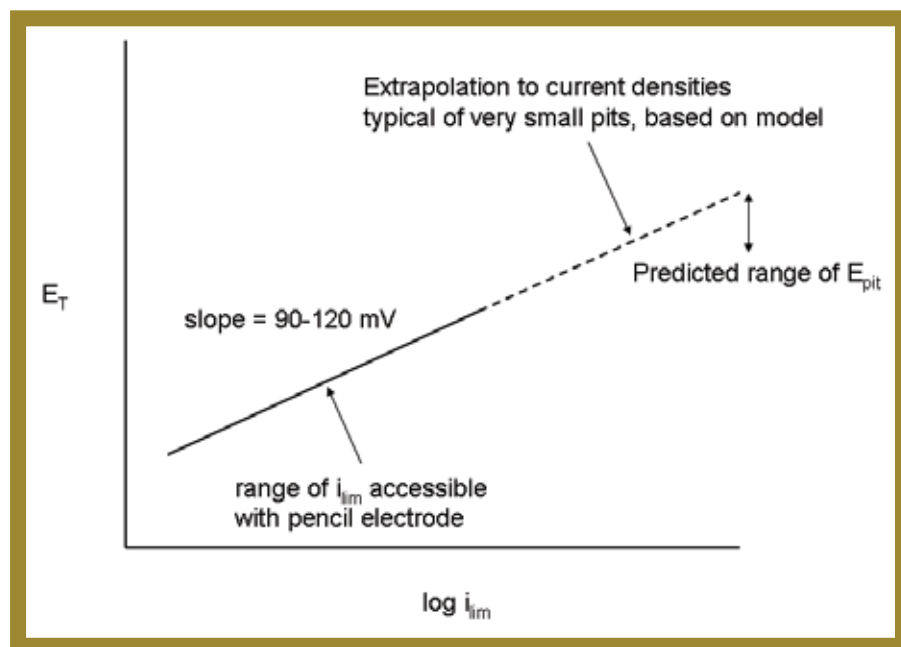15. T. Yonezawa, V. Ashworth, and R. P. M. Procter, *Corrosion,* **44**, 489 (1988).

FIG. 3. *Method used by Laycock[20] and Ernst[22] to predict pitting potentials from the results of artificial pit (pencil electrode) experiments in which the transition potential between film-free and salt-covered dissolution was measured as a function of pit depth via the limiting anodic current density (i_{lim}), drawing heavily on Galvele's pit model.*

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