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COMISION NACIONAL DE ENERGIA ATOMICA
PRESIDENCIA DE LA NACION

PROGRAMA MULTINACIONAL DE METALURGIA
(Programa Regional de Desarrollo Científico y Tecnológico-OEA)

PRESENT STATE OF UNDERSTANDING OF THE BREAKDOWN OF PASSIVITY AND REPASSIVATION

José R. Galvele

Preprint of the overview paper for the: FOURTH INTERNATIONAL SYMPOSIUM ON PASSIVITY, October 17-21, 1977, Airlie, Virginia, USA.

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José R. Galvele

Comisión Nacional de Energía Atómica, Departamento Materiales, Avda. Libertador 8250, Buenos Aires, Argentina.

The passivity breakdown literature has been reviewed by Kolotyrkin (1), Szklarska-Smialowska (2), and more recently by Kruger (3) and Hisamatsu(4). In the present review, a compilation is made of the recent information published on pitting, and a razionalization is attempted of the information available. The present review deals mainly with the pitting initiation process; information on pit propagation kinetics has not been included.

Pitting is a type of very localized corrosion that appears on metal surfaces that otherwise show very low dissolution rates. From a mechanistic point of view the present reviewer could identify three types of pitting which morphologically are similar but apparently follow different mechanisms.

The most common type of pitting is found when potentiostatic or galvanostatic polarization curves are produced in neutral or alkaline solutions containing the aggressive anions. In all these solutions the polarization curves show a passive zone up to a certain potential above which pitting starts, Figure 1-a. This type of pitting is characterized by the existence of a pitting potential, and this technique of measurement seems to be the oldest and the most frequently used in pitting studies (5-57). We will identify this type of pitting as <u>electrochemical depassivation</u>.

The second type of pitting appears when using a technique introduced by Engell and Stolica (58, 59). This technique consists in passivating the metal in an acid solution, usually H_2SO_4 solution, and then injecting a solution containing an aggressive anion, like NaCl solution. This technique has been used for iron by Engell and Stolica (58, 59), by Kolotyrkin and Freiman (60) and by Vetter and Strehblow (61); it was used

for Fe-Cr-Ni stainless steels by Hoar and Jacob (62) and Stolica (63), for Fe-Cr alloys by Stolica (63, 64) and for nickel by Ammar and Darwish (65).

One important observation is that, in general, in acid solutions there is no measurable pitting potential; this has been pointed out by various authors (59-61, 66). After injection of chloride ions, pitting is found at all the potentials where passivity was observed in the initial solution. The only exceptions are nickel and, in some cases, iron in pH 5 phthalate buffer solutions (66).

Looking to the polarization curves for iron (67), for nickel (68, 69) and for Fe-Ni alloys (70) in H_2SO_4 solutions with various amounts of chloride ions, Figures 2 and 3, it is difficult to deteot a potential where a transition from passivity to passivity breakdown can be located. This transition is not found even for very low concentrations of NaCl in H_2SO_4 solution. Actually, it is observed that, as the concentration of chloride ions increases, the current density in the passive zone increases, and eventually the current density involved is so high that it is difficult to accept that passivity of the metal is still retained. It could be argued that the pitting potential in these solutions is lower than the Flade potential, but, as shown below, the pitting potential increases when the aggressive ion concentration is decreased, so it should be detectable in Figures 2 and 3 for the lowest chloride concentration. Instead of a change in the breakdown potential, what we see in those figures is a shift in the passive current, from very low to very high current values. In the first type of pitting we find that the process starts as a result of a change in the potential; at a potential below the pitting potential, even in presence of a high concentration of the aggressive anions, the metal remains passive. In this second type of pitting the localized corrosion appears to be potential-independent, and it starts as a result of a change in the composition of the media. We will call this type of pitting: chemical depassivation.

There is a third type of pitting, described as a distinct process by Galvele, Lumsden and Staehle (71) for ferritic stainless steels in HCl solutions. The difference from the other two types is that it develops not on a passive metal surface, but on a metal that is undergoing general

dissolution. It was found for Fe-Cr-Mo ferritic stainless steels in HCl solutions, Figure 4. It is also found for niokel in $NiCl_2$ solutions (72), and most probably it would also include some of the metallographic etching solutions, like those for aluminum which are mixtures of nitric plus hydrochloric plus hydrofluoric acids (73). It was found that this type of pitting shows a olear pitting potential, but contrary to what it is observed for electrochemical depassivation, the pitting potential does not change with the content of an alloying element like molybdenum (71), Figure 4. It was reported that this pitting potential changes with crystallographic orientation (72), but no information is available about the effect of the aggressive anion concentration, the temperature, the inhibitors, etc. This type of pitting will be refered to as the HCl-stainless steel type.

EXPERIMENTAL ASPECTS OF PITTING CORROSION

Pitting Potential, Ep

The pitting potential of a metal, Ep, can be defined, in a potentiostatic polarization curve, as the potential below which the metal surface remains passive, and above which pitting nucleates on the metal surface, Figure 1-a. The pitting potential has been measured by several techniques, like potentiostatic methods, galvanostatio methods, mechanioal surface scratching, etc., and will be described by another reviewer in this conference (74).

In recent literature, pitting potentials have been reported for iron wiskers in chloride containing solutions (8), iron in ohloride solutions (21, 60, 61, 66, 75-77), in bromide solutions (60, 61, 75, 77), in iodide solutions (60, 61, 75), in perchlorate solutions (18, 60, 61, 75), and in sulfate solutions (61, 78), low alloy steels and carbon steels in chloride solutions (8, 17, 21), stainless steels in chloride solutions (19, 20, 23, 24, 28, 40, 56, 79-81) and in bromide solutions (81), nickel in halide solutions (43, 66), manganese in various aggressive anions (16), zinc in various aggressive anions (16, 52), cadmium in various aggressive anions (16, 53),

aluminum in chloride solutions (10-13, 32, 46, 47) and in other aggressive anions (10, 82), electrodeposited NiSn alloy in chloride containing solutions (83), zirconium in halide solutions (27, 57, 84-86), and in perchlorate solutions (87), titanium in halide solutions (25, 57, 88) and tantalum in halide solutions (57).

Repassivation Potential, Er

Besides the pitting potential described above, Pourbaix (89) described another potential characteristic of the pitting process. It was reported by Pourbaix that the pits, which will start to grow at a potential equal to or higher than the pitting potential, will keep growing even when the potential is lowered below the pitting potential. The pits will stop growing only when the potential is lower than a certain potential called repassivation potential, or protection potential, Er, Figure 1-b. The existence of such repassivation potential has been reported by several authors (12, 13, 19, 20, 23, 24, 28, 33, 34, 40, 90).

Wilde and Williams (19, 33) measured the repassivation potential for stainless steel in NaCl solutions, and found a correlation between the difference of these two potentials, Ep and Er, and the susceptibility of the alloy to crevice corrosion. They found that the bigger the difference the higher the susoeptibility of the metal to crevice corrosion.

Suzuki and Kitamura (40) showed that the repassivation potential for stainless steel in chloride media varied with the degree of the occlusion of the pits. The deeper the pit, the lower was the repassivation potential. Hisamatsu and Tsujikawa (90) confirmed this observation and found also that the value of the repassivation potential was dependent not only of the degree of the pit growth but also on the rate of the potential descend during the measurement of Er.

On the other hand, Broli and Holtan (12, 13) found, for aluminum in NaCl solutions, that the difference between the pitting potential and the repassivation potential was a function of the polarization rate, and that the difference between the potentials tended to cancel out when quasi-potentiostatic conditions were approached. They concluded that for aluminum

Ep and Er were equal.

Inhibition potential, Ei

Besides the pitting potential and the repassivation potential, there is a third characteristic potential, described by Schwenk (91), and usually called inhibition potential, Ei, Figure 1-c. Schwenk found, for stainless steels in chloride solutions containing nitrates, that there was a pitting potential, Ep, above whioh the pitting started, and an upper limiting potential, Ei, above whioh the sample became passive again. These observations were confirmed by Leckie and Uhlig (48). Kuzub and Novitskii (79) studied the inhibition potential of stainless steels in chloride plus nitrate solutions, and reported that an increase in the chromium oontent in the steel lowered the inhibition potential.

Freiman and Kolotyrkin (92) described for iron in sulfate solutions what they called a second passive state. Vetter and Strehblow (61) showed later that this second passivation was due to a pitting process, and identified the second passivation as the inhibition potential described by Schwenk.

The existence of an inhibition potential was also reported for iron in perchlorate solutions (61), for iron and nickel in ohloride plus nitrate solutions (61, 66, 75), for iron in chloride plus perchlorate solutions (61, 75), for iron in bromide plus perohlorate solutions (75), for iron in iodide plus nitrate solutions (75), for iron in iodide plus perchlorate solutions (75), and for nickel in bromide plus nitrate solutions (75).

Effect of temperature on the pitting potential

The pitting potential of stainless steels (40, 79, 93) and of aluminum (12, 39, 94) was found to decrease with an increase in the temperature. In the case of stainless steels, Kolotyrkin et al (23) reported that a break in the curve of Ep vs temperature was observed, and it was related, as described below, to a change in the sites for pitting.

The pitting of titanium, on the other hand, changes with temperature in a complex manner, and depends on the nature of the aggressive anion, as shown in Figure 5, (25).

As for the inhibition potential of stainless steels in mixtures of ohloride plus nitrate solutions, it was found to inorease when the temperature was increased (79).

Induction time, τ

When aggressive anions are injected in the passivating media, at constant potential, the metal remains passive for a certain time, and then pitting starts on the passive metal, with a noticeable inorease in the current density. The time spent between the injection of the aggressive anion and the start of pitting is called induction time, Figure 1-d, and has been measured in several systems.

Usually the passivating solution is a H_2SO_4 solution, and the aggressive anions are either chloride or bromide ions. Under these conditions induotion times have been reported for iron (37, 59, 95), for iron in caustic solutions (22), for nickel (65, 95, 96), for Fe-Cr alloys (38, 63, 64, 97), for Fe-Cr-Ni alloys (62, 63, 80, 98) and for aluminum (99). For iron and for nickel Strehblow (95) reported that the induction time was smaller when the prepassivation period was shorter. For Fe-13Cr alloy Broli et al (38) found that the induction time increased when the potential was decreased. Sato et al (80) reported that the induction time for stainless steel was a linear function of the potential.

Heusler and Fischer, ussing a ring-diso electrode, studied initiation for iron (37) and a Fe-5Cr alloy (97). They found that injeotion of chloride ions produced a currentless dissolution of Fe III, Figure 6. Probably it was the dissolution of the passivating gamma-Fe_2O_3. The consumption of this passivating layer would lead to pit initiation.

Effcot of temperature on the induction time

The reciprocal of the induction time, $1/\tau$, is taken as the rate of pit initiation, i.e. the number of events per unit time (62, 99). At constant

halide concentration $1/\tau$ is proportional to the constant rate, and we have the following relation:

$$\frac{1}{\tau} = A \cdot e^{-E_a/RT} \quad , \quad (i)$$

with A=constant, and E_a the activation energy of the process. Thus, a convencional Arrhenius plot of $\log(1/\tau)$ vs the reciprocal of the temperature will yield the apparent activation energy for the pitting initiation process.

For stainless steel in H_2SO_4+NaCl solution Hoar and Jacob (62) reported an experimental activation energy of about 60 kcal/mol. And for pure iron Foster and Hoar (100) reported an experimental activation energy of approximately 10 kcal/mol. For aluminum alloy type 7075, in H_2SO_4 plus halide solutions, Dallek and Foley (99) reported activation energies ranging from 4.6 kcal/mol up to 26 kcal/mol. No attempt has been made so far to correlate this activation energies with the mechanism of pitting.

Orders of reaction for pitting

The idea of orders of reaction for pitting was introduced by Hoar and Jacob (62), and it is based on the following assumption. It is supposed, as we said above, that $1/\tau$ is an approximate estimate of the rate of the breakdown process, "whatever it may be" (62). The rate equation is (99):

$$\frac{1}{\tau} = K \cdot (Me)^m \cdot (X^-)^n \quad , \quad (ii)$$

where K is the rate constant, (Me) is the metal atoms concentration, (X^-) is the halide ion concentration, and m and n are the respective orders of reaction. If K and (Me) are taken as constants, then the plot of $\log(1/\tau)$ vs $\log(X^-)$ will give the order of reaction n. Table I shows the orders of reaction reported for various systems. Hoar and Jacob suggested (62) that the order of reaction could be interpreted as being the result of the formation of a transitional complex on the metal surface. In their case complexes of three to four halide ions were suggested. In a similar way, Dallek and Foley (99) suggested for aluminum the formation of dissolved complexes of the

type: $Al_2Cl_8^{2-}$; $AlBr_4^-$; $Al(OH)_2Cl_2^-$; etc.

Some authors (103) criticize the validity of this approach to calculate the order of reaction for pitting. The criticism points to the fact that equation (ii), based on the Boltzmann's law, is valid for processes where many moleoular collisions are taking place at random, while in pitting the measurements are related to the formation of just a few isolated pits.

Heusler and Fischer (104) found that when iron is kept at a constant potential, and chloride ions are injected, a currentless dissolution of the passivating oxide film is observed at any electrode potential, immediately after chloride is added. The potential-independent dissolution rate exhibits large fluctuations with time, but the mean rate grows linearly with the chloride concentration. This observation is in agreement with the order of reaction $n = 1$ reported for iron in Table I. If this type of observation would be confirmed for the other pitting processes mentioned in Table I, then the reaction orders would not be related to a few localized pits, but to the general dissolution of the passivating film. Then, pits would appear in those places where the passivating oxide film is thinner, and would develop as an independent process.

Pitting initiation current densities

High current densities have been found for pit initiation and growth. For aluminum in NaCl solutions Kaesche (46) reported that the minimum current density inside the pits was recorded at the pitting potential and had a value of 0.3 A/cm^2. For aluminum in 4M NaCl solution, the current density in the pits increased with the electrode potential, following what seemed to be a logarithmic law with a slope of $b = 0.150$ V. At a potential 0.100 V over the pitting potential the current density inside the pits was close to 1.1 A/cm^2.

Szklarska-Smialowska and Janik-Czachor (105) measured the current density within pits for Fe-16Cr alloy in 0.7 N NaCl + 0.7 N H_2SO_4 solution. They found that the current density inside the pits was a funotion of

potential, and aocording to the interpretation made by Sato et al (80) it would follow a logarithmic law with a slope of b=+0.220 V. For the Fe-16Cr alloy Szklarska-Smialowska and Janik-Czaohor (105) reported a pit initiation potential of about 0.50 V(s.c.e.) and a pit passivation potential, Er, of -0.05 V(s.c.e.). From Sato's paper (80) it is inferred that the current density at the pit initiation potential was about 8.0 A/om^2, while at the pit repassivation potential it dropped to 0.1 A/cm^2. Novokovsky and Sorokina (106) reported, for pit initiation on stainless steel, current densities as high as 7 to 10 A/cm^3.

Sato et al (80) reported that in austenitio stainless steels, for potential higher than 0.60 V(s.c.e.) the current density inside the pits became potential independent, reaohing a value of 8 A/om^2.

For Fe-18Cr ferritic stainless steels with 0 to 5% Mo, in 1 N NaCl solutions, Galvele, Lumsden and Staehle (71) found that the mean current density inside the pits, at the pitting potential, was about 0.5 A/om^2.

Schwenk (91) working with Fe-18Cr-10Ni austenitic stainless steels, reported a current density inside the pits, at the pitting potential, of the order of 0.5 A/cm^2. He also found that the reaction inside the pit followed a Tafel law, with a slope of b=+0.087 V. For the same type of stainless steels Smialowska et al (107) reported that the current density, inside the pits would start, at the pitting potential, at a value about 1 A/om^2, and that it would drop with time and with potential.

For pure iron, Vetter and Strehblow (108) reported pit initiation current densities ranging from 0.9 up to 2.0 A/om^2. For the same metal Rousek (109) reported initial current densities of 1.7 A/cm^2, decreasing with time; and Butler et al (110) reported initial current densities of 0.5 to 1.0 A/om^2.

For nickel Tousek (109) reported pit initiation current densities ranging from 0.9 up to 3.3 A/cm^2.

Beck (25) reported for titanium that the current densitites necessary to initiate and sustain pitting in KBr solutions was about 1 A/cm^2. While for titanium in NaCl solutions the current densities necessary to initiate and sustain pitting were extremely high, of the order of 20 A/om^2.

From the above observations it is concluded that, in the initiation process, current densities of the order of the A/cm^2 are involved.

Simultaneously with the anodic dissolution process, the evolution of gas bubbles from the pits has been reported by various authors (46, 54, 82, 111, 112). It was found that the amount of gas evolved was equivalent to about 10% of the total anodic current (111, 112).

Pitting nucleation sites

The nucleation sites of pits were found to be related frequently to microscopic features of the metal surface. For example, for stainless steels (23, 30, 31, 113, 114) it was found that the location of the pits is usually related with the presence of inclusions. Smialowski et al (113) reported that pits are initiated at non-metallic inclusions, being the mixed manganese sulphide inclusions the most effective. According to these authors, in absence of the sulphide inclusions, the chromium oxide particles can nucleate the corrosion pitting.

According to Kolotyrkin et al (23), at temperatures around 20° to 35°C, pits on stainless steels were nucleated on inclusions of mixed oxides containing, apart from oxigen, some two to four elements, such as Si, Ca, and more rarely Al and Mg, with traces of S, K, and P. No Ti or Mn appeared in any of these inclusions. At 95°C, on the other hand, pits were nucleated on particles composed by many-component oxysulfides, and, apart from O and S, they contained at least five to seven elements, among whioh were always Mn and Ti.

Glazoova et al (30) found for Fe-Cr-Ni-Si stainless steels containing silicon oxide inclusions that the pits nucleated preferentially on the silicon oxide particles.

Janik-Czachor et al (114) studied the effect of nitrogen on the pitting behavior of 18Cr-5Ni-10Mn stainless steel. They reported that the most susceptible sites for pit nucleation were boundaries between the austenite matrix and some second-phase precipitates, presumably carbides.

For low alloy steels the preferential sites for nucleation of pits were found to be manganese sulfide particles (9, 21, 115). For nickel

it was reported that the pits nucleate either on soratches of the surface, on grain boundaries (116), or on Ni_3S_2 inclusions (117).

Kolotyrkin et al (31) suggested that the preferential nucleation of pits on sulfide partioles was due to a catalytic action of the sulfide ions.

Effect of alloying elements on the pitting potential

The pitting potential of a metal is strongly affected by alloying elements. This effect has been described by previous reviewers (1, 2). For example, for stainless steels, it is known that chromium increases the pitting potential of the alloy (24, 35, 44, 79, 118), nitrogen is also beneficial (44, 114, 119), as well as nickel (24), molybdenum (56, 71, 120-123), silicon (120), vanadium (120), rhenium (5, 120), etc.; while alloying elements like manganese and sulfur were detrimental (119, 124). Nitrogen would inhibit pitting of stainless steels by inhibiting the acidification of the solution inside the pit. The presence of NH_4^+ was detected inside the pits (44) and the production of this cation would consume hydrogen ions present in the media.

In the case of aluminum, it is known that the pitting potential is increased by copper (51, 125, 126) and manganese (127), it is decreased by zinc (125, 128, 129), mercury (127), tin (127), galium (127, and indium (127), and it is slightly affected by magnesium (125, 128), silicon (129), chromium (127), iron (127), etc.

Pit-border morphology

For a detailed model of pit initiation and propagation it is important to know how the transition from fast dissolution to passivity takes place at the border of the pits. According to Vetter and Strehblow (130), the edges of the pits are sharp, and the transition from fast dissolution to passivity takes place in a distance smaller than 10^{-6} cm, Figure 7-a. This description cannot be taken as a general property of pitting, as these authors suggested, since covered pits have been reported in many cases, as for example for stainless steels (91, 106, 131-136), for nickel (69, 133, 137-139) and for iron (133). Yahalom, Ives and Kruger (140) have shown that the film

covering the openings of the pits was the original passive film. Then, it is found that in many cases of pitting, a model like the one in Figure 7-b would give a better description of the pitting process. The potential gradients, concentration gradients, and pH changes calculated by Vetter and Strehblow (130) for the borders of pits of the type shown in Figure 7-a would not apply to pits of the type in Figure 7-b. More substantial solution composition changes should be expected for pits of the second type than those for type a.

Minimum concentration of aggressive anion

Several authors have reported the existence of a minimum concentration of the aggressive anion, below which no pitting is observed. Part of these data is shown in Table II. Broli et al (38) rised doubts about the validity of the extrapolation techniques for determination of the minimum chloride concentration. These authors suggested that the extrapolated values were not the same at every potential.

With regard to the chemical-depassivation type of pitting, it is interesting to look at the polarization curves of Nobe and Tobias (67), Figure 2. It is found that iron could not be passivated in H_2SO_4 solutions if the media contained a small amount of NaCl, but normal passivation could be found if the H_2SO_4 solution contained less than 0.001 M NaCl. Similarly, Piron et al (68) reported for nickel in 1 N H_2SO_4 solution, Figure 3, that the presence of 0.017 M NaCl (0.1 % NaCl) produced an increase of almost two orders of magnitude in the passive current density. When the content of NaCl in the solution was raised to about 0.085 M, the passive zone for nickel was completely lost. Thus, the minimum chloride concentration for pitting is that which will not affect the polarization curve of the metal in an acid medium.

Aggressive anions

In most of the published work on pitting of metals, chloride ion has been used as the aggressive anion. Nevertheless, it is well known at present that many other anions can act as aggressive anions. Table III shows some of the aggressive anions reported in recent literature. From this table

it is concluded that for those metals forming highly insoluble oxides, only anions of strong acids are aggressive, while for those metals forming less stable oxides, like zinc or manganese, anions of relatively weak acids can also produce passivity breakdown.

Effect of the aggressive anion concentration on Ep

It is usually observed that the pitting potential of a metal is lowered by increasing the concentration of the aggressive anion. In general, a relation of the type:

$$Ep = A - B \log C_X \qquad \text{(iii)}$$

is found, where A and B are constants, and C_X is the aggressive anion concentration. Table IV shows a compilation of B values found in recent literature. Galvele (148, 149) has shown that if the migration of the chloride ions inside the pit is the only variable considered, a value of B = 0.059 V is obtained. The contribution of other factors could lead to higher B values. When buffers are used in the measurement of C_X vs Ep the slope B can be affected by the change in the buffer/C_X ratio. As shown by Augustynski (14) and by Heusler and Fischer (37), Figure 8, a change in the buffer concentration at constant C_X, will produce a change in the pitting potential. Also Böhni and Uhlig (47) have shown that above a certain Weak Salt/C_X ratio pitting is inhibited. The value of B also depends on the type of buffer used (37, 66), as shown in Figure 9. The value of B could also be affected by the measurement technique. It has been reported (45) that values of B obtained by potentiokinetic techniques were higher than those obtained by potentiostatic techniques.

Effect of pH on Ep

There is no general agreement about the effect of pH on the pitting potential. It was found in several systems, and in a wide range of pH values, that the pitting potential is not affected by the pH of the solution (46,61,66,87,145). On the other hand, several authors reported pH effects that range from small changes in the pitting potential, to a complete inhibition of pitting

For iron in chloride solutions Strehblow and Titze(66) reported that there were no changes in the pitting potential for pH values from 8 up to 13. On the other hand, Heusler and Fischer(37) reported, for iron in chloride solu-

tions, that the pitting potential was independent on the pH on a wide range of pH values, but that no pitting could be found for a pH higher than 10.4. Alvarez and Galvele(76) working with pure iron in NaCl solutions found that the pitting potential measured galvanostaticaly, was constant for pH values from 7 to 10, but increased with the pH for pH values higher than 10, Figure 10.

Augustynski et al(14) reported that the pitting potential of zinc in perohlorate solutions increased with an inorease in the pH. The effeot of the pH was higher the lower the concentration of the aggressive anion.

For aluminum in perohlorate solutions(82) the pitting potential reported at pH 7 was -0.04 V, while in perohloric aoid solution, of the same concentration, it was found that the pitting potential was 50 mV lower.

The inhibition of pitting in strong alkaline solutions has been reported by various authors. It was found(17) that pitting of iron in alkaline NaCl solutions was inhibited when the ratio of Cl^-/OH^- concentrations was equal to or higher than 1/1. For austenitic stainless steels it was reported (48, 147) that the pitting potential was not affected by the pH over a wide range of values, but inhibition of pitting was found for pH values higher than 8. For nickel in KCl solutions, Prazhak et al (118) reported that the pitting potential of the metal increased linearly with the increase of the logarithm of the NaOH concentration.

Inhibitors for pitting

One important property of pitting processes is that they can be inhibited by certain anions present in the aggressive solution. For example, Kolotyrkin et al (81) reported for iron that an increasing ratio of sulfate to halide ion concentration, in the aggressive solution, inoreased the pitting potential. The effect of the ratio of sulfate ion to chloride ion concentration on the value of pitting potential was also described by Rosenfeld and Danilov (131) and by Leckie and Uhlig (48) for stainless steels, by Kolotyrkin and Gilman (27) for zirconium, by Szklarska-Smialowska (69) for nickel, by Böhni and Uhlig (47) and by De Micheli and Galvele (50) for aluminum, and by Dugdale and Cotton (146) for titanium. The effect of $SO_4^=$ ions on pitting in Cl^- solutions was explained by Galvele (149) as being due to the preferential

accumulation of $SO_4^{=}$ ions inside the pits by a transport process.

Several inhibitors for pitting of aluminum were studied by Böhni and Uhlig (47) and by De Micheli and Galvele (50). Leckie and Uhlig (48) studied inhibitors for pitting of stainless steels, and Uhlig and Gilman(150) and Schwenk (91) reported that nitrate ions inhibited pitting of stainless steels in chloride solutions but not in bromide solutions (91). Awad and Hoar (6) found that the pitting potential of mild steel in chloride solutions increased by the addition of sodium carbonate or mixtures of sodium bicarbonate plus sodium phosphate.

As we saw above (37) the pitting potential of iron in chloride solutions was a function of the concentration of the buffer. Augustynski et al (14) found that the higher the concentration of the borate buffer, the higher the pitting potential of zinc in chloride and in perchlorate solutions. According to Wilson (151) buffers inhibit localized corrosion by preventing marked changes of pH on the metal surface.

Use of buffers in pitting measurements

The use of buffers is the usual approach in chemistry and in electrochemistry when changes in pH are to be avoided. This use is made with the implicit assumption that buffers will not interfere with the process under investigation. Buffers have been used by many authors in the study of pitting (9, 14, 37, 46, 61, 66). Nevertheless the assumption that the buffer does not interfere with the studied process is not valid in the case of pitting corrosion. It was shown (149) that for neutral or alkaline solutions substantial pH changes will take place inside the pit, at the very initial stages, and even in the presence of buffers. This fact invalidates the use of buffers in pitting corrosion studies. On the other hand, we saw above that the buffers act as inhibitors for pitting (14, 37, 151) and that they even modify the type of film formed on the metal, like in the case of iron in phthalate buffer(66).

All this shows that when developing a model of pitting, it must be taken into consideration that buffers, if present in the solution, will influence the mechanism in study.

Effect of the scanning rate on Ep and Er

The pitting potential, Ep, can be measured, among other techniques, by potentiostatic and potentiokinetic methods. Several authors have studied the effect of the potential scanning rate on the pitting potential (4, 9, 13, 28, 45, 91). The general conclusion was that a high scanning rate produced a high pitting potential, and it was suggested that very slow scanning rates, or potentiostatic techniques, should be used for the measurement of the pitting potential. The Ep measurements made by scanning techniques usually show big scattering. The probability distribution of this pitting potentials for stainless steels was studied by Sato (152) and by Shibata and Takeyama (15, 153). According to Shibata and Takeyama, the pitting potentials measured under these conditions are controlled not by an electrochemical process, but rather by an electromechanical breakdown of the passive films. It has been reported (29) that the high pitting potential values obtained under such unstable conditions are reduced if the samples are irradiated with ultraviolet light. The Ep values obtained under stable conditions are not affected by the ultraviolet light.

As for the pitting repassivation potential, Er, it was found for aluminum (13, 125) that the higher the scanning rate, the lower the pitting repassivation potential. For stainless steels, on the other hand, Hisamatsu (89) reported that the higher the scanning rate, the higher the repassivation potential Er. Since it is also known (19) that the repassivation potential is a function of the size of the pits, we conclude that there is no general agreement with regard to what is the most reliable method for measuring Er.

THEORIES OF PITTING

We have seen above the most frequent observations of the pitting processes. We will see now the most common mechanisms proposed for pitting, and the experimental evidences either in favor or against these mechanisms.

Flaws and oxide film defects

There is abundant experimental evidence pointing out that pit nucleation is somehow related to the presence of defects in the oxide film. As regards to the formation of those defects, they may be easily produced,

they may pre-exist in the oxide film, or they may be continuously produced by a dynamic process of film rupture and repassivation.

It is known that pit formation is strongly affected by the surface preparation technique (15, 154). Besides, using iron whiskers, it was found (8) that pitting depends on the degree of twisting of the iron whisker, indicating that in this case pits grow only when breakdown of the passive film occurs at the emergent dislocation sites introduced by twisting. It is also known that passive films which have not reached the steady state are more sensitive to chloride attack than those prepassivated for a longer time (52, 64, 108), Figure 11. Frequently (95, 108, 130) pit nucleation is favored by a potential change in the positive or negative direction. This suggests that potential changes introduce defects in the passive film. On the other hand, noise analysis of passive films, at constant potential, either in presence or in absence of aggressive anions, suggest that in the passive film there is a dynamic balance between film rupture and selfrepair (155-157).

As for the way by which this breakdown takes place, some theoretical explanations have been attempted. Sato (158) reported that breakdown of anodic films on metals can be produced through electrostriction pressure. Fromhold (159) suggested that the migration of ionic species through a compact anodically-produced passive film produces stresses large enough to cause plastic deformation or mechanical breakdown of the passive film, and that the stresses could transform a crystalline structure into an amorphous form. Another explanation for the initiation of pits at specific sites is offered by Wood et al (160, 161). These authors suggest that pitting starts at flaws in the oxide film, and that those flaws are already present when the metal is immersed in the aggressive solution. Nevertheless, Wexler and Galvele (54) have shown that neither the existence of preformed flaws, nor the mechanical breakdown of the passive film, would explain by itself pitting nucleation in the electrochemical-depassivation type processes. When the passive film is intentionally broken, for example by straining the metal, no pits are nucleated on the slip steps if the potential is lower than the pitting potential, Figure 12 (162). On the other hand, if straining is done at a potential higher than the pitting potential pits will nucleate on the slip steps (162),

Figures 13 and 14. The above observations were made with aluminum straining. at constant potential, in NaCl solutions and in $NaNO_3$ solutions. Similar observations were made on zirconium strained in NaCl solutions (85); the same conclusions were reached through the use of surfaoe soratching techniques on zinc (52), cadmium (53), iron (76), and nickel (76).

As for the chemical-depassivation type, Heusler and Fischer (37, 97,104) have shown the existenoe of a currentless dissolution of FeIII during the induction time, Figure 6. If to start pitting, in this cases, it is necessary to dissolve first the passivating film, then the role of the film breakdown in pit initiation is not olear. If, on the other hand, pits initiate on flaws and other deffeots as soon as the chloride ions are injeoted in the solution, then it is not clear why Heusler and Fischer could not detect Fe II during the induction time. It is known that Fe III is produced by the passive zones and FeII originates in the pits (59). This is clearly an area were more research should be done.

Ion migration and oxide film contamination

One of the first questions that appears when studying pit initiation is what happens to the composition of the passivating oxide film, when it is exposed to the action of the aggressive anions. Several mechanisms have been proposed on ion migration and contamination of the oxide films. Some of them have been criticized, but it is only now that new surface analysis techniques are available, that direct information about contamination processes can be obtained. Nevertheless, as we will see below, contradictory information has been published, and more research is necessary in this field.

The migration of chloride ions into anodized aluminum films has been studied by Pryor et al(163) using impedance measurements. These authors suggested that chloride ions entered the film by a substitution process. Hoar Mears and Rothwell (164) suggested that in solutions containing chloride ions, at and above the pitting potential, there was a field-stimulated anion entry into the passivating oxide film at singular points. Nevertheless, Vetter and Strehblow (130) pointed out that a migration polyatomic aggressive anions such as $SO_4^=$, ClO_4^-, or SCN^- through a solid layer was not conceivable.

Mc Bee and Kruger (165), through ellipsometric studies on pure iron, found that the injection of chloride ions in the media produced changes in the properties of the oxide film, probably by penetration of the film. The changes were reversible, and the properties of the oxide film were recovered after removing the chloride ions from the media. The same authors (166) found that there were also changes in oxide films on Fe-Cr and Fe-Cr-Mo alloys, when exposed to chloride ions. The changes were less pronounced than those found with pure iron. The Fe-Cr film did not recover its properties after removal of the chloride ions. The presence of Mo in the alloy did not change the properties of the oxide film in the presence of chloride ions.

Lumsden and Staehle (167) made Auger electron spectroscopy (AES) measurements of Fe-25Cr-1 Mo and Fe-25Cr-5 Mo alloys polarized in a neutral 1 M Na_2SO_4+1 M NaCl solution. No molybdenum enrichment was observed in the passive film of either alloy, and some chloride was detected near the surface film. The amount of chloride ions present was very small, and the penetration was only a few atom layers beneath the surface.

Szklarska-Smialowska et al (168) by X-ray electron spectroscopy (ESCA) and AES observed, for iron exposed in a borate buffer plus 0.1 M KCl solution, that chloride ion was present only at the passive metal surface, and it was rather weakly bonded to the passive film.

The above observations would indicate that for iron and iron alloys there is no penetration of chloride ions in the passive film. Another metal on which extensive surface analysis was performed is aluminum. In this case the results published are contradictory. While some authors reported contamination of the oxide film, others claimed that no such contamination could be detected.

Abd Rabbo et al (160) using secondary ion mass spectroscopy (SIMS) for aluminum samples covered with ca. 7.2 10^{-6} cm thick barrier type anodic film, found that a substantial amount of chloride ion was detected at the oxide-solution interface, but no chloride ion was detected through the bulk of the material itself. They also reported (169) that although there was no penetration of chloride ions in the aluminum film, incorporation of chromate and phosphate ions was detected. On the other hand, Maitra and

Verink (170) using AES found chloride ion migration in aluminum exposed to chloride ions solution, Figure 15, confirming the results by Pryor et al (163).

Painot and Augustynski (144) studied by ESCA the anodic films of aluminum formed in various solutions. They found that sulfate ions were incorporated in the films formed in sulfate solutions. Incorporation of chloride ions was found in films formed in chloride solutions and in perohlorate solutions. No ClO_4^- ions could be detected in the films formed in perohlorate solutions, and the presence of chloride ions indicated that the ClO_4^- ions underwent reduction inside the aluminum oxide film.

Koudeltova et al(171) studied aluminum films formed in presence of chloride plus chromate ions by ESCA. They reported that the chromate ion had no special merit in preventing the chloride penetration of the protective oxide film. The amount of chloride ion in the film formed in chromate plus chloride solutions was similar to the one produced in absence of chromate ions. On the other hand, chromate ions underwent reduction in the oxide film.

Augustynski et al(172) reported, from ESCA studies on aluminum immersed in nitrate solutions that no nitrate ion could be found inside the film, but that nitrogen containing species were present, indicating that nitrate underwent reduction inside the film.

Competitive adsorption

Several authors have suggested that competitive adsorption is an important condition for pitting initiation. Pitting starts with the adsorption of aggressive anions on the metal surface and displacement of the adsorbed passivating species (18, 27, 36, 47, 48, 66, 79, 118, 131, 138, 173). This mechanism is intimately related to the idea that passivity is caused by an adsorbed monolayer of oxygen or another passivating species. This idea has lost ground from the moment that it was found that passive films in general are not adsorbed monolayers of oxygen, but rather tridimentional oxide films. On the other hand, it was difficult to explain, based on competitive adsorption ideas, why, for example, chromate ions inhibit pitting of aluminum in chloride containing solutions, without changing the chloride content in the oxide film (171), or why it is that perohlorate ions adsorb preferentially inhibiting pitting

of iron in chloride solutions, at low potentials, but act as aggressive anions at higher potentials (66), or why nitrate ions adsorb preferentially inhibiting pitting of aluminum in chloride solutions (50), and again by competitive adsorption, produce by themselves pitting of aluminum at a different potential(10).

There is, however, a possible way by which adsorption can play an important role in the mechanism of pitting. As we will see below, under certain circumstances there is no doubt that salt films are formed inside the pits, with the dissolution rate of those salts accounting for the propagation rate of the pits. It is known that the dissolution kinetics of salts is greatly affected by the presence of contaminants adsorbed on the salt surface. There are cases where a contaminant could accelarate the dissolution rate of a salt(174), while in others the adsorption of various ions inhibited the dissolution rate of the salts(174-176). For example, inhibition of pitting of stainless steels in chloride solutions by molibdate ions(177) could be explained by adsorption of the molybdate ions on a $CrCl_3$ layer inside the pits(71).

Nucleation of pre-pits

Janik-Czachor et al(7), working with high purity iron, found that at potentials lower than the pitting potential there was a local accumulation of chloride ions on the metal surface. These authors suggested that this local chloride accumulations could be pre-nucleis of pits, and that their formation could be a necessary condition for pit initiation. The existence of such prepits was supported also by Heusler and Fischer(37), but it is not known so far if this is a general property of pitting.

Critical concentration of chloride ions

Various authors(26, 77, 81, 90, 109, 136) have suggested that there is a critical concentration of chloride ions to start pitting. Only when such concentration is locally exceded will pitting start. The idea of a significant change in concentration of chloride ions at the initial stages of pitting does not agree with transport calculations for small pits (108, 148, 149). Besides measurements of the composition of the electrolyte inside the pits(132) showed that chloride concentration increased with the size of the pits, reaching a

maximum conoentration (6 to 12N) when a pit size of about 0.5 mm diameter was obtained. For smaller pits there was a rapid decrease in the ohloride conoentration, and eventually it would be expected that at the very small pits the conoentration of chloride ions inside the pits would be very close to that of the bulk solution.

It is important to notice that if the key factor is not the build up or chloride ion alone, but the accumulation of chloride ions plus other corrosion prodructs, as suggested by Freiman et al (77), this mechanism oould hardly be distinguished from the localized aoidification meohaniem desoribed below.

While there is no clear proof that local chloride ions accumulation is responsible for pit initiation, it seems olear at least that, as shown by Hisamatsu et al (90,136), local chloride ions accumulation plays an important role in accelerating pit propagation in stainless steels.

Salt film formation and pitting

According to some authors (108) pit initiation is olosely related to the formation of a salt layer on the metal/solution interfaoe. There are evidences that in many cases of pitting important ohmic drops are located on the metal surface inside the pit. The ohmio drop was attributed to a salt film, and the presence of such film was generally connected to an hemispherioal morphology of the pits. In the absenoe of such films orystallografio etching is usually found.

Evidence was found on the existence of an important potential drop on the metal surface inside pits in titanium(25, 112). Beck(25) suggested that the ohmic drop was due to the presence of a salt film of titanium tetrahalide (or oxyhalide) on the metal surface inside the pit.

Schwenk (91) found a high Tafel slope for the current density inside the pits of stainless steel, and suggested that the polarization effect was probably due to a film on the pit surface. Isaacs (43) estimated the thickness of that film in about 10^{-6} cm.

Gary et al (72) observed the formation of a green orystal layer on nickel electrodes anodized in a $NiCl_2$ solution, as it would be the case

inside a pit. Galvele, Lumsden and Staehle (71) applied AES analysis on molybdenum containing ferritic stainless steels anodized in acid chloride solutions, and found a high concentration of chlorine in the film, Figure 16. No such chloride enrichment was found on stainless steels anodized in neutral chloride containing solutions (167).

Let us see now under what circumstances a salt layer could be formed on a metal surface, and what could be its dissolution rate. It was reported that the dissolution of iron in acidic chloride solutions leads to the formation of a $FeCl_2$ layer (178,179). Nevertheless, induction time studies have shown (178, 179) that supersaturation was necessary on the metal-solution interface, before the salt film initiated precipitation on the metal surface. In a similar way, Alkire et al (180) found on copper artificial pits that extended periods of dissolution lead to precipitation of a salt on to the electrode surface, owing to supersaturation of the solution. From transport considerations (149) it was found that supersaturation conditions could not be reached during pit initiation with current densities of the order of some units of A/cm^2. According to this, in most cases of pitting the salt layer formation would not take place during pit initiation but during pit propagation. Current densities as high as 100 A/cm^2 would be required to reach supersaturation in, for example, a 10^{-6} cm long diffusion path.

As for the expected dissolution rates, the dissolution rate of a crystalline salt is function of the solubility of the salt. The higher the solubility the higher the dissolution rate (181-183). According to Shchukarev's equation (183) the rate of dissolution of salts in water is proportional to their solubility:

$$v = K \cdot C_{sat} \qquad \text{(iv)}$$

being v the dissolution rate, K a constant, and C_{sat} the solubility of the salt in the solution.

If a salt layer is formed inside the pit, and a steady state is reached, the thickness of the film will remain constant with time. That means that the anodic current leading to the salt formation should be compensated by the dissolution rate of the salt. If the salt formation current density is lower than the dissolution rate, the salt will be consumed by dissolution.

On the other hand, if the current density is higher than the dissolution rate, accumulation of salt will take place on the metal surface, hindering further current circulation, and the system will reach a stationary state.

From the kinetic data on dissolution rates of salts, published by Karazhanov et al(182) it is found that the dissolution rate, for example, of NaCl is equivalent to a current density of 12 A/cm^2, and that of NaI is 21 A/cm^2. While for a less soluble salt, like LiF, the value would be 5.8×10^{-2} A/cm^2. Since the dissolution rates vary in parallel with the solubilities, and decrease in the same order, it would be expected that, as found by Augustynski for zinc (14), those anions giving high solubility salts would produce passivity breakdown. In the above treatment we have assumed that the film was an anhydrous salt layer. It could also be some oxyhalide layer, or a similar compound. There is no sufficient information available to be certain about the composition of the layer. Nevertheless, it is clear that, in view of the high current densities involved it must be a highly soluble substance.

There are two other factors that should be considered. One is the overpotential necessary to reach a current density that would balance the dissolution rate. The other, is how to avoid precipitation of metal hydroxides over the salt layer, due to hydrolysis of the metal ions.

In several cases (21, 52, 53, 76) it has been reported that the pitting potential is very close to the corrosion potential of the metal in the acidified solution. In those cases pitting growth takes place under low current densities, of the order of 10^{-1} A/cm^2, and most probably the metal inside the pit is undergoing active dissolution without any salt films. In such cases rough surface pits should be found. On the other hand, when pits are grown with higher polarizations, the supersaturation conditions inside the pits could be reached, and the metal will dissolve through a salt film. The current density inside the pit could change with the potential, since it was found that the dissolution rate of a salt is accelerated by the presence of an electric field (184).

As for the hydrolysis problem, the only way of avoiding precipitation of hydrolysis products over the salt film is to have a sufficiently acid solution inside the pit. For most metals, when working in alkaline or

in neutral solution, this acidification will be found only when the anion of the salt belongs to a strong acid. This leads to the observation made by Hoar (186) in 1937 that only salts of strong acids will act as aggressive anions. This subject will be discussed in more detail below.

Those variables affecting the dissolution rate of the salt film will also affect the pitting behavior of the metal. For example the dissolution rate of $CrCl_3$ is accelerated by reducing agents like Cr II, and it is inhibited by oxidizing agents (175). This property could explain the beneficial effect of molybdenum on the pitting resistance of stainless steels in chloride solutions. The molybdenum, which is not enriched in the film (167), would be oxidized to molybdate, and the molybdate adsorbed on the $CrCl_3$ salt layer will inhibit its dissolution rate (71). Inhibition of dissolution rate by adsorption of ions has been reported in the literature (175, 176).

Localized acidification

One mechanism of pitting, that applies to the electrochemical depassivation type of pitting, says that pitting starts as a result of the localized acidification that takes place on the metal-solution interface, and that hinders the reformation of the passive film.

For the analysis of passivity breakdown, the following facts should be considered (52, 54). When a metal dissolves in an electrolyte containing anions of a strong acid, the following reactions will take place:

$$Me = Me^{z+} + ze \qquad (v)$$

followed by:

$$Me^{z+} + zH_2O = Me(OH)_z + zH^+ . \qquad (vi)$$

If the electrolyte is an alkaline unbuffered solution, the pH of the solution near the anode will drop. The maximum pH drop expected should be given by reaction (vi) at equilibrium, and will depend on the solubility of the metal hydroxide. Similar results should be obtained if, instead of an hydroxide, an oxide is formed.

If a in Figure 17 is the initial pH of the solution, and b the pH in the locally acidified zone, pitting will occur only when reaction (v) becomes thermodynamically possible, i.e. pitting will start at a potential

higher than $\underline{a}_2$. Between $\underline{a}_1$ and $\underline{a}_2$ only the reaotion:

$$Me + zH_2O = Me(OH)_z + zH^+ + ze \qquad (vii)$$

will take place, and the metal will repassivate. Above the potential $\underline{a}_2$, the localized acidity produced by reaotion (vii) could give the oonditions for reaction (v) to occur. This reaction, followed by reaction (vi) will maintain the acidity near the metal surface.

Aocording to Figure 17, the pitting potential of the metal will be given by the equilibrium potential of reaction (v). Such a meohanism was proposed by Van Muylder, Pourbaix and Van Laer (186) for the pitting potential of copper, but it failed when applied to metals with equilibrium potentials outside the range of stability of water, such as iron, aluminum, zino, etc., or when reduoible anions, such as nitrates, were present in the solution. This mechanism was modified by Galvele <u>et al</u> (21, 51-54, 128, 1481 149) to explain the pitting potential of metals like zino, aluminum, oadmium or iron, and the pitting potentials found in presence of reducible anions or inhibitors.

The main point in the above desoribed mechanism is that there exists heterogeneity in the solution, close to the dissolving metal surfaoe. The perpetuation of this heterogeneity is a necessary condition to maintain the dissolution process. When the steady state is reached, the rate of proton pruduction, (v) plus (vi), will be equal to the rate of proton consumption. In an unbuffered NaCl solution, there will be two processes reponsible for the proton consumption. One will be the hydrogen evolution reaction:

$$2H^+ + 2e = H_2 \qquad (viii)$$

and the other will be proton diffusion from the anodic zone to the bulk of the solution:

$$H^+_{(anode)} \xrightarrow{\text{diffusion}} H^+_{(bulk\ solution)} \qquad (ix)$$

The rates of reaotions (v), (vii) and (viii) are potential dependent. If reaction (vi) is fast, reaction (v) will give the rate of proton production, and the higher the potential, the higher the rate of proton production will be. On the other hand, the lower the potential, the higher the rate of reaction (viii), <u>i.e.</u> the rate of proton consumption. The potential at which the rates of reaotions (v) and (viii) are equal is the corrosion potential

or open circuit potential of the metal in the acidified solution close to the anode, E_c^*. This potential could be measured in a separate experiment, by exposing the metal to a solution resembling that near the anode. If the metal in the alkaline, unbuffered solution, is exposed at a potential equal to E_c^*, no localized acidity can be produced, since at such potential the rate of reactions (v) and (vi) will be equal to the rate of reaction(viii), and no net production of protons will take place. Meanwhile, process (ix) will dissipate any previously existing localized acidity. Then at any potential up to E_c^*, the metal will form proteotive oxide films, and any disruption of the oxide film will lead to its reformation. At potentials higher than E_c^*, the filmed metal will be under an unstable condition. A disruption of the oxide film could result from a meohanical or electrochemical action, as described above. Once bare metal is exposed to the solution no protective film will be reformed. The idea that E_c^* is a limiting potential for pit growth agrees with the experimental observation made by Kitamura and Suzuki (42), who found that pit growth in austenitic stainless steels occurs only at potentials more noble than the open circuit potential of pit anodes.

A different picture is found if instead of working in a solution of an indiferent anion of a strong acid, like NaCl solution, a reactive anion is used. In $NaNO_3$ solutions, for instance, not only reactions (v), (vi), (vii), and (viii) will have to be considered, but also a new reaction:

$$NO_3^- + 10\ H^+ + 8e = 3\ H_2O + NH_4^+ \quad . \qquad (x)$$

Reaction (x) is proton consuming, the same as reaction (viii), and localized acidity in $NaNO_3$ solutions will take place at potentials much higher than in NaCl solutions. A new E_c^* value will apply in this case, and it will be the open circuit potential of the metal in acid nitrate solutions. As observed by Alvarez and Galvele (52), passivity breakdown of zinc in 1M $NaNO_3$ solutions only occurs at potentials higher than -0.66 V(n.h.e.), while the open circuit potential of zinc in 1 M HNO_3 solution was found to be between -0.66 and -0.65 V(n.h.e.).

Any other impediment for the formation of the locally acidified zone will produce inhibition of the pitting process. This is the case when buffers are present in the solution. In this case the higher the concentration

of the buffer, the higher the pitting potential will be.

Vetter and Strehblow (108, 130) questioned the meohanisms of pitting based on local changes in the composition of the solution, on the grounds that no signifioant changes oould be expected at the initial steps of pitting, when the pits were very small. Galvele (148, 149) repeated the calculations made by Vetter and Strehblow, ussing a simplified model for a pit, and taking into account the hydrolysis of the metal ions, and found that, although the chloride ion changes were not significant in the initial stages of pitting, the pH changes were very important, even for the earliest stages of pit growth. From this calculation concentration diagrams for ions inside the pits were obtained, Figure 18. To determine the conditions of pit initiation, a value had to be chosen for the critical H^+ concentration above which pit would start. In a first approximation the same criteria used by Pourbaix for his diagrams (187) was applied here. The critical acidification was assumed to be equal to the pH at which the passivating oxide film is in equilibrium with a concentration of 10^{-6} M of the metal ions. Calculations were made for zinc, nickel, cobalt, aluminum and chromium, and in all the cases it was found that the critical acidification was reaohed for $\underline{X}.\underline{i}$ values aproximately equal to 10^{-6} A/cm. Being $\underline{X}$ the depth of the pit, in cm, and $\underline{i}$ the current density in the pit, in A/cm^2. For current densities of the order of 1 A/cm^2, a pit size of 10^{-6} cm will be big enough to have at the bottom the critical acidification. By this diagrams it was possible to explain the effect of the buffer ion conoentration on the pitting potential (Figure 19) the effect of the OH^- on the pitting potential, (Figure 20) the existence of a repassivation potential, Er (Figure 21) as well as the effect of the aggressive anion concentration on the pitting potential, and the passivating action of $SO_4^=$ ions on Cl^- ions pitting.

The explanation for the existence of a repassivation potential is obtained in the following way. As mentioned above, the oxide film on the passive metal will suffer continuous breaks, thus exposing metal to the solution. The current density circulating in those fissures will be a function of the electrode potential. At each potential the cracks in the oxide film will show a characteristic $\underline{X}.\underline{i}$ value given by the current density and the

length of the crack (Figure 21-a). As soon as the system reaches the critical $\underline{X.i}$ value, $\underline{X.i} = 1$ in Figure 21, the pit will start to grow. If the potential remains constant, the current density will also be constant, but $\underline{X}$ will increase with time, as will do $\underline{X.i}$ ($\underline{X.i} = 2$ in Figure 21). If the potential is then lowered, the current density will drop, but the pit will continue to grow while the $\underline{X.i}$ value is higher than 1. This means that pits will grow at potentials lower than the initiation potential. Finally the pit will stop growing either because the value $\underline{X.i}$ is lower than the minimum for pit growth, or because the electrode potential is lower than E_o^*. This mechanism explains the observation made by Suzuki and Kitamura (40) that the deepest the pit the lower was the repassivation potential.

As for the inhibition potential, Ei, there is not sufficient data available, but the explanation of such potential, from the point of view of the localized acidification would be the following. The metal inside the pit will behave as a metal in an acidified solution. In certain acidified solutions, like HCl solutions, metals like iron will dissolve at high overpotentials with very high current densities, and an increase in the overpotential will produce a monotonic increase in the current density. In H_2SO_4 solutions, on the other hand, there will be not a monotonic increase in the current density with the overpotential. There is a potential above which the dissolution of the metal will be drastically reduced, and the metal will became passive. In the case of a pit, for example for iron in Na_2SO_4 solutions, when the electrode potential reaches the value of passivation of metal in the acid solution, the metal inside the pit will become passive and the pitting will stop. Then the pitting inhibition potential, Ei, should be close to the passivation potential of the metal in the acidified pit-like solution. Figure 22 shows the Ei values reported by Vetter and Strehblow (61) for iron in perchlorate and in sulfate solutions. It was reported that the pH inside the pits in iron is between 3 and 4 (188). As it is shown in Figure 22, there is a very good correlation between the reported Ei values and the passivation potential for iron in a pH 3-4 solution.

As we have seen above, there is a potential below which no localized acidification can be mantained on the metal/solution interface. This potential is given by the corrosion potential of the metal in the

acidified solutions, E_c^*. When measuring the pitting potential, a positive polarization, η, is added to the corrosion potential to maintain a net anodic current density inside the pit, and secure the minimum $\underline{X.i}$ value. From transport considerations (149) it was concluded that a further contribution has to be accounted for, due to the effect of inhibitors in the solution, E_{inh}. Finally, since the current density inside the pits is high, there is a contribution due to the electrical potential, ϕ, that must be added. In this way, the measured pitting potential is the total of the above mentioned factors:

$$E_p = E_c^* + \eta + E_{inh} + \phi \quad . \qquad \text{(xi)}$$

The alloying elements will change the value of the pitting potential mainly by changing the values of E_c^* and η. Equation (xi) has been tested with binary aluminum alloys (128) and with ferritic stainless steels (71), and a very good correlation was found between the values calculated with equation (xi) and those found experimentally, as shown in Table V.

From the theory of localized acidification we see that the pitting potential has no special meaning. It is only the potential necessary to reach the necessary current density for the critical $\underline{X.i}$ value. This would mean that a growing pit will do it under a constant $\underline{X.i}$ value. Novokovsky and Sorokina (106) working with a stainless steel pit model, found that the pit growth was related to a constant $\underline{X.i}$ value. Another case of constant $\underline{X.i}$ is found in the work by Beck for titanium (112), where he measured the minimum current density to maintain a pit active for different pit depths. His results fit well with an equation of the type $\underline{X.i}$ = constant.

Crevice corrosion

It has been reported that crevice corrosion starts at lower potentials than pitting (19, 33, 35, 121, 147), and the initiation of crevice corrosion is attributed to a localized acidification (189-191). The same mechanism described above for pitting can be used to explain crevice corrosion.

When describing the localized acidification mechanism for pitting we assumed that the current density inside the pit was of the order of 1 A/cm^2.

For some metals, as it is probably the case with chromium, it might happen that such a high current density could not be reached. Then the metal would not be susceptible to pitting. Nevertheless, the critical $\underline{X.i}$ value can be reached even with a small current density, provided that a sufficiently long diffusion path is present. That would be the case in a crevice. In this way, a metal could be resistant to pitting, but susceptible to crevice corrosion. From the eleotrochemical point of view both processes would be equal, the only difference being the length of the diffusion path.

For most of the metals studied (149) the $\underline{X.i}$ value for critical acidification was close to 10^{-6} A/cm, Figure 18. For a defect 10^{-6} cm long the current density necessary to reach the critical acidification would be 1 A/cm^2. If the deffect has a size of 10^{-4} cm, a current density of only 10^{-2} A/cm^2 would be high enough to start localized corrosion. Since the current density is function of the potential, the corrosion at the 10^{-6} cm deffects will start at a different potential than that at the 10^{-4} cm deffects. The difference between the two potentials will be given, in first approximation by the Tafel slope of the metal in the acid pit-like solution. If the Tafel slope is of 30 mV, the difference between both potentials will be only 60 mV. But if the Tafel slope for the metal is 400 mV, the difference will be 800 mV. In this case the corrosion at crevices will start at a potential 800 mV below the pitting potential. This explains the empirical relation found by Wilde and Williams (35) who showed that the bigger the difference between Ep and Er, the more susceptible was the metal to crevice corrosion.

The degree of susceptibility of a metal to crevice corrosion will be given by the value of η in equation (xi). Table VI shows some values for η, and it is observed that those metals not susceptible to crevice corrosion have η values lower than 200 mV, while those susceptible to crevice corrosion have η values between 470 and 1000 mV.

CONCLUSIONS

1.- The transport processes inside a pit were used to explain the nature of the pitting potential and the repassivation potential. It is evident from this description that both potentials have no thermodynamic value, and that they depend not only on the kinetics of the processes involved,

but also on the geometrical characteristios of the samples in study. While a smooth surfaoe will give high Ep values, the presenoe of crevices will lead to the same type of corrosion starting at a lower potential, and will be defined as crevice corrosion.

In a similar way, the repassivation potential Er will be function of the occlusion of the pit.

2.- From the three types of pitting, the electroohemical depassivation type seems to be the best known. The chemical depassivation type, in some cases, could be transformed to the electroohemical type by the change in the pH of the solution, but there is no experimental evidenoe on this matter.

The HCl-stainless steel type it the type of pitting on whioh we have less information.

3.- No convinoing proofs were found yet on the meaning of the reaotion orders of pitting, and the validity of their measurement.

4.- Equation (xi) gives us a tool for developing alloys resistant to the electroohemical pitting. It shows that the quickest way of evaluating the resistance of an alloy to aggressive neutral or alkaline solutions is by measuring its behavior in the acid solutions. If various alloying elements are studied, the effect of these elements on E_c^* and on η can be evaluated.

5.- We need more information on the composition and nature of the films formed inside the pits, and techniques like ESCA and AES seem to be very promising. It seems that the resistance of stainless steels to pitting as well as the beneficial effeots of ohromium as alloying element in thoee steels, is related to the abnormaly slow dissolution rate of $CrCl_3$. The investigation on the kinetics of dissolution of salts like this could lead us to the development of more resistant alloys.

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TABLE I

ORDERS OF REACTION FOR PITTING

Metal	Aggressive anion	Order of reaction n	Reference
Iron	Cl^-	1	59
Iron	Cl^-	1	100
Mild Steel	Cl^-	1.7 to 2.6 (*)	22
Nickel	Cl^-	1.4 to 1.9 (*)	65
Nickel	Br^-	ap. 1.2	96
Fe-5.6%Cr	Cl^-	1	64
Fe-11.6%Cr	Cl^-	1	64
Fe-Cr-Ni	Cl^-	2.5 to 4.5	62
Fe-Cr-Ni	Cl^-	2	101
Fe-Cr-Ni	Br^-	4 to 4.5	62
Zirconium	Cl^-	0.03 to 0.10	26
Aluminum	F^-	3	99
Aluminum	Cl^-	2 to 8(**)	99
Aluminum	Cl^-	0(***) to 0.9(****)	102
Aluminum	Br^-	2 to 4(**)	99
Aluminum	I^-	2	99

(*) Potential dependent

(**) pH dependent

(***) Low Cl^- concentration

(****) High Cl^- concentration.

TABLE II

MINIMUM AGGRESSIVE ANION CONCENTRATION NECESSARY FOR PITTING OF VARIOUS METALS AND ALLOYS

Metal	Aggressive anion	Minimum concentration (N)	Reference
Iron	Cl^-(*)	0.0003	37, 63
Iron	Cl^-(**)	0.0005	61
Fe-5.6%Cr	Cl^-(*)	0.017	63
Fe-11.6%Cr	Cl^-(*)	0.069	63
Fe-20%Cr	Cl^-(*)	0.1	63
Fe-24.5%Cr	Cl^-(*)	1.0	63
Fe-29.4%Cr	Cl^-(*)	1.0	63
Fe-18.6Cr-9.9Ni	Cl^-(*)	0.1	63
Nickel	Cl^-(*)	0.001	65
Titanium	Br^-(***)	0.002	25

(*) H_2SO_4 + NaCl solution

(**) Phthalate buffer + NaCl, pH 5

(***) KBr solution

TABLE III

ANIONS PRODUCING PASSIVITY BREAKDOWN

Metal	Aggressive anion	Reference
Iron	Cl^-	21, 60, 61, 66, 75, 76
	Br^-	60, 61, 75
	I^-	60, 75, 76
	ClO_4^-	18, 60, 61 75
	$SO_4^=$	61, 78, 141
Nickel	Cl^-	65, 66, 75, 76
	Br^-	75, 96
	I^-	75
Stainless steel	Cl^-	5, 24, 62, 81, 91
	Br^-	5, 24, 62, 81, 91
Aluminum	Cl^-	10, 50, 99, 142, 143
	Br^-	10, 50, 99, 142
	I^-	10, 50, 99, 147
	ClO_4^-	10, 50, 82, 142, 147
	NO_3^-	10, 50, 54, 142, 145
	SCN^-	50, 142
Titanium	Cl^-	25, 57, 88, 146
	Br^-	25, 57, 146
	I^-	25, 57, 146
Zirconium	Cl^-	27, 57, 85, 86
	Br^-	27, 57, 86
	I^-	27, 57, 86
	ClO_4^-	87
Tantalum	Br^-	57
	I^-	57

TABLE III (cont.)

Zinc	Cl^-	16, 52
	Br^-	14, 16
	I^-	14, 52
	NO_3^-	14, 52
	$SO_4^=$	14, 16, 52
	ClO_4^-	14, 16
	ClO_3^-	14
	BrO_3^-	14
	HCO_2^-	14
	$CH_3CO_2^-$	14
Cadmium	Cl^-	16, 53
	Br^-	16
	ClO_4^-	16
	$SO_4^=$	16, 53
Manganese	Cl^-	16
	Br^-	16
	ClO_4^-	16
	$SO_4^=$	16
	NO_3^-	16
	$CH_3CO_2^-$	16

TABLE IV

VALUES OF THE SLOPE B IN EQUATION (iii).

Metal	Aggressive anion	Buffer	B V	Reference
Iron	Cl^-	none(pH 10)	0.058	76
Iron	Cl^-	Borate(pH 8)	0.13	66
Iron	Cl^-	Phthalate(pH 5)	0.08	66
Iron	Cl^-	Borate(pH 8.4)	0.10	45
Iron	Cl^-	Borate(pH 8.4)	0.15 to 0.20	60
Iron	Cl^-	various	0.03 to 0.08	37
Iron	ClO_4^-	Phthalate(pH 5)	0.14	61
Low alloy st.	Cl^-	Borate(pH 8.4)	0.08 to 0.11	9
Carbon steel	Cl^-	Borate(pH 8.4)	0.45	9
Fe-5Cr	Cl^-	Borate(pH 7.3)	0.68	97
Fe-18Cr	Cl^-	none	0.20	81
Fe-18Cr	Br^-	none	0.20	81
Fe-18Cr	Cl^-	none	0.17	147
Fe-19Cr-8Ni	Cl^-	none	0.16	147
Fe-18Cr-8Ni	Cl^-	none	0.13 to 0.23	24
Fe-18Cr-8Ni	Cl^-	none	0.044	40
Fe-18Cr-8Ni	Cl^-	none	0.088	48
Nickel	Cl^-	none	0.071	49
83Ni-17Cu	Cl^-	none	0.078	49
66Ni-34Cu	Cl^-	none	0.074	49
Aluminum	Cl^-	none (pH 7)	0.073	10
Aluminum	Cl^-	none	0.12	11
Aluminum	Cl^-	none (pH 11)	0.13	46
Aluminum	Cl^-	none	0.127	47
Aluminum	NO_3^-	none	0.06 to 0.10	145
Al-4%Cu	Cl^-	none (pH 7)	0.046	10
Al_2Cu	Cl^-	none (pH 7)	0.055	10
Titanium	Br^-	none	0.11	25
Zirconium	Cl^-	none	0.065	27
Zirconium	Cl^-	none	0.058	86
Zirconium	ClO_4^-	none	0.100	87

TABLE V

COMPARISON BETWEEN THE THEORETICAL PITTING POTENTIAL VALUE CALCULATED WITH Eq (xi) AND THE EXPERIMANTAL PITTING POTENTIAL VALUE MEASURED IN 1.0 M NaCl SOLUTION.

Alloy	E^*_c V(sce)	+ η V	+ ϕ V	= Ep(theor.) V(sce)	Ref.	Ep(exp.) V(sce)	Ref.
Al 99.99%	-0.76	+0.17	+0.05	-0.54	128	-0.53	10
Al-3%Cu	-0.52	+0.04	+0.05	-0.43	128	-0.43	51
Al-3%Mg	-0.76	+0.15	+0.05	-0.56	128	-0.53 to -0.57	128
Al-3%Zn	-0.82	+0.01	+0.05	-0.76	128	-0.75	128
Fe-18Cr	-0.55	+0.67		0.12	71	0.10 to 0.14	56
Fe-18Cr-1Mo	-0.49	+0.74		0.25	71	0.16 to 0.22	56
Fe-18Cr-2Mo	-0.48	+0.88		0.40	71	0.22 to 0.34	56
Fe-18Cr-5Mo	-0.45	+1.00		0.55	71	0.52 to 0.56	56

TABLE VI

OVERPOTENTIAL VALUES, η , FROM Eq.(xi), vs CREVICE CORROSION SUSCEPTIBILITY

Metal	η (mV)	Crevice corrosion	Reference
Iron	ap. 30	no	76
Zinc	ap. 20	no	52
Cadmium	ap. 20	no	53
Aluminum	170	no	128
Al-3%Mg	150	no	128
Al-3%Cu	40	no	128
Al-3%Zn	10	no	128
Nickel	470	yes	76
Fe-18Cr-XMo (X= 0 to 5)	670 to 1000	yes	71

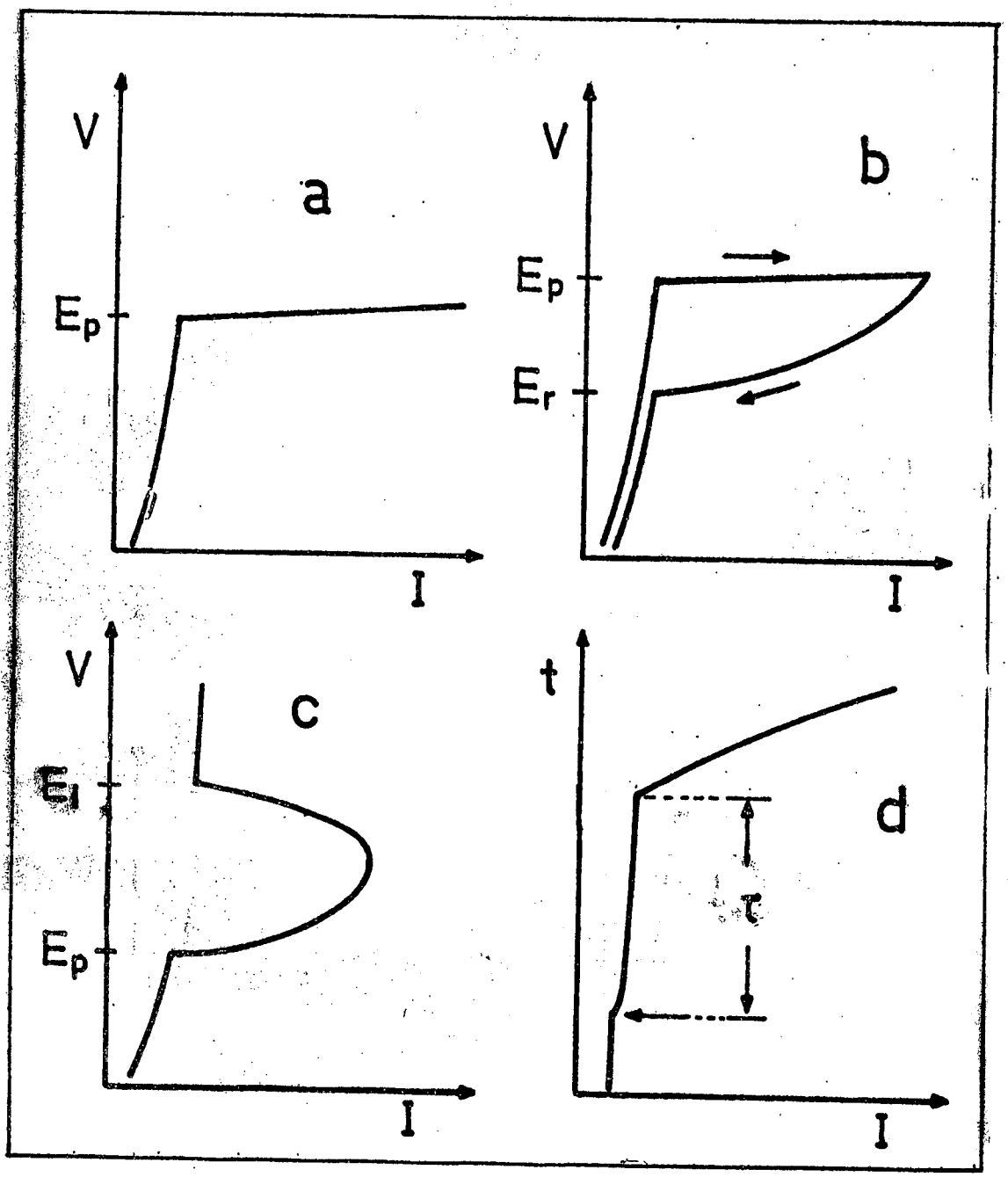

FIGURE 1.-Definition of a: pitting potential; b: repassivation potential (Arrows indicate polarization direction); c: inhibition potential and d: induction time (Arrow indicates injection of aggressive anion solution).

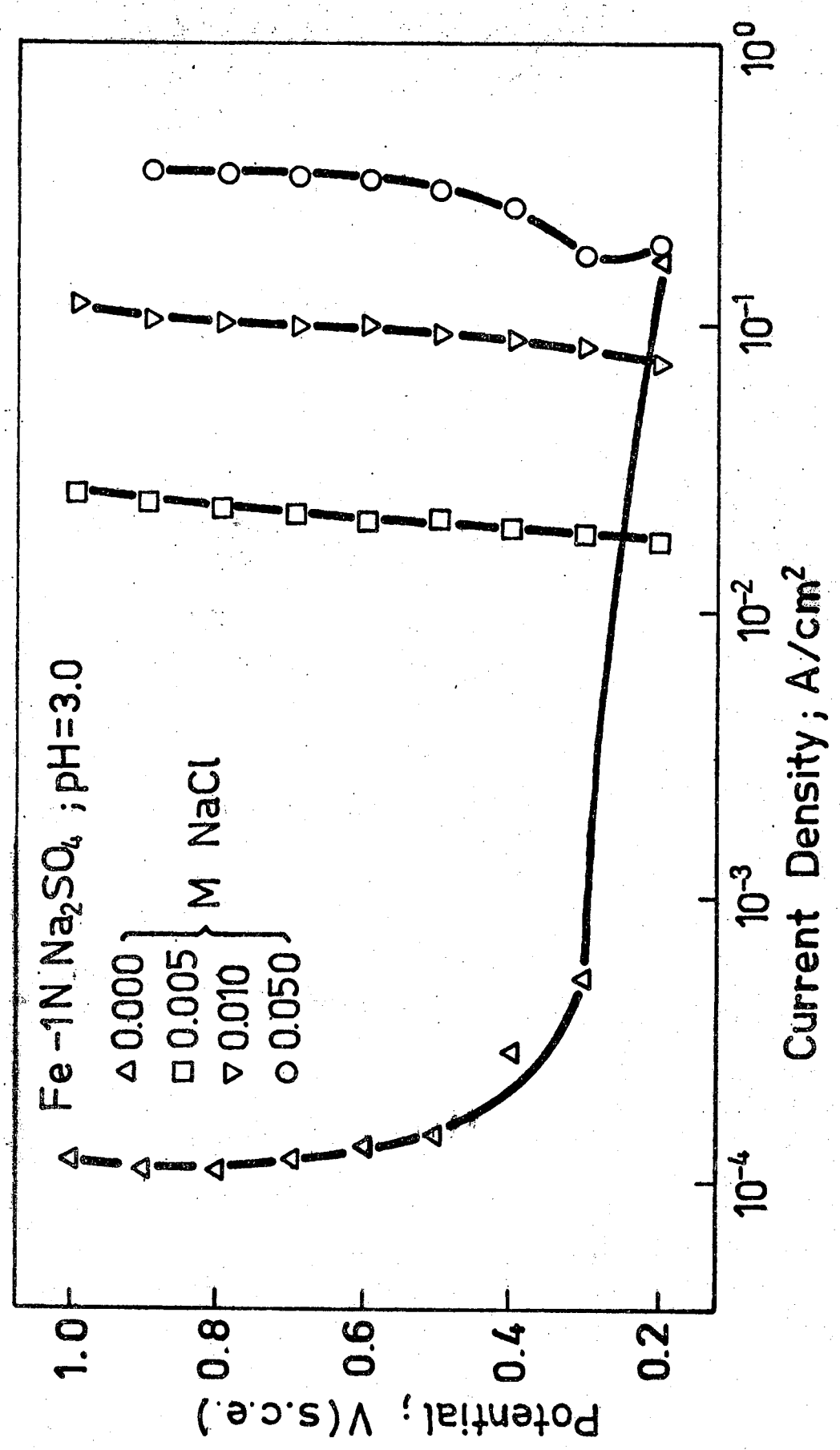

FIGURE 2.- Effect of chloride ion on passivity of iron in 1 N Na_2SO_4 solution (pH = 3.0) (67).

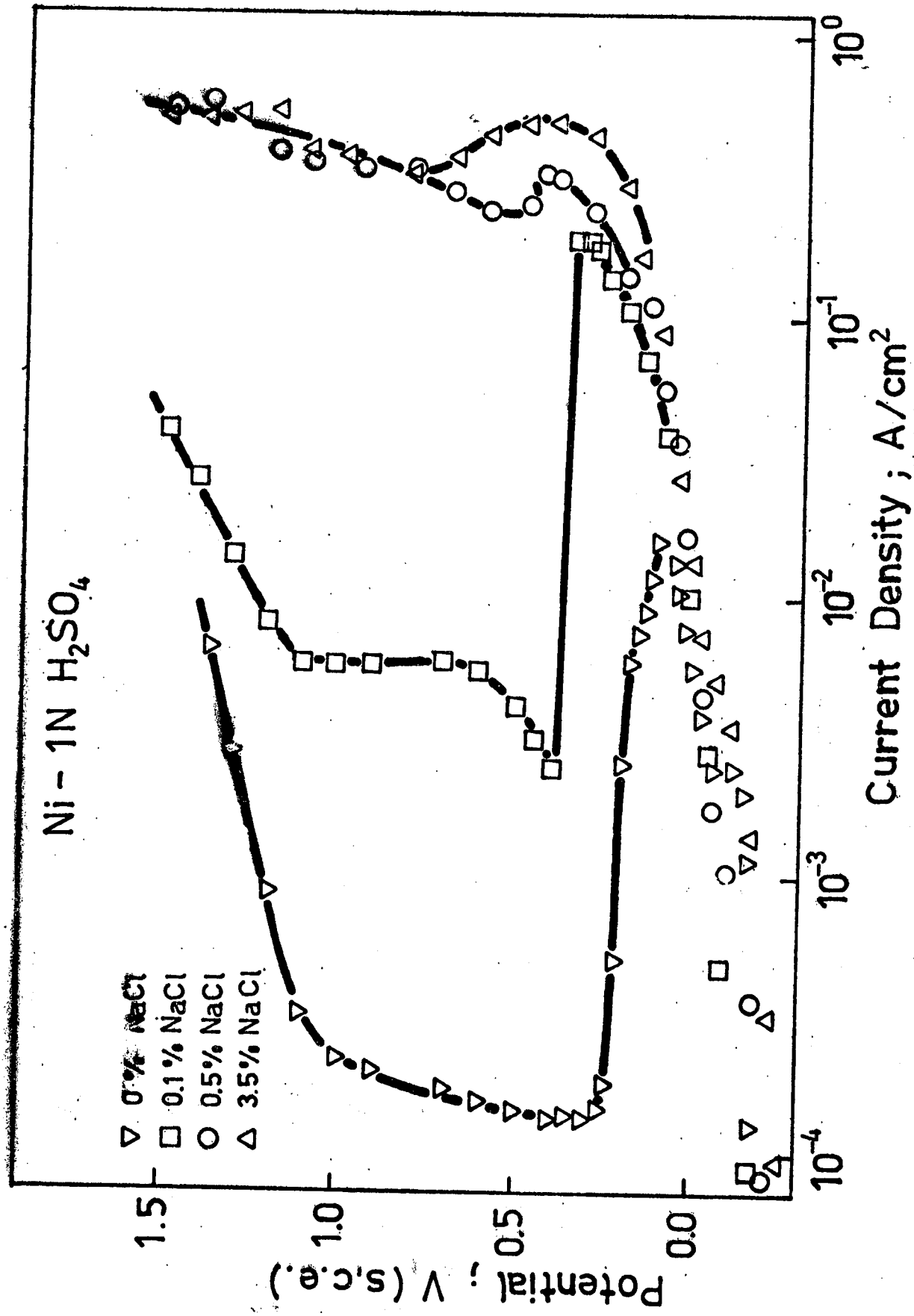

FIGURE 3.- Effect of chloride ion on passivity of nickel in 1 N H_2SO_4 solution (68).

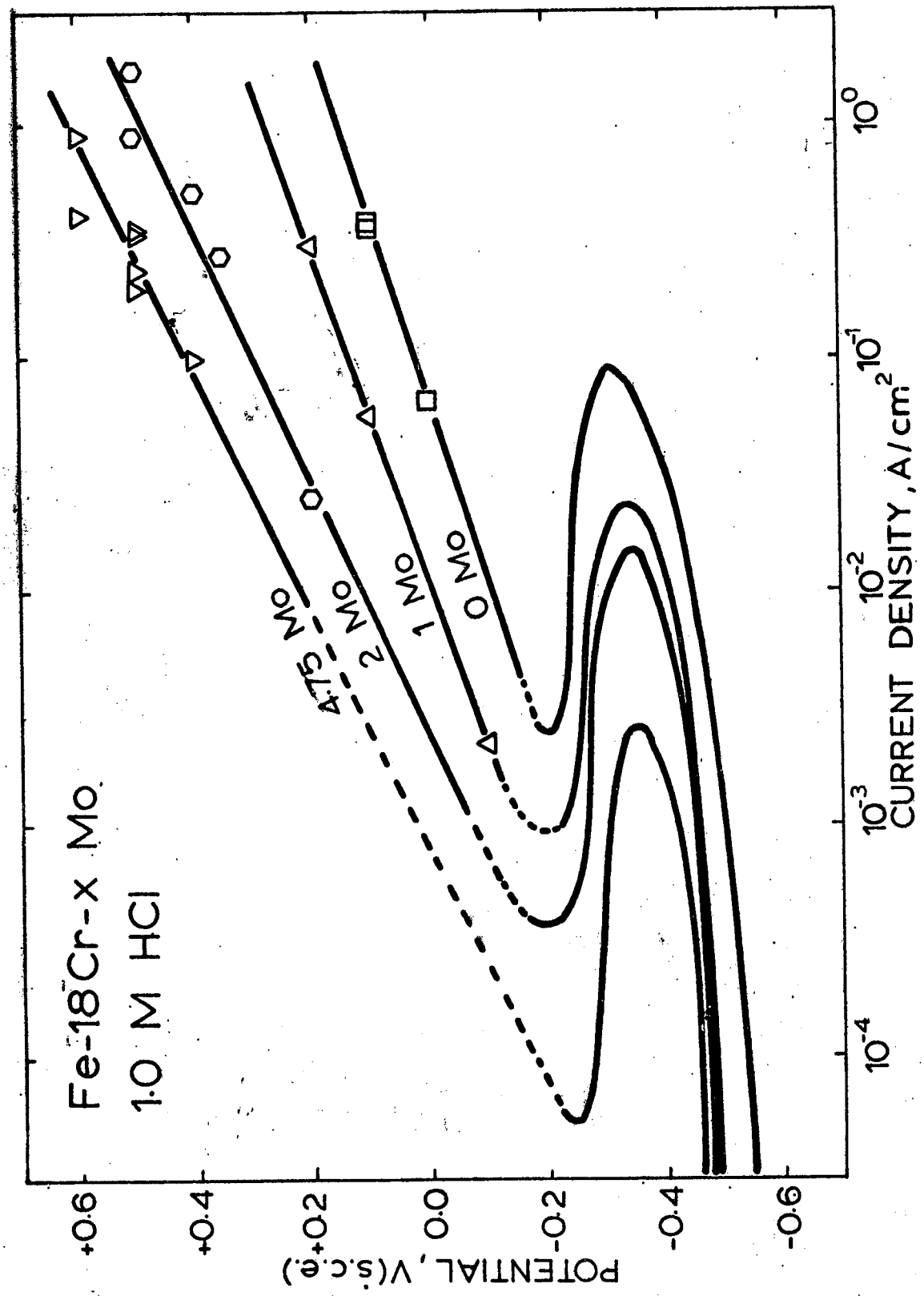

FIGURE 4.- Anodic polarization curves for type 18 Cr-X Mo ferritic stainless steel in deaerated 1 N HCl solution at 24°C. Pitting potential at -0.2 V(s.c.e.) (71).

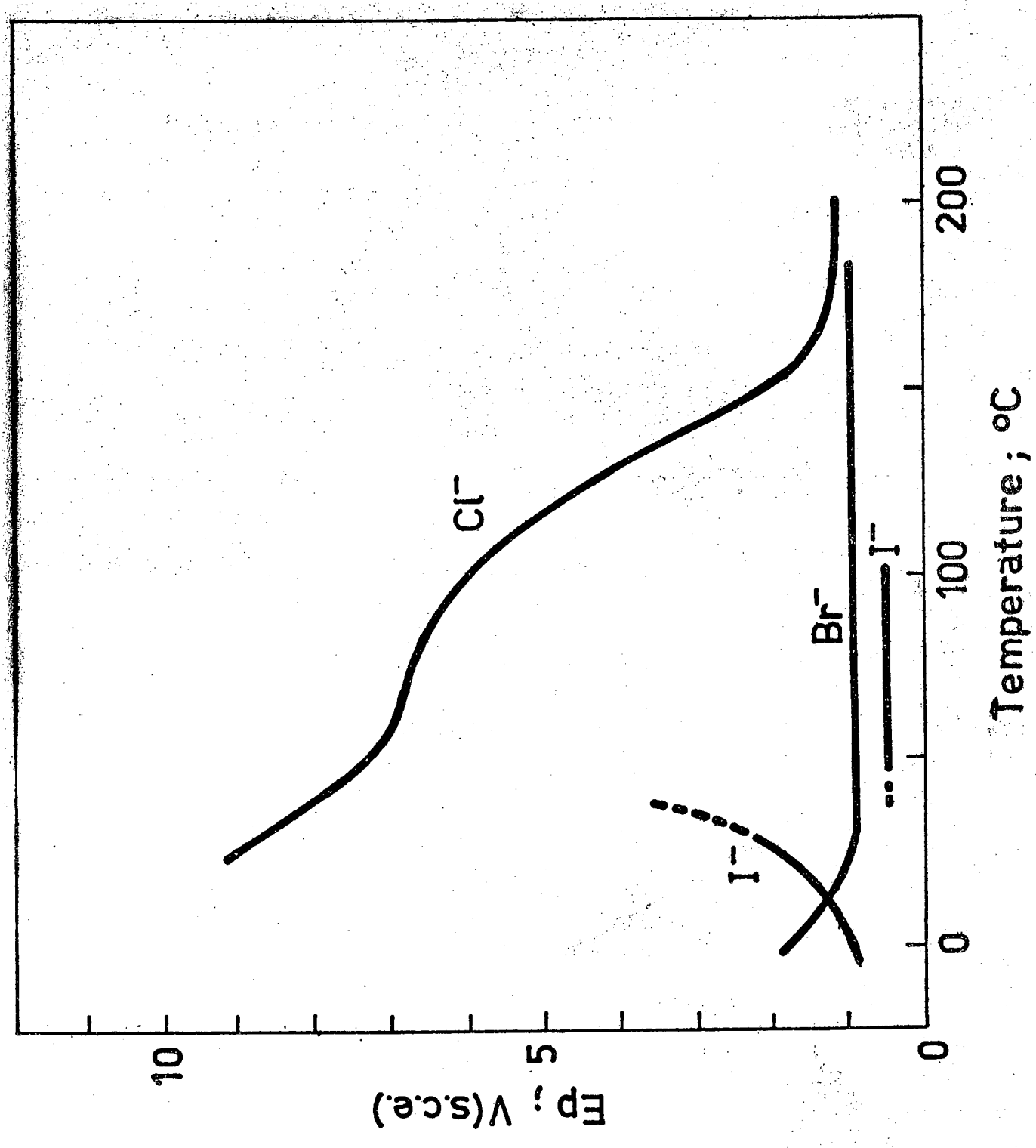

FIGURE 5.- Effect of temperature on steady-state pitting of titanium in 0.6 - 1 M halide solutions (25).

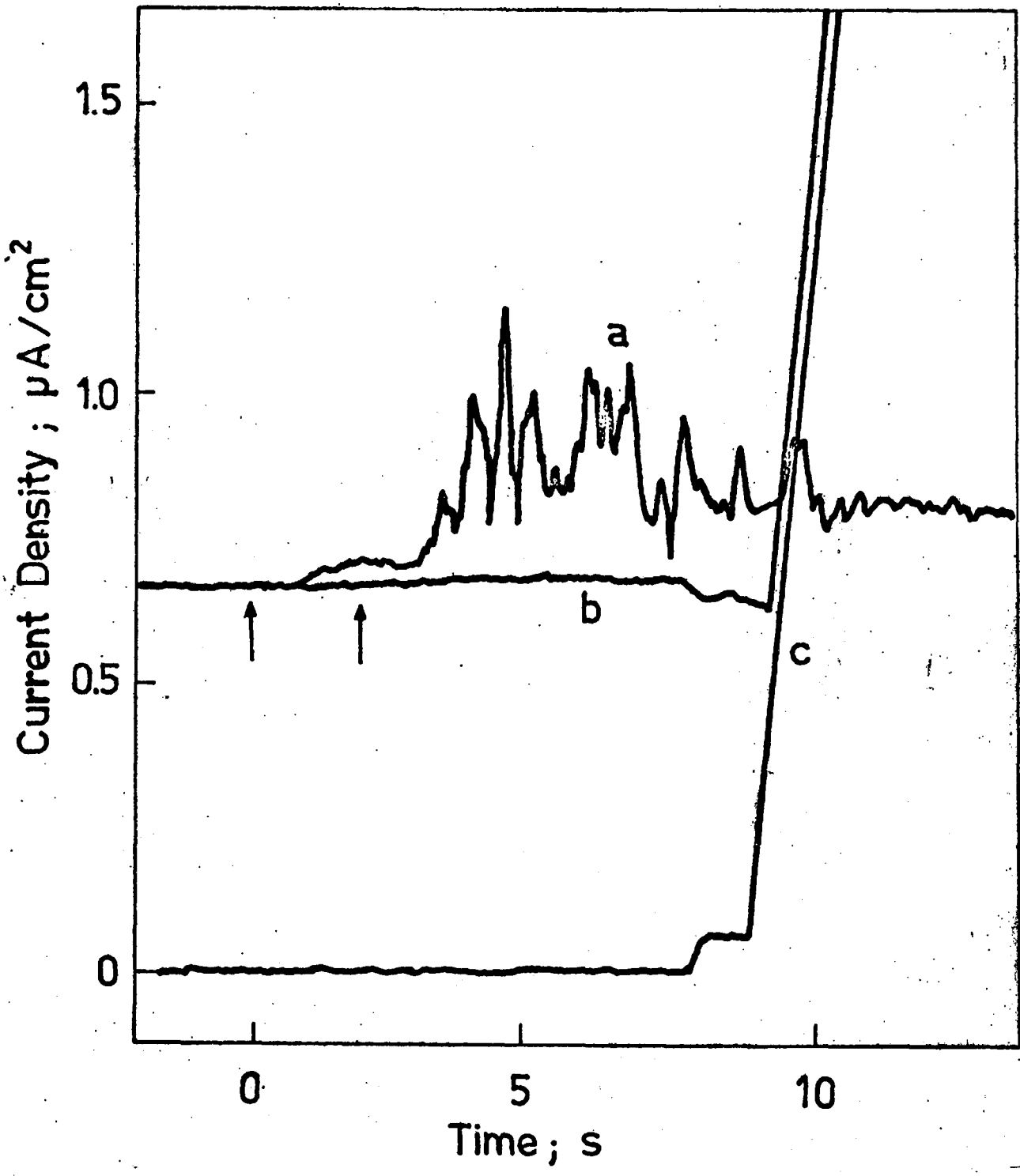

FIGURE 6.- Current-time changes after injection of chloride ions in a borate buffer solution (pH 7.3), for iron at 0.3 V(s.c.e.). a: Fe III dissolution rate; b: total anodic current; c: Fe II dissolution rate. The arrows indicate the time required to establish a constant chloride concentration of 0.01 M NaCl.(37).

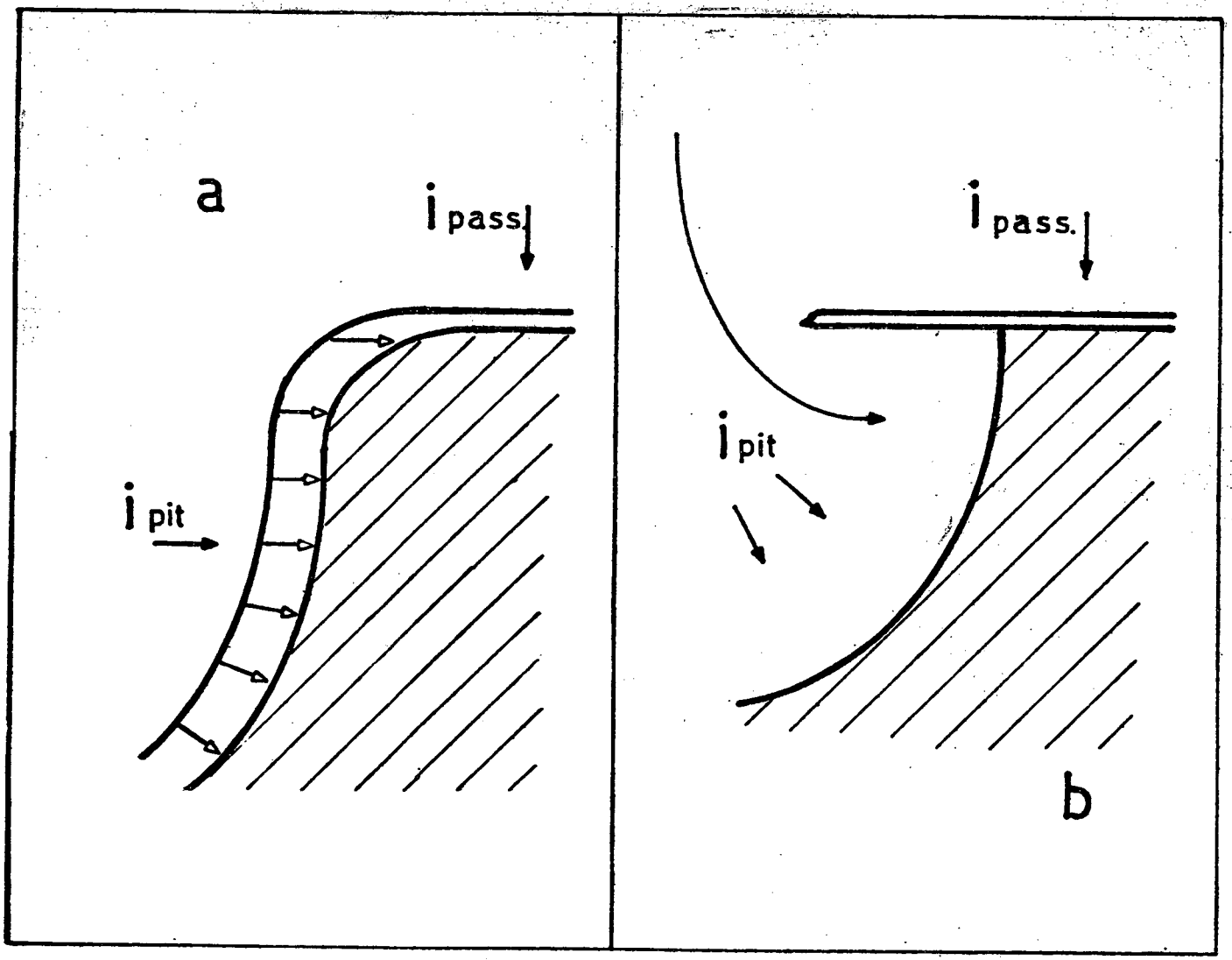

FIGURE 7.- a: Pit borders according to Vetter and Strehblow (130); b modified model based on the existence of oxide covered pits.

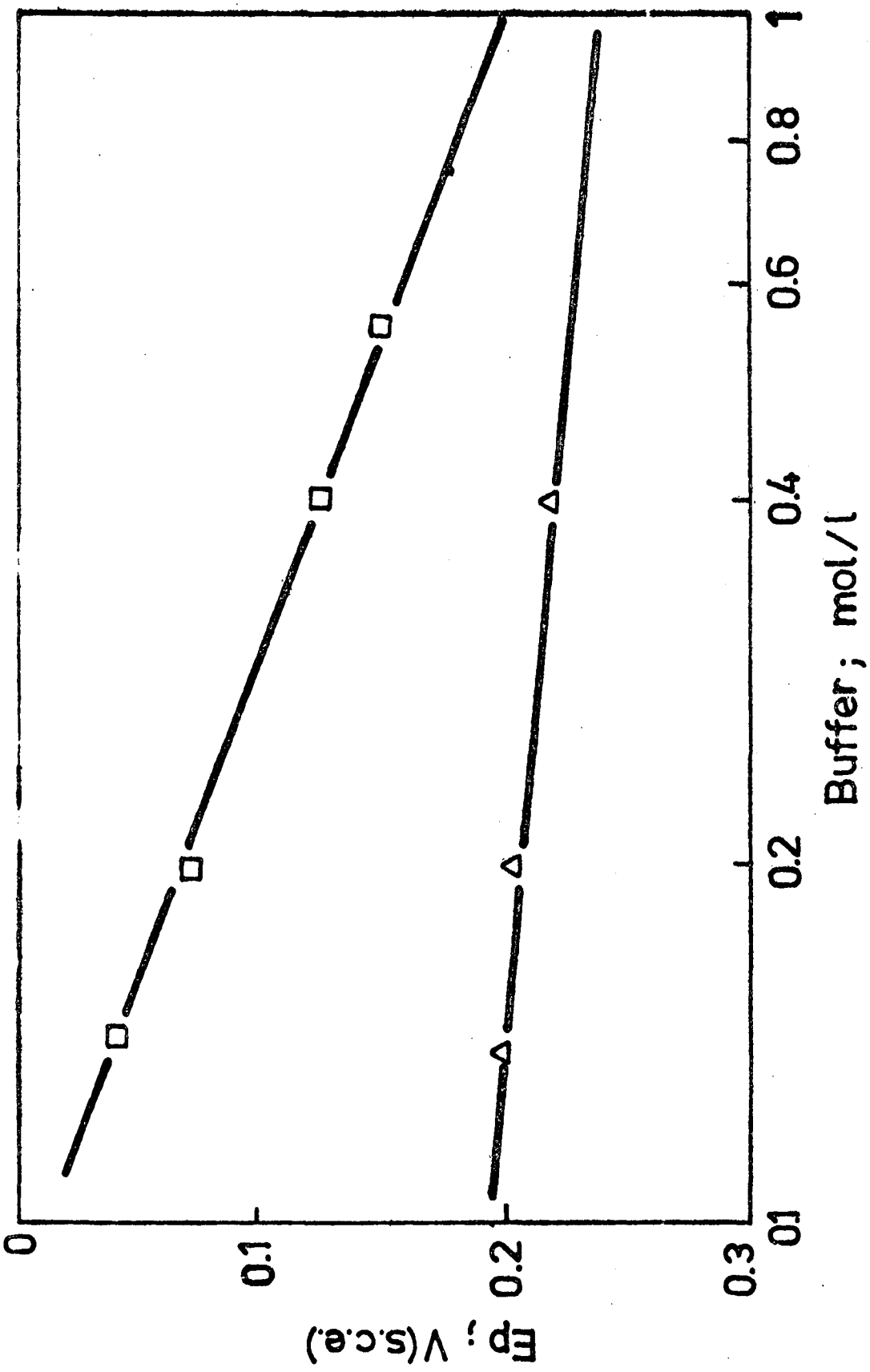

FIGURE 8.- Dependence of the pitting potential of iron, at constant chloride concentration (0.01 M NaCl) on the concentrations of borate (□) and of phthalate (Δ), (37).

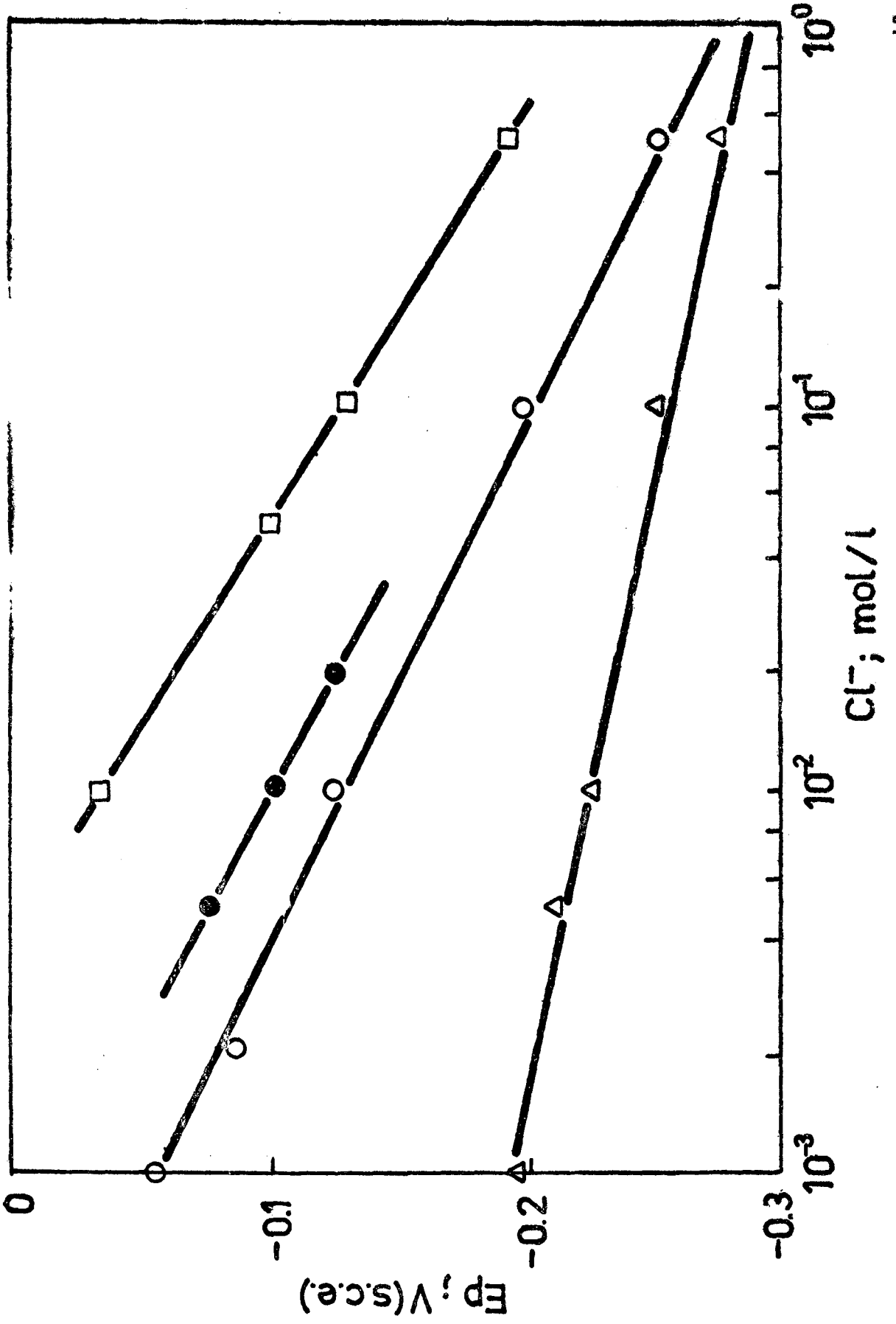

FIGURE 9.- Dependence of the pitting potential of iron on the concentration of NaCl for various supporting electrolytes. □ : 0.13 M borate buffer; ● : 0.2 M borate buffer, pH 7.3; ○ : 0.4 M borate buffer; △ : 0.2 M borate buffer + 0.15 M phthalate buffer. (37).

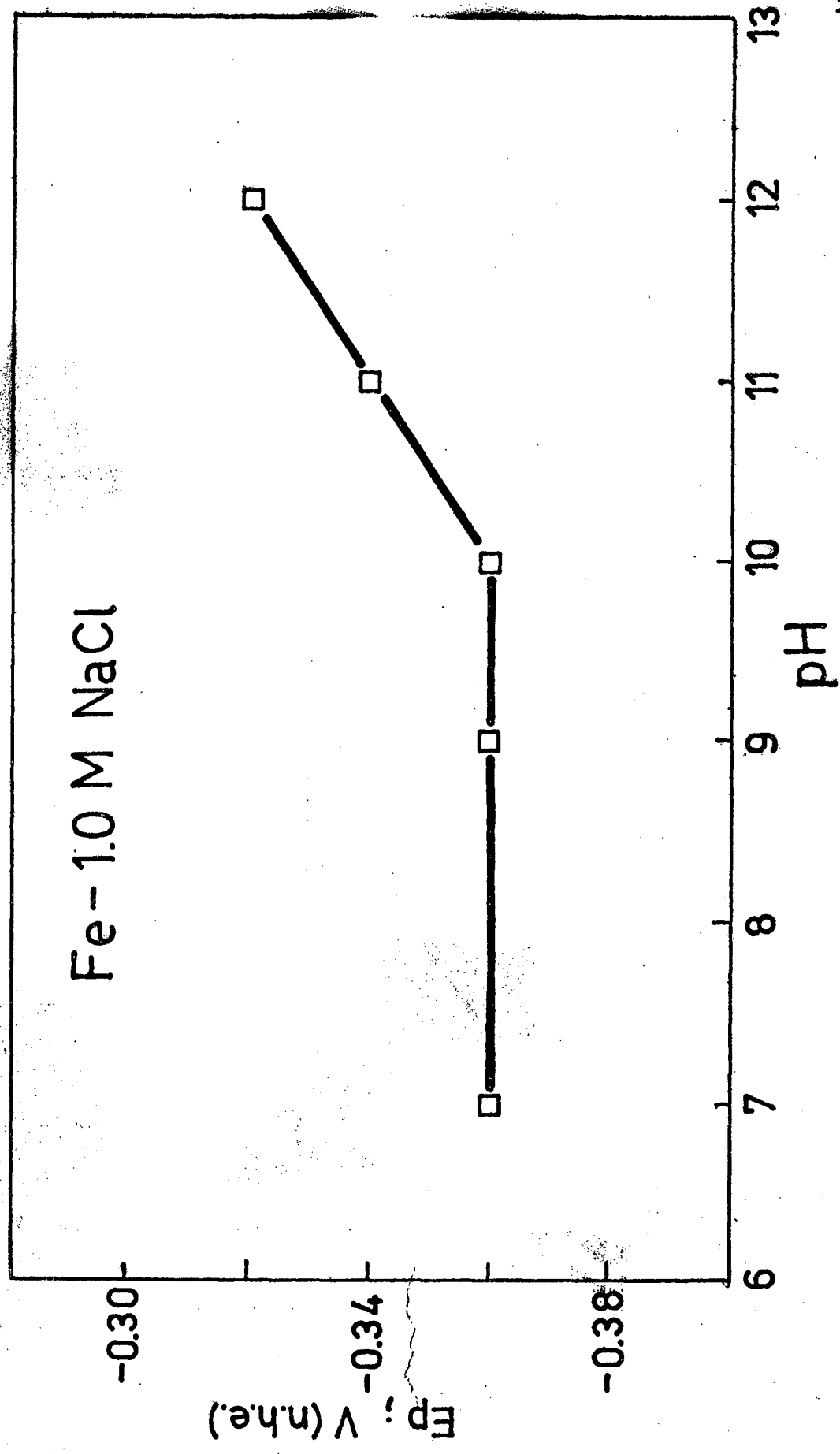

FIGURE 10.- Effect of the pH on the pitting potential of iron in deaerated 1 N NaCl solution, at 25°C, (76).

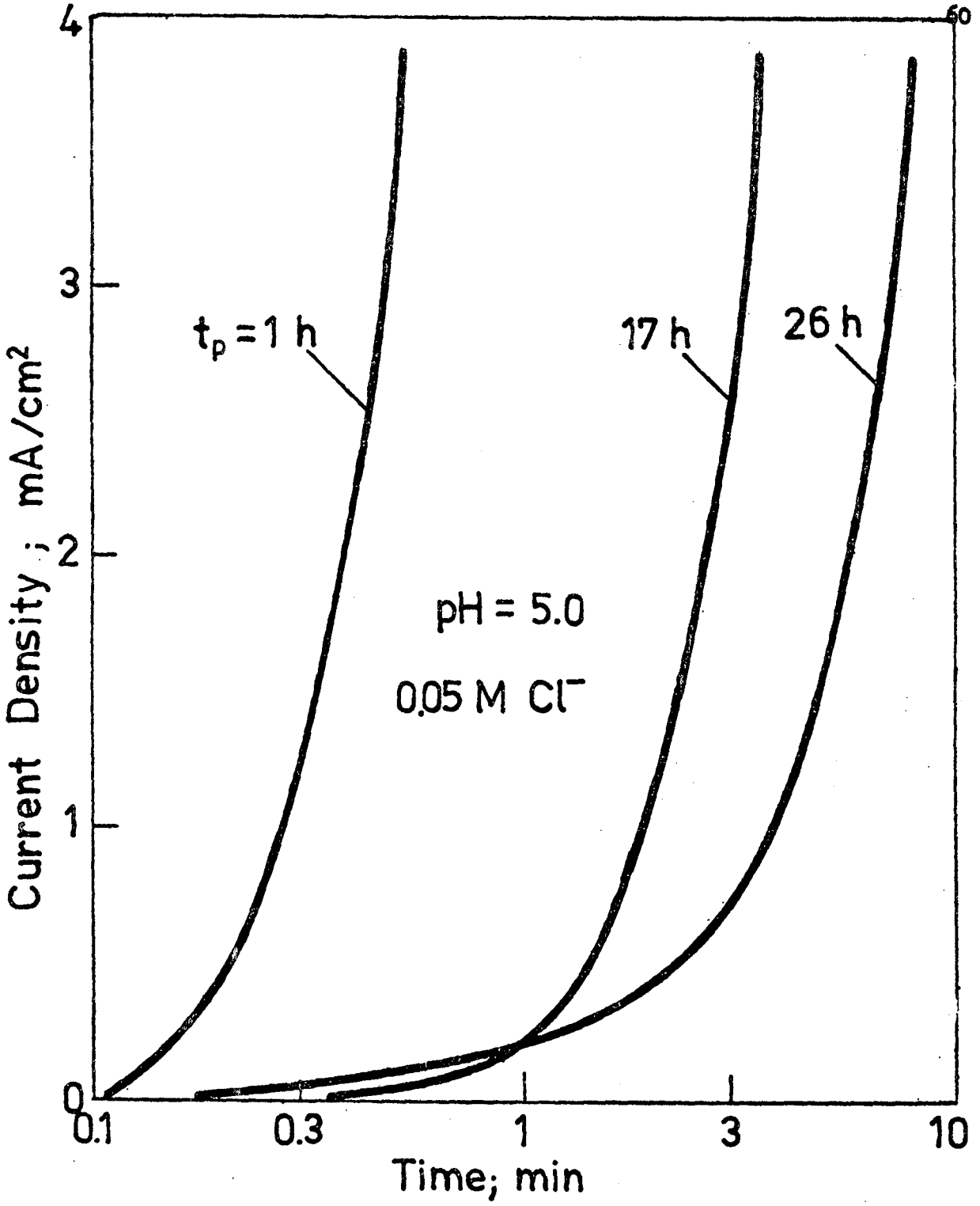

FIGURE 11.- Effect of the prepassivation time (t_p) on the pitting of iron in a pH 5 phthalate buffer with 0.05 M NaCl, at constant potential E = 1.18 V(n.h.e.).(108).

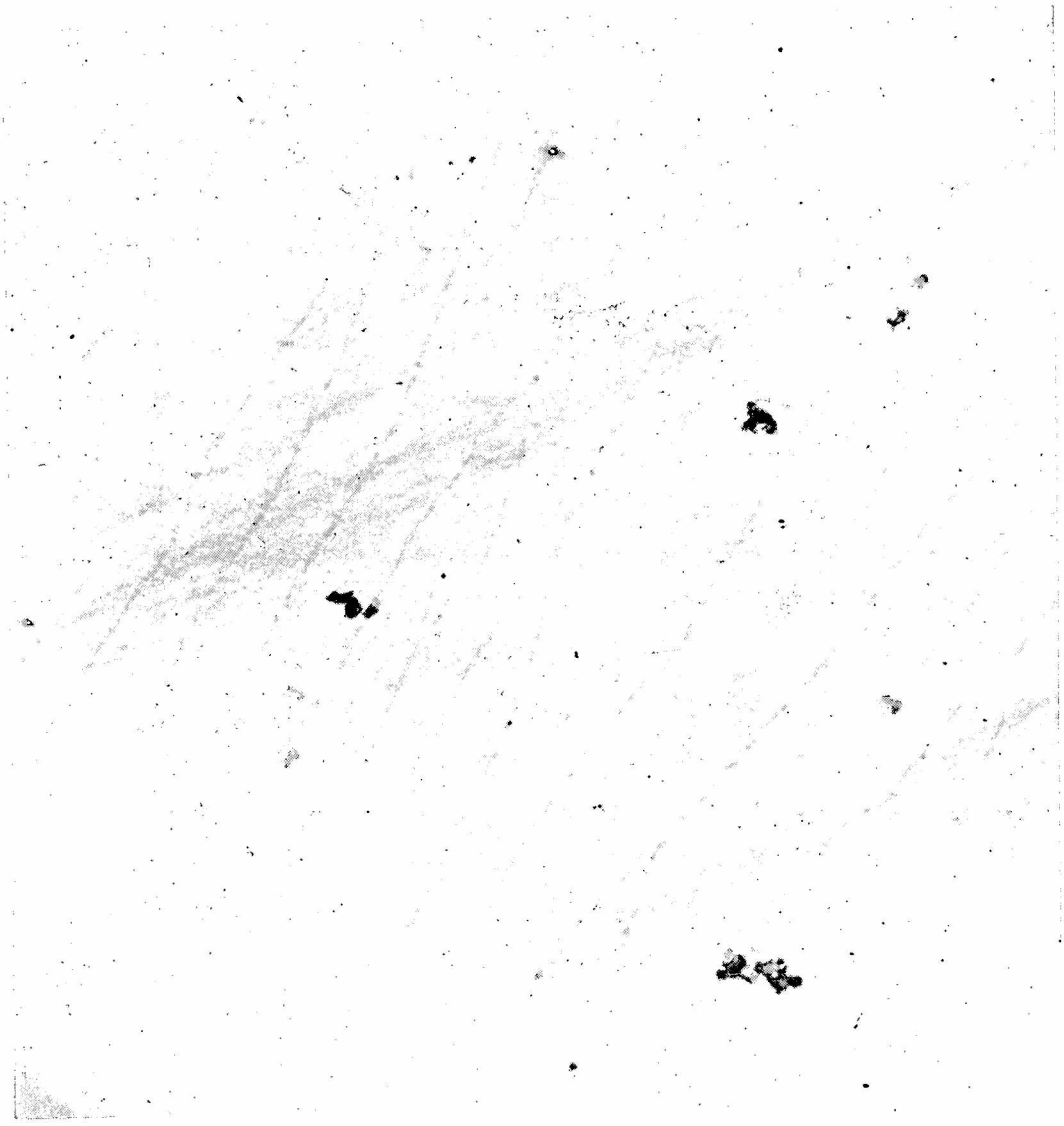

FIGURE 12.- Aluminum strained in 1 M NaCl solution below the pitting potential (E = -0.53 V n.h.e.). No corrosion is observed on the slip steps. Oxide replica, 16000 X (162).

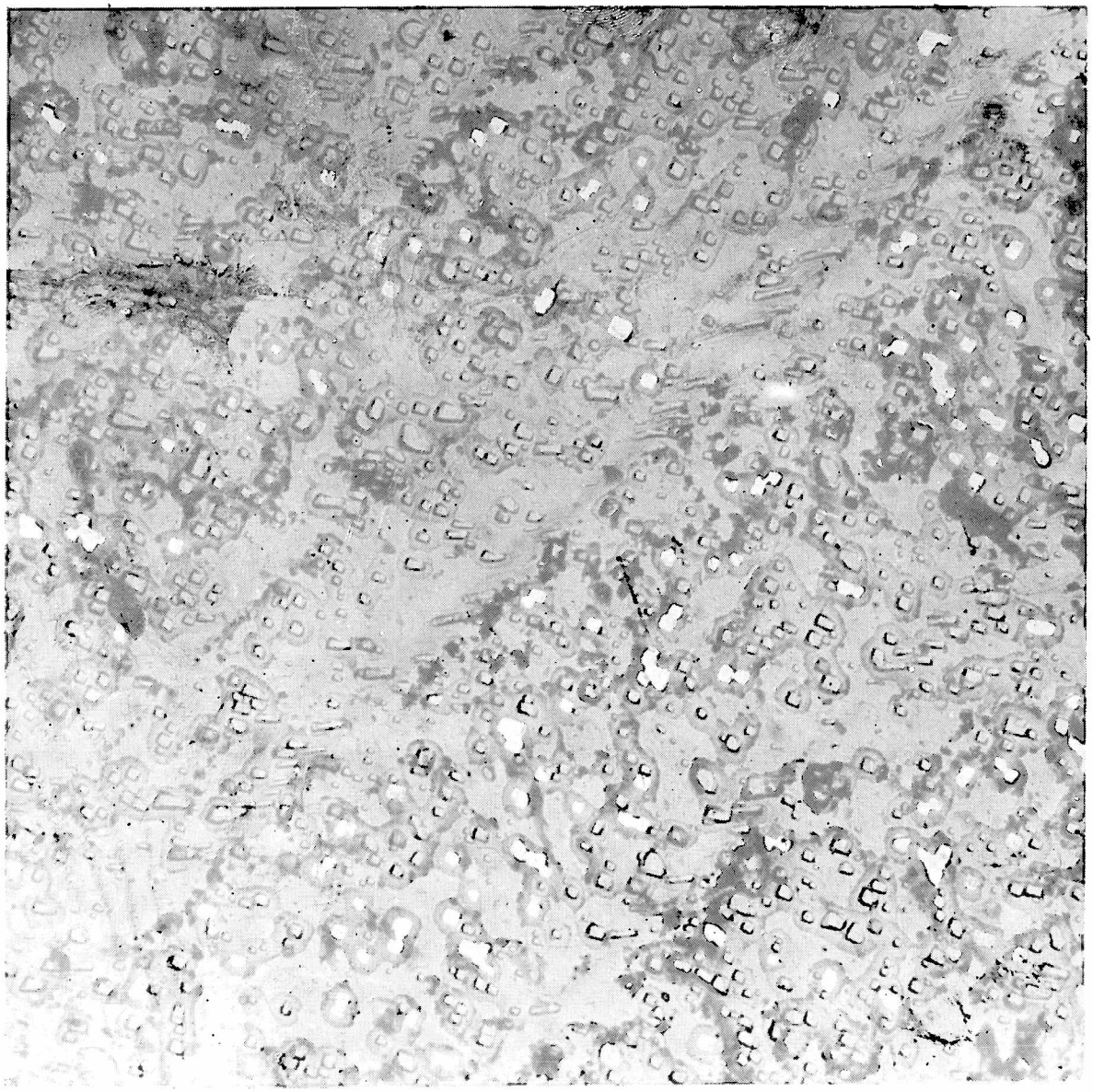

FIGURE 13.- Aluminum strained in 1 M NaCl solution above the pitting potential (E = -0.50 V n.h.e.). Extensive corrosion of the sample. Carbon replica, 7000 X (162).

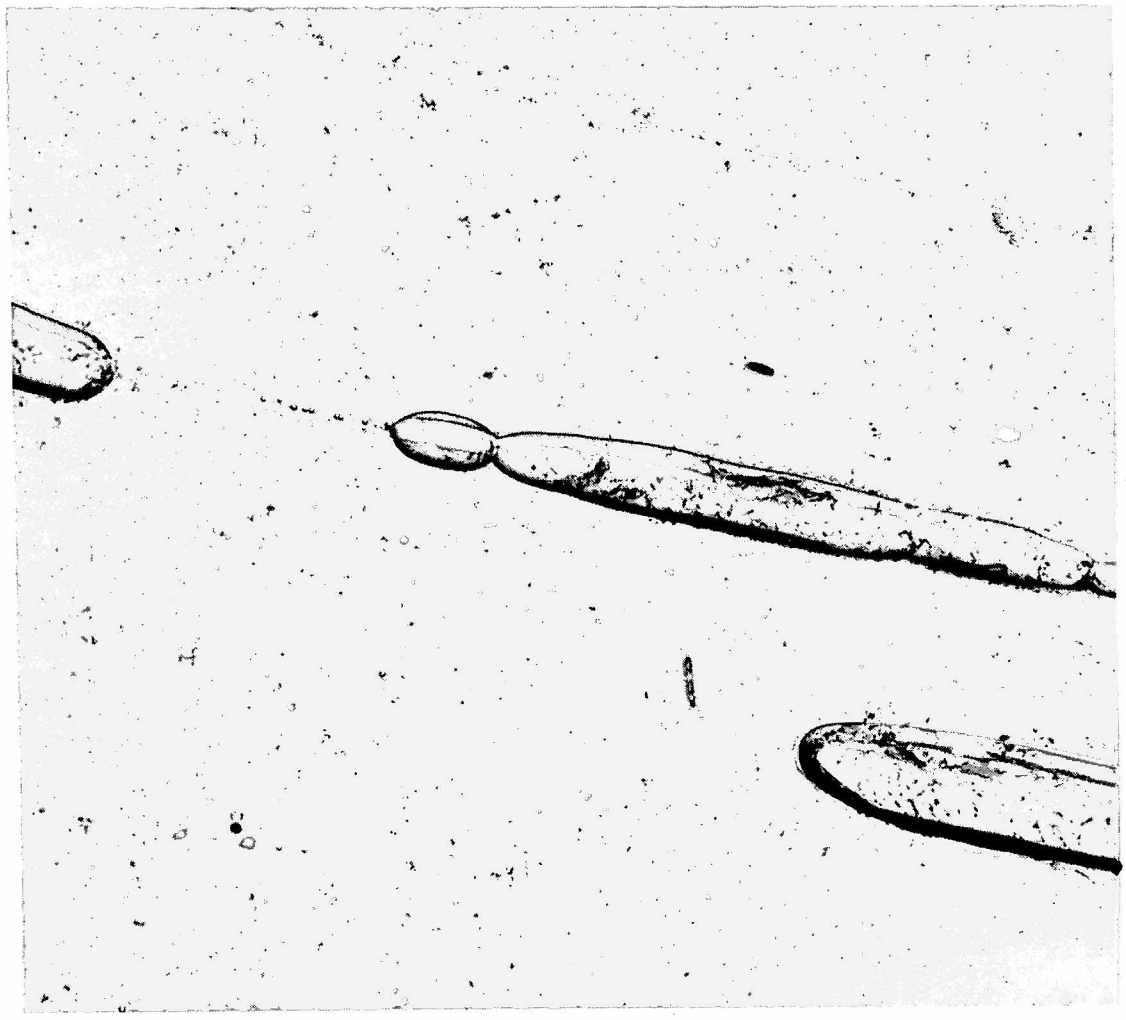

FIGURE 14.- Aluminum strained in 1 M $NaNO_3$ solution above the pitting potential (E = 1.8 V n.h.e.). Pitting nucleates on the slip steps. Oxide replica, 4000 X (162).

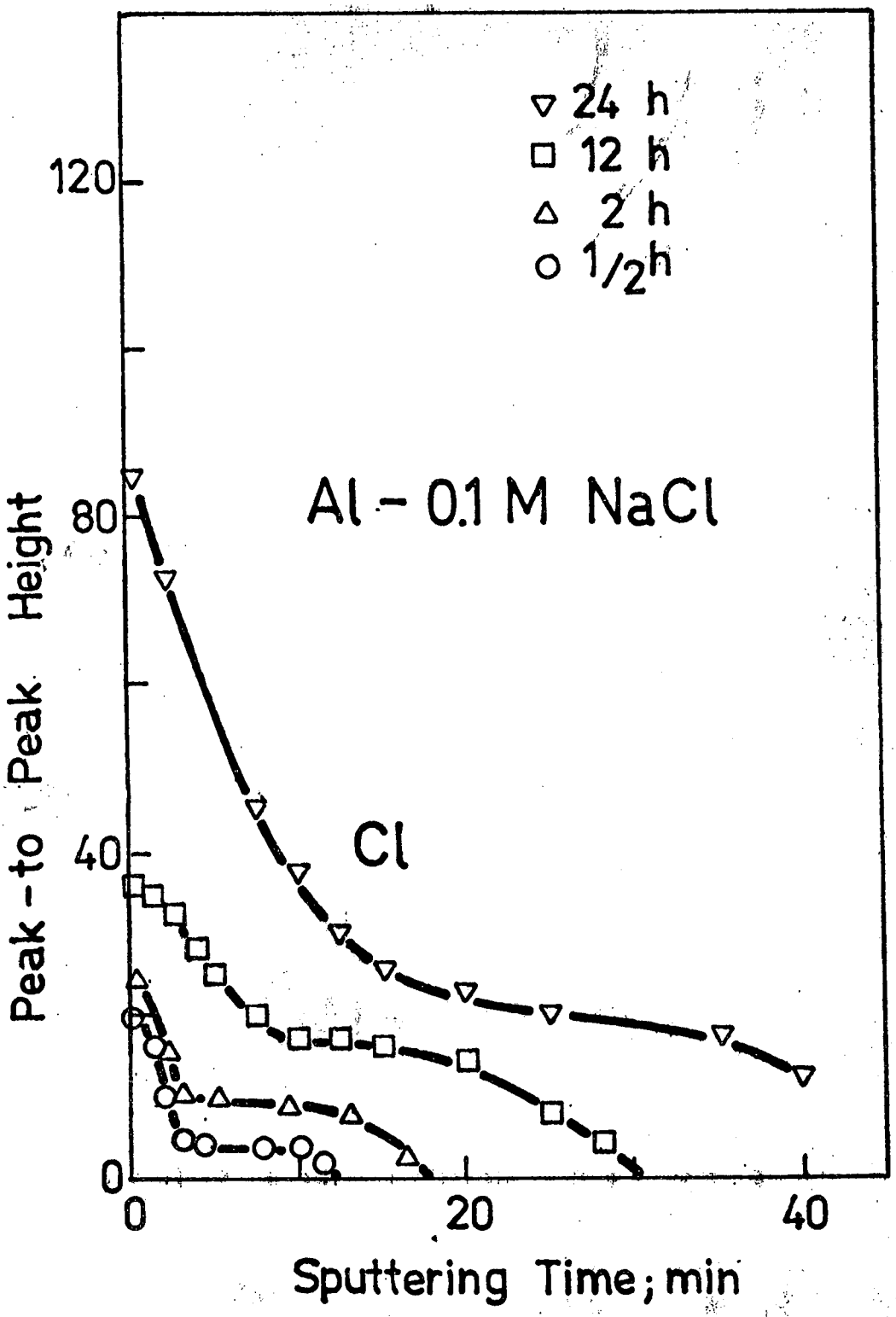

FIGURE 15.- Chloride ion penetration in aluminum films exposed to a 0.1 M NaCl solution. Measurements by Auger electron spectroscopy (170).

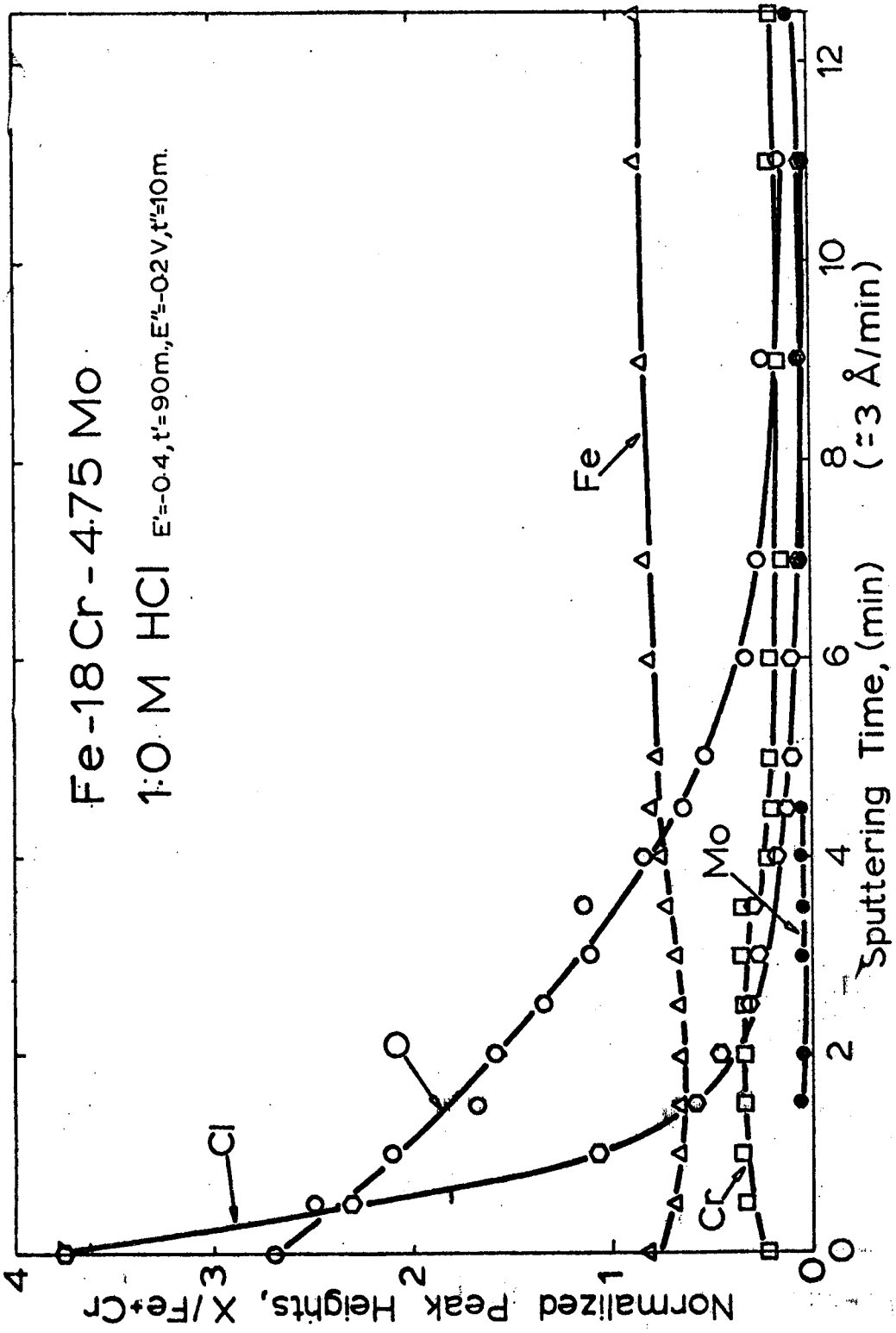

FIGURE 16.- Auger normalized peak heights vs. sputtering time for type 18Cr-2Mo ferritic stainless steel polarized for 20 min at -0.400 V(s.c.e.) plus 10 min at -0.200 V(s.c.e.) in deaerated 1 M HCl solution (71).

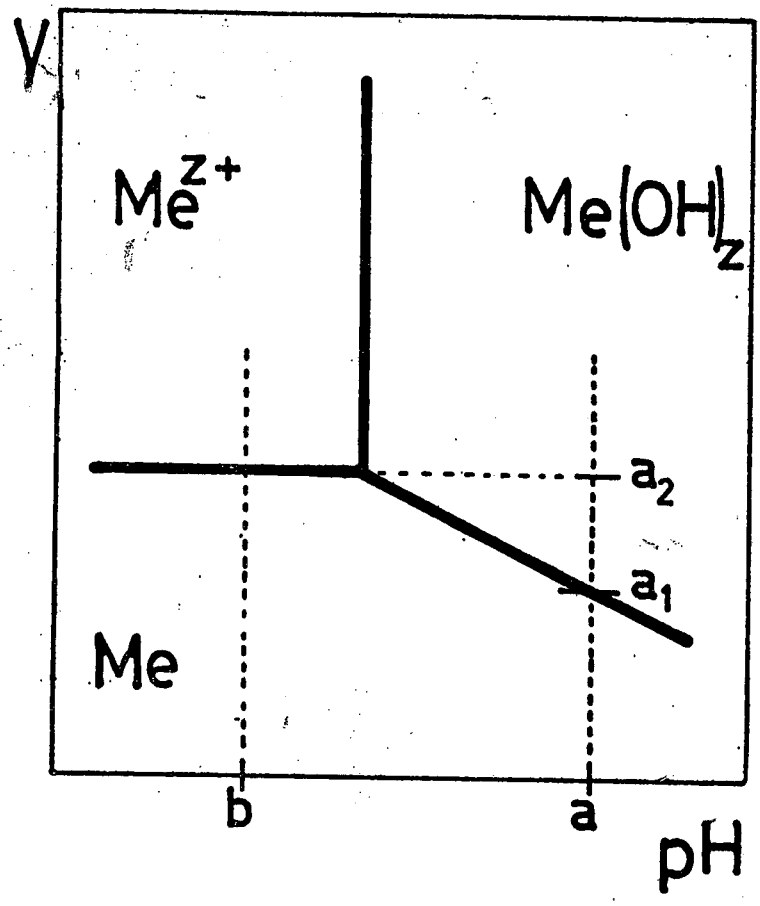

FIGURE 17.- Sohematio Potential-pH diagram. a: pH of the bulk solution; a_1-a_2: passive zone; a_2: pitting potential; b : pH of the locally acidified zone, (52).

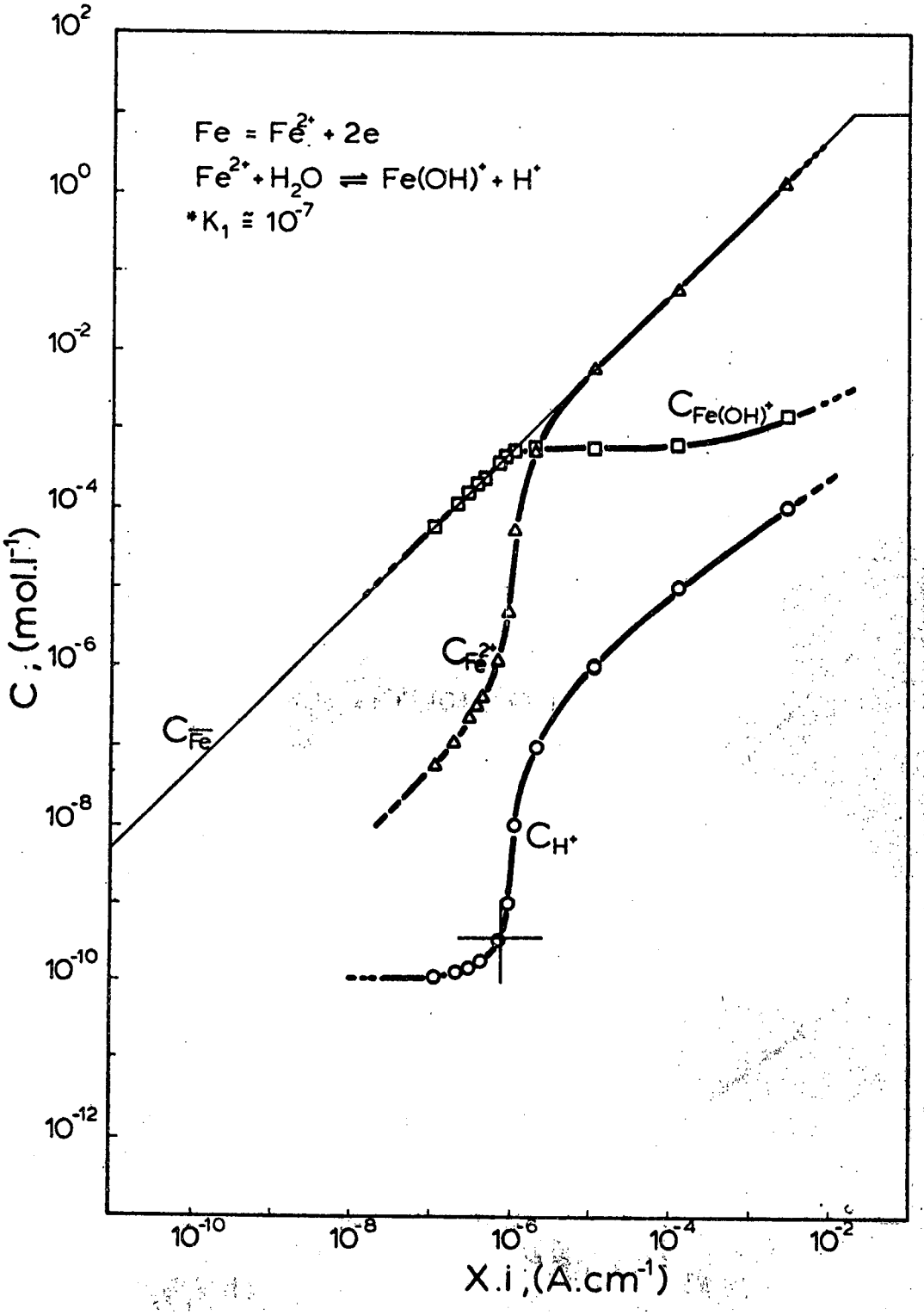

FIGURE 18.- Concentrations of Fe^{2+}, $Fe(OH)^{+}$, and H^{+} as a funotion of the produot of the depth X and the current density i in a unidirectional pit, (149).

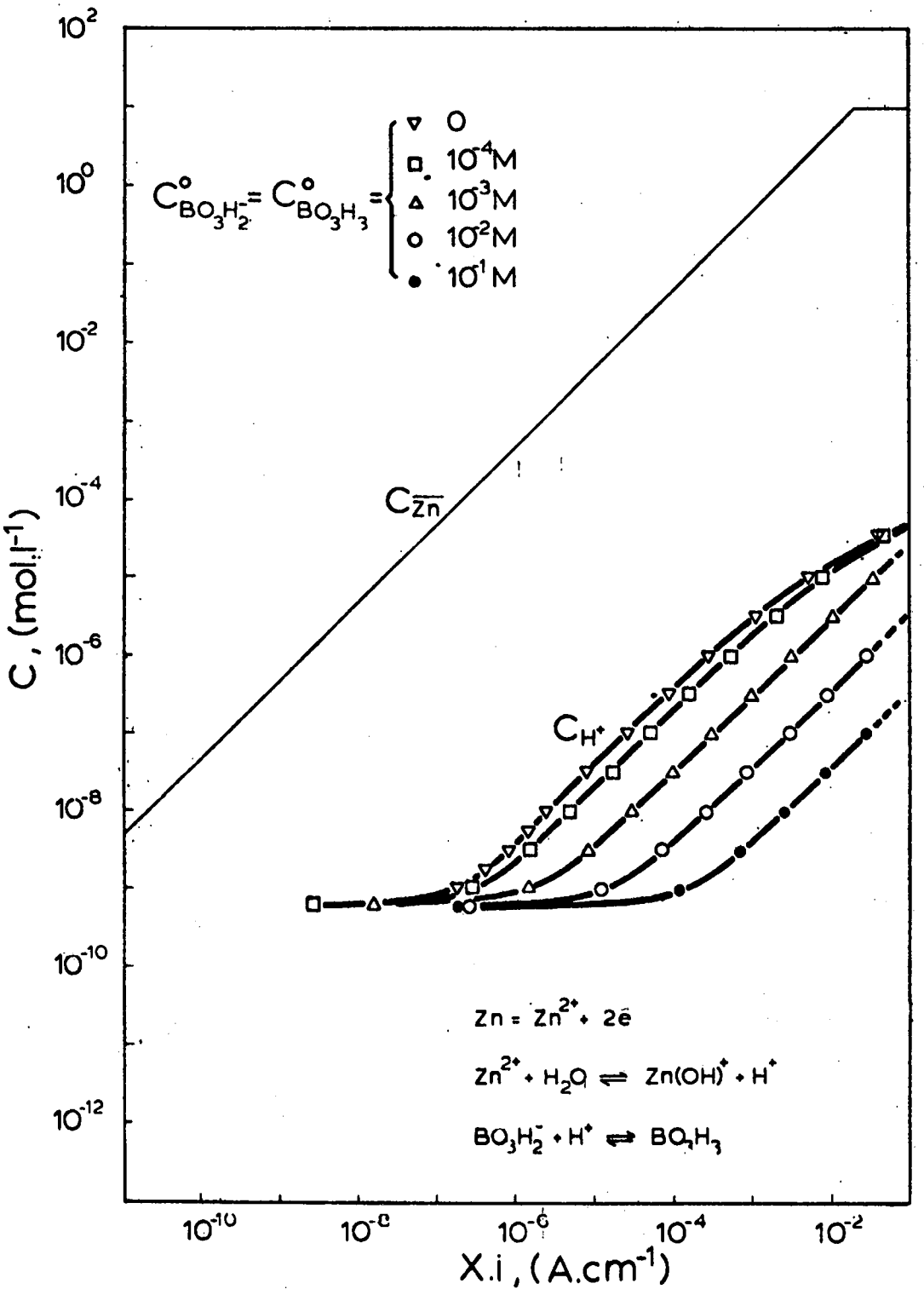

FIGURE 19.- Effect of the borax concentration on the H^+ concentration as a function of the product of the depth X and the current density i in a unidirectional zino pit, (149).

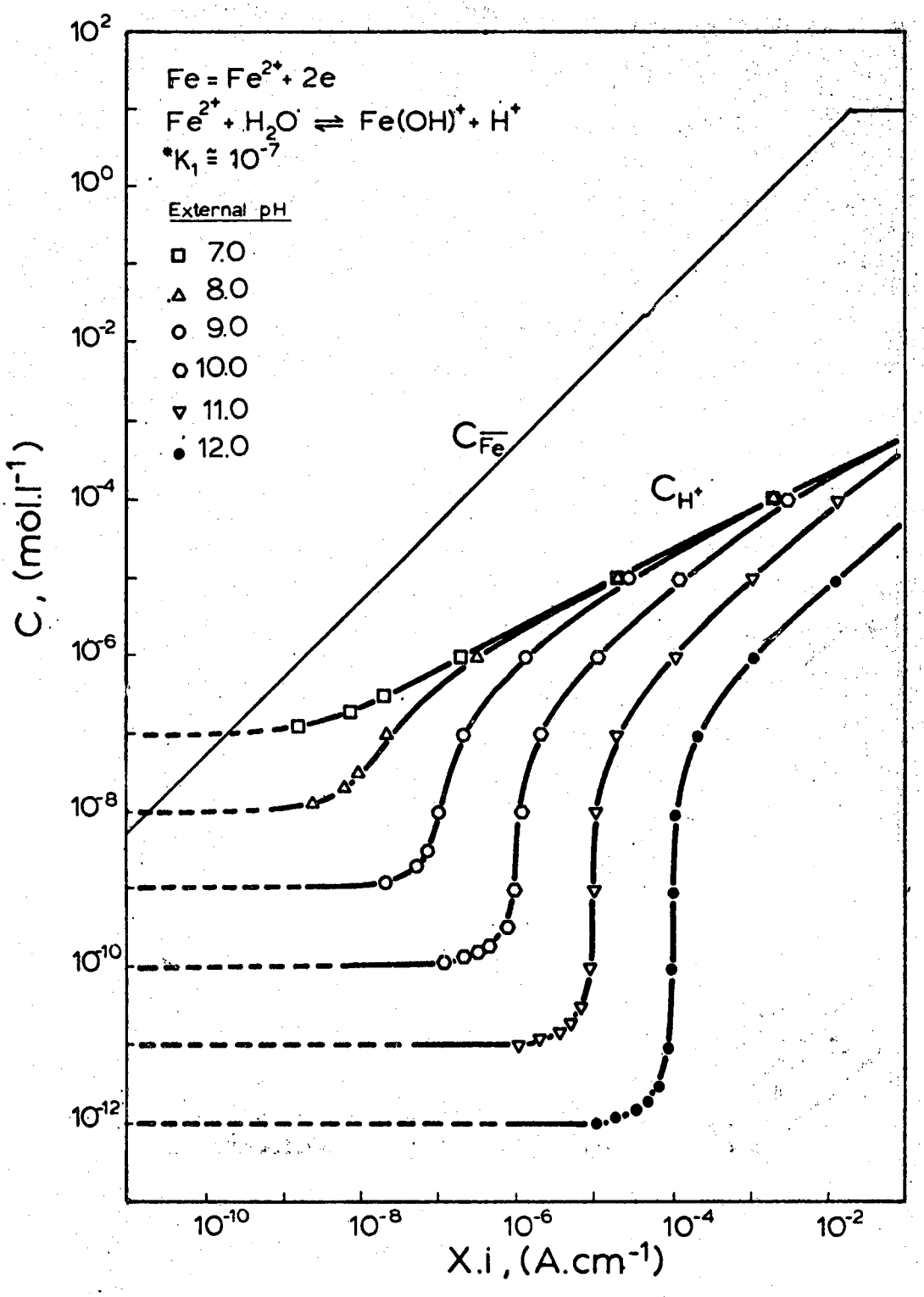

FIGURE 20.- Effect of the external pH on the concentration of H^+ as a function of the product of the depth X and the current density i in a unidirectional iron pit, (149).

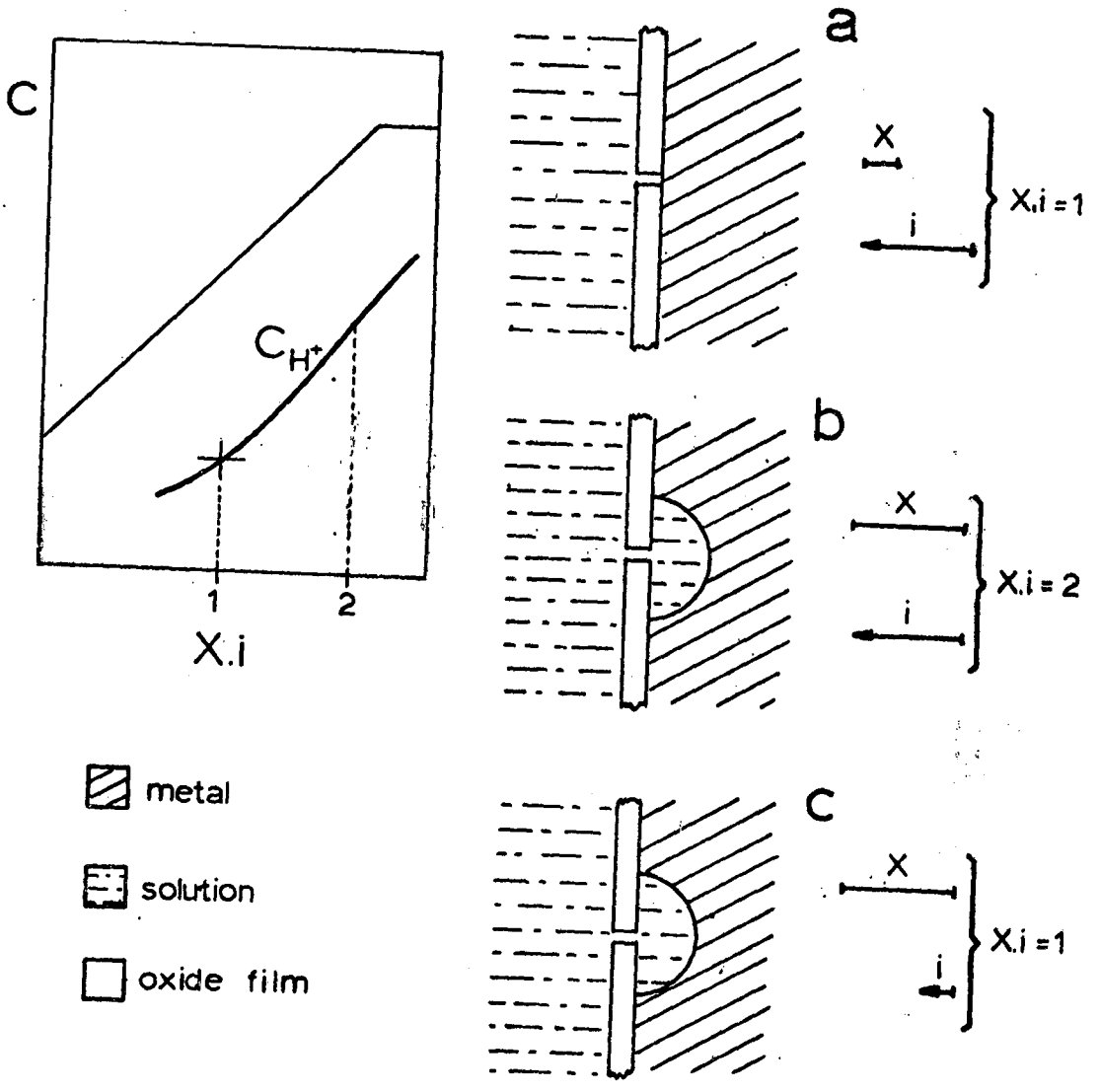

FIGURE 21.- Events leading to the measurement of pitting repassivation potentials, Er, different from the pitting potentials, Ep (149).

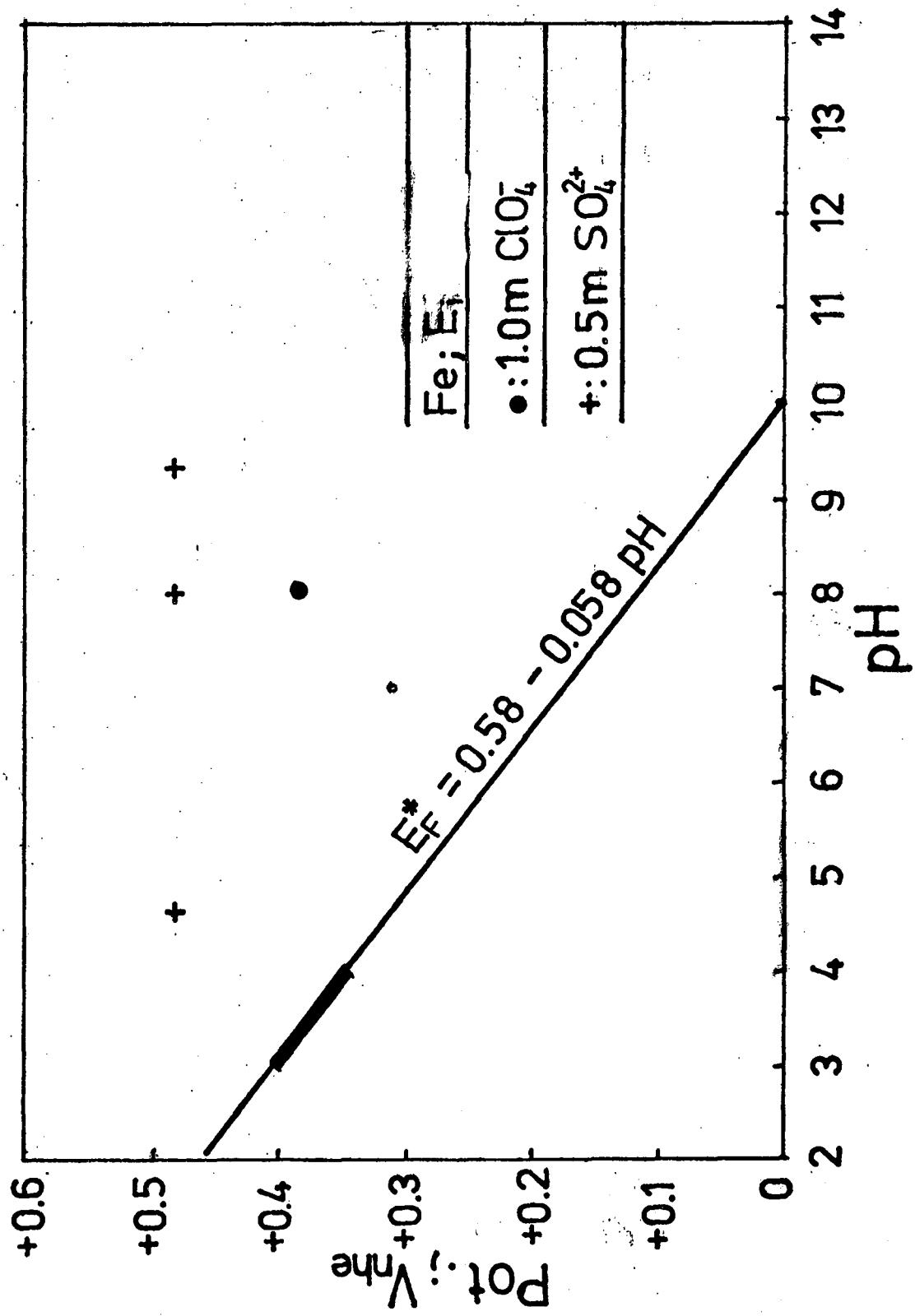

FIGURA 22.- Pitting inhibition potentials for iron, reported by Vetter and Strehblow (61), compared to the Flade potential of iron in a pit-like solution.