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MECHANISM OF CORROSION WITH LIMITED ACCESS OF ELECTROLYTE

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1. INTRODUCTION

Many engineering structures, items of chemical equipment, and instruments corrode most strongly, strange as it may seem, at those places to which access of the corrosive medium is difficult (flanged unions, shut-off equipment, hydraulic seals, constructional gaps and crevices, etc.).

This dangerous and widespread type of corrosion, which at first was most definitely and clearly exhibited in structural gaps and crevices, was called in the literature "crevice corrosion". Nowadays this term no longer reflects the variety of corrosion phenomena which arise as a result of restricted access of electrolyte to individual parts of fabrications and equipment. However, since this term has already taken deep root in the literature, we shall preserve it in the present review, but use it in a wider sense to cover, besides corrosion in crevices, selective linear dissolution of metals at the boundary of several phases, the corrosion of structures along the water-line, the development of pitting, etc.

Crevice corrosion plays an important part in the breakdown of structures in chemical equipment, diesel engines, atomic reactors, and instruments. Intense corrosion

develops not only in existing structural clearances and cracks, but also in those which arise during operation of the articles. Very important automatic devices, for example valves, often fail to operate owing to crevice corrosion, which entails serious consequences. The operation of devices having calibrated dispensing apertures breaks down in time, producing an excessive consumption of fuel, reagents, and occasionally even a failure in industrial processes.

Although great attention has been paid to crevice corrosion in several researches[1-17], the mechanism of the process has remained relatively little studied. This has impeded the development of rational methods of protection against corrosion, as well as the correct choice of materials for the manufacture of equipment and appliances.

Interest in crevice corrosion has revived recently, mainly owing to the requirements of industry, and these processes have begun to be widely studied, both in the Soviet Union and abroad.

In the explanation of crevice corrosion, the greatest currency has been attained by the ideas of differential aeration developed by Evans and Mears[2,4]. Further investigation has shown, however, that the mechanism of crevice corrosion cannot be reduced to differential aeration alone. Intensified crevice corrosion is often observed even in acid electrolytes, as well as in electrolytes which have been completely freed from oxygen. The processes which develop in crevices are in actual fact more complicated, and are governed by several factors. A far larger number of processes than had previously been assumed were found to occur by a mechanism of crevice corrosion. In particular, the corrosion of polyphase contacts in acid electrolytes[9-11], the pitting of stainless steels[12], and corrosion processes developing along the water-line[13,14] must be included in the above type of corrosion.

Electrochemical methods of investigating crevice corrosion[9,10,18] have been extremely fruitful, and have helped to establish several general laws and yield fresh results revealing the mechanism of crevice corrosion. They have shown convincingly that these phenomena are not associated with any special properties of the interface, but are caused by the change in the electrochemical properties of the metal at sites to which access of electrolyte is impeded.

It is now possible, on the basis of results obtained from a systematic study of a large number of metals[9,11,19,20], to elicit the most characteristic features of the process for most metals, and hence to formulate very general views on the mechanism of crevice corrosion.

The present paper reviews the most important results obtained in the study of crevice corrosion.

2. PECULIARITIES OF THE ELECTROCHEMICAL BEHAVIOUR OF METALS IN NARROW GAPS AND CREVICES

The specific character of electrochemical reactions occurring on metals in narrow gaps is due to difficulties in the access of corroding agents and passivators from the bulk of the electrolyte to the gap and the slow removal from it of the products of the electrochemical reactions[19,21,22]. Primarily it is the access of oxygen to the narrow gap that is greatly impeded, and this is responsible for several peculiarities in the course of anodic and cathodic reactions. The polarisation curves reproduced in Fig. 1 for iron in gaps show, for example, that in neutral electrolytes the rate of the anodic process is appreciably increased in the gap, while the cathodic process is retarded.

The accelerated ionisation of a metal in a gap is due to the fact that, as a result of the diminished concentration of oxygen in the crevice, anodic dissolution occurs at more negative potentials. The lower concentration of oxygen on the metal surface in the gap results in predominant formation of ferrous compounds, which possess no protective properties.

For the group of metals whose passive state is due to the presence of oxygen or other oxidant, obstacles to the access of these reagents to the crevice may so accelerate the anodic process that these metals begin to dissolve as active metals.

The diminished oxygen concentration in the gap has the opposite effect on the cathodic process: it makes both kinetic and diffusion stages of the process difficult. This is shown by the general displacement of the cathodic polarisation curves to more negative potentials (Fig. 1*b*) and the lower limiting diffusion current.

It is noteworthy that, after the gap has reached a certain width (0.25 mm) the limiting diffusion current becomes practically constant. The explanation is that the whole volume of electrolyte in such gaps is no longer mixed by convection, and transport of oxygen is effected only by diffusion.

The corrosion behaviour of metals in crevices and gaps can be predicted from the change in the kinetics of the electrochemical reactions. Metals which under normal conditions corrode with anodic control should be especially sensitive to crevice corrosion. Where, however, the rate of corrosion is governed by the kinetics of the cathodic reaction, corrosion in crevices will be slower than on a freely washed surface, since only the anodic reaction is accelerated, and in the given case does not govern the rate of spontaneous dissolution. It is assumed here, of course, that the duration of contact between metal and electrolyte is the same in the crevice and outside it. Actually, however, in atmospheric corrosion or even in corrosion under

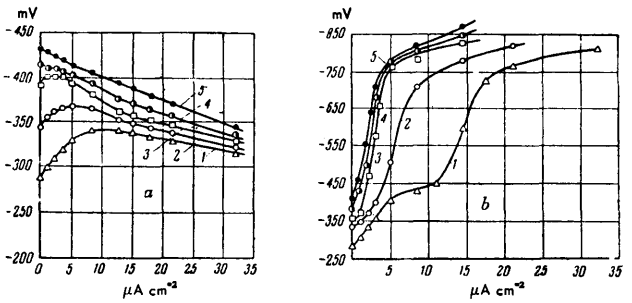


Fig. 1. Polarisation curves for iron in 0.5 *N* NaCl: *a*) anodic; *b*) cathodic: 1) in bulk; and in gaps of different width (in mm): 2) 1; 3) 0.5; 4) 0.35; 5) 0.25–0.05.

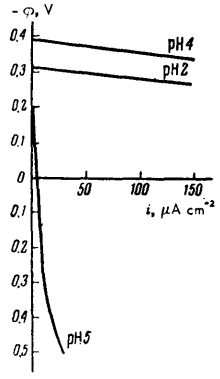


Fig.2. Potential dependence of rate of anodic ionisation of iron at various pH values.

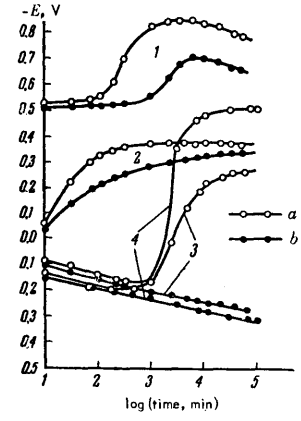


Fig.3. Time variation of steady-rate potentials of metals in 0.5 *N* NaCl: *a*) in a 0.05 mm crevice; *b*) on an open surface; for: 1) aluminium; 2) iron; 3) iron in (per litre) 70 mg Na_2SO_4 + + 30 mg NaCl + 250 mg $NaNO_2$; 4) stainless steel (13% Cr).

conditions of periodic wetting, electrolyte is retained considerably longer in the crevices, and for this reason corrosion is always more rapid in crevices than on an open surface.

The restricted supply of electrolyte to difficultly accessible sites results in a relatively rapid change in pH, which can be in either direction, as will be shown below. It is therefore necessary to consider how such changes influence the electrochemical behaviour of metals. As has been shown by one of us[23] and also by Iofa and Larin[10], an increase in pH in acid electrolytes (pH 1–4) accelerates the anodic ionisation of iron. In neutral electrolytes the opposite effect is produced, the anodic process being slowed down. These regularities are well illustrated by the polarisation curves in Fig. 2.

Study of the corrosion of many metals in gaps[19] confirms the theoretical prediction that crevice corrosion will depend on the nature of the controlling factor. Such metals as iron, zinc, and aluminium alloys of the Al–Zn–Mg–Cu (V95) and Al–Cu (D16) systems, in which corrosion is controlled by the rate of the cathodic reaction, corrode more slowly inside than outside crevices (with the same time of contact with the electrolyte). However, such alloys as Kh13, Kh17, AMTs, and AMG, which corrode with anodic control, are attacked more strongly in crevices than on a surface which is freely washed by the electrolyte.

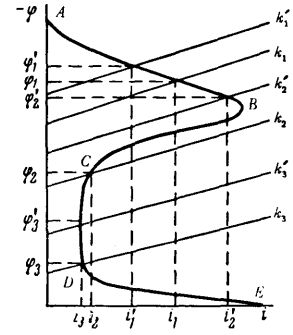


Fig.4. Potentiostatic curve representing behaviour of metals in crevices: *ABCDE*) anodic polarisation curve; k_1)–k_3) cathodic polarisation curves for open surface; k'_1)–k'_3) corresponding curves for surface in crevice; φ)–φ') steady-state electrode potentials.

3. CHANGE IN STEADY-STATE POTENTIALS AT SITES TO WHICH ACCESS OF ELECTROLYTE IS IMPEDED

The acceleration of the anodic ionisation of metal and retardation of cathodic depolarisation processes at sites to which access of electrolyte is impeded should result in the steady-state potential of metals being less noble at such positions. This has been confirmed by measurements on several metals in crevices[19] (Fig. 3), the potential in which may show a quite considerable shift to more negative values.

The change is especially great with stainless steels: with the steels Kh13 and Kh17, for example, the potential of the metal in a crevice is 0.55–0.60 V more negative than in bulk. The explanation is that, as a result of the insufficient supply of oxygen, the stainless steel passes from the passive into an active state, whereas iron, both in the bulk of the electrolyte and in a crevice, lies within the range of potentials characteristic of the active state, where there is no such strong dependence of potential on oxygen concentration.

In order to ascertain the possible consequences of the above changes in the kinetics of electrochemical reactions, it is useful to consider the potentiostatic curve for the anodic process (Fig. 4). Analysis of this curve shows that in principle crevice corrosion can develop in three ways: (1) when the steady-state potential of the metal is in the

active range, the negative shift in this potential occurring in a crevice, caused by the diminished efficiency of the cathodic process, should result in a lower rate of corrosion ($i_1 - i_1'$); and (2) and (3) when the steady-state potential of the metal is more positive than the potential of complete passivation, alloys may or may not be activated as a result of the hindrance to the cathodic process, depending on whether the steady-state potential of the metal is (2) close to the potential of complete passivation or (3) remote from the latter. In case (2) the negative shift in the steady-state potential in the crevice ($k_2 - k_2'$) results in activation of the metal and its intensified breakdown in the crevice ($i_2 - i_2'$); but in the last case ($k_3 - k_3'$) the passive state will not be disturbed ($i_3 - i_3'$).

It follows from the above that metals which are in a passive state should be especially sensitive to crevice corrosion, but the diminished efficiency of the cathodic process and the accelerated anodic process in crevices should not always produce activation of the alloy. If these changes in the kinetics of the electrochemical reactions do not bring the steady-state potential beyond the potential of complete passivation, activation will not occur. Although stainless and ordinary steels (the latter in the presence of inhibitors) are often activated in crevices the stable passive state of these metals can be preserved even in crevices provided that the chromium content of the alloy is sufficient or the solution contains sufficient inhibitor of oxidising type.

Hence it can be concluded that appliances which for engineering reasons contain gaps and crevices must be made of more highly alloyed steels, especially with higher contents of chromium and molybdenum.

4. CHANGE IN NATURE OF CORROSION MEDIUM IN GAPS

Strong crevice corrosion is to be expected in cases in which there is a clearly marked dependence of rate of corrosion on oxidant concentration, and especially in the presence of a critical concentration above which the alloy passes into the passive state. In this respect, the behaviour of iron in nitric acid is typical. Iron is passive in 8.6 N HNO_3. In crevices, however, where conditions for the continual renewal of the acid do not exist, and its concentration falls quite rapidly, corrosion is intensified (Fig. 5*a*).

Similar phenomena are observed when corrosion inhibitors, are used (Fig. 5*b*). Effective protection by an inhibitor depends on a constant supply of the latter to the metal surface[23]. Since such conditions do not obtain in crevices, the inhibitor concentration falls to critical values, which have been shown[23] to intensify instead of diminishing corrosion. Such a situation occurs in the presence not only of $NaNO_2$ and $K_2Cr_2O_7$ but also of Na_2HPO_4. In the last case strong corrosion is caused both by diminution in the phosphate concentration and also by inadequate supply of oxygen, in the absence of which phosphates are ineffective[24,28].

The dependence of intensity of corrosion on width of gap is interesting. Maximum corrosion is observed not with the minimum gap, to which access of reagent (HNO_3, $NaNO_2$) is most greatly impeded, but with some intermediate gaps. Such a relationship depends on the degree of breakdown of the passive state. The narrower the gap, the greater the proportion of the surface over which passivity has broken down, and corrosion becomes uniform

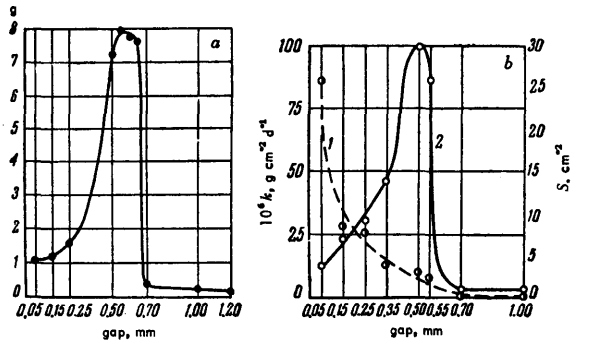


Fig.5. Dependence on width of gap of crevice corrosion of iron in oxidising agents: *a*) 8.6 N HNO_3; *b*) NaCl (30 mg litre^{-1}) + + Na_2SO_4 (70) + $NaNO_2$ (250): 1) corroded area; 2) intensity of corrosion.

in character. In intermediate gaps the concentration of oxidant is diminished to a smaller extent, and corrosion becomes local in character, penetrating to a relatively great depth.

In structures containing gaps and crevices, for example the cooling systems of diesel engines, which often break down, the total concentration of inhibitors must therefore be increased. This can be illustrated by results which we have obtained for the inhibitor concentrations required to ensure protection of a freely washed metal and of metal located in crevices (Table 1).

Apart from the above generalisations, the possibility of a change in character of the corrosion medium located in a gap must be taken into account. The small volume of the gap and the limited extent to which corrosion products diffuse away create conditions for more rapid saturation of the electrolyte by the corrosion products than in the bulk of the electrolyte. The formation of sparingly soluble hydroxides results in the rapid establishment of a definite pH in the gap, the value of which is controlled by the solubility product of the hydroxide. Thus saturation of a solution with $Fe(OH)_2$, $Al(OH)_3$, and $Mg(OH)_2$ respectively establishes pH values of 6.8–6.9,[25] 8.5, and 10.5.

With iron such a shift in pH is advantageous. With aluminium, however, the limit of the corrosion resistance of which in 0.5 NNaCl lies[26] within the pH range 6.5–8.0,

TABLE 1. Inhibitor concentrations required to protect steel in crevices (0.05 mm) and on open surface. Initial composition of electrolyte (mg litre^{-1}): 30 NaCl + + 70 Na_2SO_4.

Metal	$NaNO_2$, g litre^{-1}		$K_2Cr_2O_7$, g litre^{-1}		Na_2HPO_4, g litre^{-1}	
	open surface	crevice	open surface	crevice	open surface	crevice
Iron	0.1	2.0	0.07	1.20	3.60	30.0
Cast iron	0.95	11.5	0.08	1.00	—	—

displacement of the pH beyond these limits produces strong corrosion. For this reason the corrosion of aluminium is far greater in a gap (0.04 mm) than in bulk[20]. With decrease in the concentration of chloride ions, the pH limits of the corrosion stability of aluminium become wider[26], and therefore corrosion in crevices diminishes.

Hence it follows that the negative shift in the potential of aluminium in a gap is caused not only by the difficult access of oxygen but also by a change in the character of the corrosion medium. Moreover, as will be shown below, the greatest changes in corrosion medium in gaps result from the formation of macrocells of crevice–open surface type.

5. FORMATION OF MACROCELLS OF CREVICE–OPEN SURFACE TYPE

So far we have confined our discussion to the electrochemical and corrosion behaviour of metals in crevices alone. In reality, a metal in a crevice is always in contact with metal which is freely washed by electrolyte, and this circumstance substantially changes the character of the process[19]. Since, as was shown in Fig. 3, the potential of a metal in a crevice differs appreciably from its potential under free access of oxygen or other passivating agent, favourable conditions are created for the formation of macrocells, in which the metal in the gap constitutes the anode. The curves in Fig. 6, representing the time variation of the current arising between an electrode which is freely washed with electrolyte and an electrode located in a crevice, show that quite powerful cells can operate on various metals under such conditions.

A noteworthy feature is the presence of an induction period, during which the current from the cell is very small. With the steel Kh13, for example, a current was produced in 0.5 *N* NaCl after about 30 h, and with Kh17 after 28–30 d. This indicates that differential aeration cannot by itself initially secure the effective operation of such cells. Consequently there must be other factors producing a large current in the system. One of these we have already discussed, and this is the gradual loss of the passive state by the metal, owing to the restricted access of passivating agent. However, the change in the character of the corrosion medium in the crevice is no less important. Since the metal in the crevice has the more negative potential, it begins to act as anode in the corrosion cell, which immediately produces acidification of the corrosion medium in the crevice.

For example, our calculation for aluminium[20] decomposing water according to the equation $Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$ ($K_{AlOH^{2+}} = 1.4 \times 10^{-5}$) has shown that, with a current of 160 μA, the hydrogen-ion concentration in a gap (δ = = 0.04 mm, v = 60 mm³) must be established at pH 3.5 after only 1 h. Experimental determinations give similar values (3.2–3.4).

With aluminium and stainless steels, such acidification of the medium causes further acceleration of anodic reactions in the crevice and produces stable operation of the macrocells, with ultimate breakdown of the metal in the crevice[20,27].

Differential aeration is thus merely the initial cause. The main attack on the metal in the crevice, however, is due to the appearance of active–passive macrocells, the functioning of which results in acidification of the corrosion medium in the crevice.

Hence the main requirement of material to be used for equipment containing structural gaps and crevices is relative insensitivity to change in pH.

In order to be able to predict the behaviour of metals in crevices, it was of interest to study the functioning of cells of crevice–open surface type, and determine the relation between the polarisation resistance and the ohmic resistance. Fig. 7 shows the corrosion diagram for the stainless steel Kh13, from which it follows that the existing view that ohmic control predominates in such systems is incorrect†.

Even in extremely fine gaps (0.05 mm) the system is practically completely polarised in 0.5 *N* NaCl. Owing to the facilitation of the anodic reaction in the crevice, the proportion of anodic control is small, and the working of

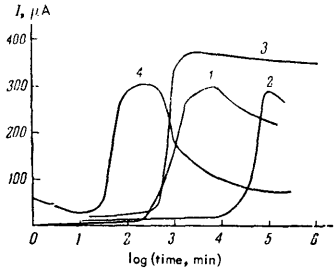


Fig. 6. Time variation of current flowing between two identical electrodes (of area 30 cm²), one being in a crevice and the other freely washed with electrolyte (0.5 *N* NaCl): 1) stainless steel Kh13 (13% Cr); 2) stainless steel Kh17 (17% Cr); 3) brass L62 (62% Cu); 4) aluminium.

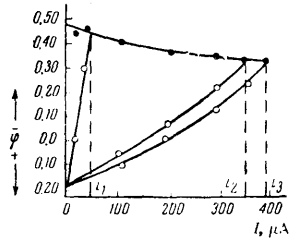


Fig. 7. Actual corrosion diagram for cell of type metal in gap (0.05 mm)–open surface of metal (stainless steel Kh13, 13% Cr) with 0.5 *N* NaCl as electrolyte and area of electrode in gap 30 cm². Ratio of areas: i_1) 1 : 1; i_2) 1 : 10; i_3) 1 : 15.

† An ohmic potential drop can be observed only in deep crevices.

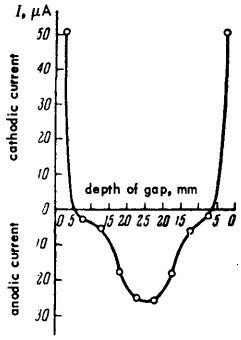


Fig.8. Distribution of current at different depths in crevice and polarity of different parts of metal in 0.5 *N* NaCl, with gap 0.1 mm wide and 25 mm deep.

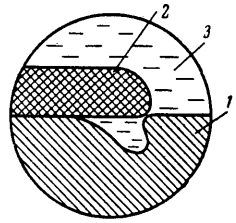


Fig.9. Corrosion structure produced in the corrosion of iron in contact with a dielectric in an acid; 1) metal; 2) paraffin wax; 3) acid.

such cells is controlled mainly by the rate of the cathodic reaction. With stainless steels of the Kh13 and Kh17 type, ohmic control proved to be so small that it could not be determined graphically. The proportion of anodic control was 4–20%, and that of cathodic control 80–96%. Since cathodic control predominates in the operation of such cells, as the diagrams show, the crevice corrosion of stainless steels and other passivated alloys should greatly depend on the cathode area, since the effectiveness of the cathodic process will increase with increase in the area of electrode which is freely washed by the electrolyte. Experiments which we have carried out under laboratory conditions[27], and by Ellis and La Que in natural seawater[8], have shown that the intensity of the crevice corrosion of stainless steels is directly proportional to the area of metal which is freely washed by electrolyte.

It must be noted that macrocells may arise within a crevice itself, owing to the difference between its edges and its centre in the rates of supply of depolarisers or corrosion medium and of removal of reaction products. This is clearly illustrated by the curve showing the distribution of current in a crevice (Fig. 8), which indicates that, as a result of the electrochemical inhomogeneity, the edges of the crevice act as cathodes, and the middle as anode[9].

6. SELECTIVE LINEAR DISSOLUTION AT PHASE BOUNDARY

The selective linear dissolution of iron at a three-phase boundary in acids occurs by the above mechanism, as our own work[9,11] and also that of Larin and Iofa[10] has shown. When in contact with a dielectric, iron and low-alloy steels break down in acids in a characteristic manner: a peculiar corrosion structure in the form of a deeply etched grove (Fig. 9) appears along the whole perimeter of the metal–dielectric boundary (the dielectric can be, for example, a blob of paraffin wax).

This interesting type of breakdown at one time attracted the attention of numerous investigators. Many hypotheses and guesses were made. Evans[2] assumed that the phenomenon was due to differential aeration; Kistyakovskii[29] and Mirlis[30] attributed it to the specific properties of dielectrics; and Tikhonov[31] supposed that portions of the surface on which bubbles of evolved hydrogen were resting became anodic zones.

The first experiments showed, however, that selective linear dissolution is observed even in electrolytes which have been completely freed from oxygen. Hence the phenomenon cannot be explained by differential aeration. Nor can the specific properties of dielectrics be used, since experiments have shown that the rate of selective linear dissolution along the perimeter is independent of the nature of the dielectric. Furthermore, such dissolution has been observed even on contact between two uniform metal surfaces.

Actually, the phenomenon is due to the formation of concentration cells. In the narrow gap along the perimeter between dielectric and metal, the pH of the electrolyte rises quite rapidly owing to reaction between metal and acid. Since access of fresh acid from the bulk of the electrolyte to the narrow gap is difficult, the difference in pH between crevice and bulk is maintained. It appeared that the rise in pH in the crevice should result in a diminished rate of corrosion. However, the situation is changed fundamentally by the existence of a contact between the metal in the crevice and the metal which is freely washed with electrolyte. As has been shown by one of us[23] and also by Larin and Iofa[10], increase in the pH of acid electrolytes makes the steady-state potential of a metal less noble and accelerates the anodic ionisation of the metal. It was found that, the greater the alkalinity of the electrolyte, the more easily does ionisation of metals occur.

$p H_2SO_4$ (*N*)	0.4	0.2	0.1	0.01	0.002
$\log i_a$	−3.90	−3.50	−2.70	−0.40	+0.1

This can be illustrated by the accompanying results obtained by Larin and Iofa[10] for the rate of dissolution of iron in sodium sulphate solution acidified with sulphuric acid, the electrolyte concentration being constant ($p + q$ = = 0.5 *N*). When the total concentration of sodium sulphate (q) and of sulphuric acid (p) was 0.5 *N*, the rate of anodic dissolution (i_a) at a potential of -0.250 V increased greatly with decrease in the concentration of sulphuric acid.

Similar results, indicating that the ionisation of iron becomes more rapid with increase in pH, were obtained by Kabanov and Leikis[32] and also by Bonhöffer and Heusler[33].

The former workers explained this interesting fact by the influence of hydroxide ions adsorbed on the surface, which facilitates ionisation of a metal. A relation between potential and pH such as that[23] illustrated in Fig. 10 provides conditions for the formation of a macrocell, with the metal in the gap as anode and the remainder of the surface as cathode.

The validity of the above mechanism can be demonstrated by the following striking experiments. If two identical iron sheets are taken, one of them is coated with a dielectric in such a way that a narrow crevice exists between metal and dielectric, and they are immersed in an electrolyte solution, an e.m.f. of 80–100 mV is established quite rapidly between the two electrodes, and a current (15–20 μA cm^{-2}) begins to flow. The anode in such a cell is the metal which forms the crevice with the dielectric.

Similar results can also be obtained with two identical electrodes which are connected to one another if the electrolyte (0.2 N H_2SO_4) around one of them is gradually made alkaline. A current flows in this case, too, its direction indicating that the metal in the more alkaline electrolyte is the anode (Fig. 11). This relation is maintained over a wide pH range, and only when this solution has become strongly alkaline (pH 12–13) does the metal in the more acid electrolyte become the anode. This is explained by the strong passivating effect of alkali, which makes the potential of the steel more positive.

A similar change in electrolyte pH takes place in the narrow gap between metal and dielectric, but in this case the increase in pH results from reaction of the acid with the metal, not from its neutralisation with alkali. The variation in pH in the crack is limited, since the anodic reaction products from the corrosion cell undergo hydrolysis and reacidify the electrolyte[20,27]. Ultimately a definite relation is established between the two processes, the pH usually reaching 2.5–3.5, *i.e.* the level which precisely favours the most efficient operation of the macrocell (see Figs. 2 and 11).

Interesting results have been obtained in a study of the functioning of similar concentration cells produced by change in the hydrogen-ion concentration (Table 2). When the concentration cell

$$Fe\,|\,(m+n)Na_2SO_4\,|\,mH_2SO_4+nNa_2SO_4\,|\,Fe$$

is on open circuit, the electrode in the acid electrolyte corrodes the more strongly. When, however, the electrodes are short-circuited, the situation is changed: corrosion of the electrode washed by the neutral electrolyte

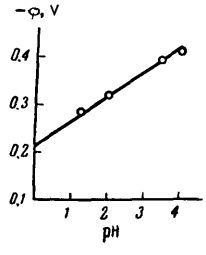


Fig. 10. Dependence of electrode potential of iron on pH.[23]

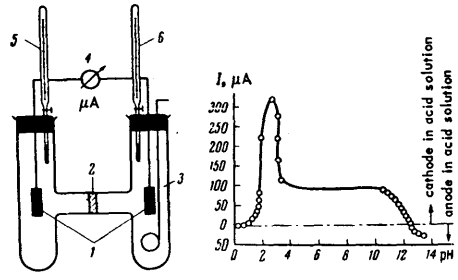


Fig. 11. Current flowing between two identical iron electrodes immersed in 0.2 N H_2SO_4 as function of pH of electrolyte around one of them (right-hand side). The left-hand side shows the apparatus for measuring such currents: 1) iron electrodes; 2) porous diaphragm; 3) stirrer; 4) microammeter; 5) and 6) microburettes.

TABLE 2. Rate of corrosion of iron electrodes (area 30 cm^2) of concentration cell in sulphate mixtures.

No.	Experimental conditions	I, μA	Rate of corrosion $\times 10^6$, g m^{-2} d^{-1}		
			in absence of contact	in contact with anode	in contact with cathode
1	0.2 N Na_2SO_4	—	5.23	—	—
2	0.2 N H_2SO_4	—	35.20	—	—
3	−Fe/0.2 N Na_2SO_4/0.2 N H_2SO_4/Fe, $S_a : S_c = 1 : 1$	200	—	30.26	33.09
4	−Fe/1 N Na_2SO_4/0.2 N H_2SO_4 + 0.8 N Na_2SO_4/Fe, $S_a : S_c = 1 : 5$	260	—	77.30	34.10

increases sharply‡. This is because the latter electrode becomes the anode, and anodic processes take place preferentially on it while the cathodic processes are in this case concentrated on the electrode in the acid electrolyte, the potential of which is kept at a more positive value by the high concentration of hydrogen ions and the slight polarisation. As a result of anodic polarisation, the rate of corrosion of the iron electrode in the neutral electrolyte is increased almost sixfold. The corrosion current of such a cell is 200 μA (Table 2). This occurs when the ohmic potential drop in the cell has been 90% of the initial potential difference§. If both internal and external resistances of the cell are reduced to a minimum, *i.e.* if the system is completely polarised, the current is increased

‡ Schikorr[34] and Liebreich[35] pointed out at one time that, if one sheet is placed in NaCl and another in HCl, and they are short-circuited, the sheet in the NaCl will corrode. In fact both electrodes corrode, and it is only under certain conditions, which will be discussed later, that corrosion of the electrode in the more alkaline electrolyte can be greater than that of the electrode in the acid electrolyte.

§ The high resistance is due to the diaphragm separating the anolyte from the catholyte.

by a factor of almost 18, and reaches about 3 mA. If, with the aim of decreasing the internal resistance of the cell, the concentration of the sulphate mixture is increased to 1 *N* and the area of the anode is diminished, which does occur in selective linear corrosion at a three-phase boundary, the rate of corrosion of the electrode in the neutral electrolyte (anode) is more than double the rate of corrosion of the cathode, *i. e.* the electrode in the acid solution.

7. CORROSION IN THE WATER-LINE ZONE

Very many structures are subject to strong attack in the region of the water-line (ships, gas-holders, cisterns, apparatus, etc.), corrosion being observed both directly at the water-line and below it (Fig. 12). At one time the mechanism of such processes was reduced to differential aeration[2]: *i. e.* it was supposed that, owing to the differential access of oxygen to portions of the metal situated along the water-line and below it, differential aeration couples were formed. The potential of the more aerated portion of the metal directly at the water-line became more noble, and the metal itself became the cathode; the portions below the water-line formed the anodes, and underwent corrosion.

However, strong corrosion along the water-line is often observed in acid medium, as well as in thoroughly stirred electrolytes, where differential aeration cannot play any important part. In order to explain such cases, the idea was put forward[2,14] of "surface competition", according to which products formed by reaction of the metal with the medium, which are usually protective in character, are deposited preferentially at the meniscus on the water–air interface, rather than at the water–metal interface.

Marshakov and Zanina[14] have recently made a detailed quantitative study of these phenomena, and established that most of them occurred by the mechanism of crevice corrosion discussed above. According to the views developed in this work[2,14], the meniscus at the metal–electrolyte–air boundary and the water-line is to be regarded as a narrow crevice, to which continuous access of electrolyte is greatly impeded. As a result, for example in acid media, the electrolyte near the meniscus becomes alkaline fairly rapidly, and the metal in this zone becomes more negative. A cell is formed in which the metal located directly at the water-line forms the anode, and undergoes intensified attack.

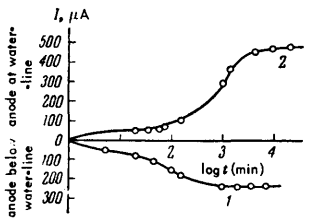


Fig. 12. Anodic zones arising at the water-line on iron[14]: 1) anodic processes concentrated below water-line in 0.1 M Na_2SO_4; 2) anodic processes concentrated at water-line in 0.1 M H_2SO_4. Perimeter along water-line 12 cm; area of electrode 50 cm^2.

It is interesting that a quantitative determination of the relation between ohmic and polarisation resistances has shown that, in spite of the narrow crevice formed by the meniscus, the ohmic resistance of the cell is low in this case, too. It has also been shown that the breakdown of steel in the water-line zone in inhibited media containing an incorrect quantity of the inhibitor likewise takes place by the mechanism of crevice corrosion. Very frequently cases of strong attack on structures along the water-line have been observed in media containing a concentration of inhibitor which, it would appear, should completely exclude corrosion. It has been found that these phenomena, too, are caused by the peculiarities of electrochemical behaviour of the metal at the meniscus, which forms a narrow crevice at the surface of the metal: as a result of inadequate access of inhibitor to this portion of the electrolyte, the concentration of inhibitor in it falls fairly rapidly, and the potential of the metal becomes more negative. It can be shown that under these conditions a quite powerful voltaic cell is formed, in which anodic processes are concentrated in the region of the meniscus, which also results in corrosion of the metal along the water-line. As these processes are not caused by any special properties of the water-line, but are due solely to a change in the concentration of inhibitor, dangerous corrosion at the water-line can be eliminated by using for such structures higher inhibitor concentrations than are usual, so that the concentration in the meniscus does not fall to dangerous levels.

8. PITTING

Stainless steels and other readily passivated alloys, usually distinguished by great resistance to oxidising media, are readily activated by halide ions. Activation takes place at a limited number of points, at which intense corrosion begins to develop rapidly, accompanied by the appearance of deep pits.

Such selective dissolution can be explained by variation, between different points on the surface, in the strength of bonding of the metal with the oxygen responsible for the passive state. At points where for some reason such bonding is weak, the oxygen is displaced by halide ions, and corrosion starts at these points. Once having begun, it must, in Kolotyrkin's opinion[36], accelerate, since halide ions, being the majority current carriers, begin to move towards these centres, increasing the concentration of activator.

Rozenfel'd and Danilov[12,37] have recently obtained results which enable the development of pitting to be explained on the basis of the above theoretical ideas concerning crevice corrosion. The new concept has been put forward, and confirmed experimentally, that pitting is to be regarded as the main form of crevice corrosion. Pits formed on the surface of stainless steels are mostly enclosed foci of corrosion, to which access of oxidant is impeded.

The diminished effectiveness of the cathodic process in a pit brings the steady-state potential of the latter beyond the potential of complete passivation, this being accompanied by loss of the passive state by the metal and acceleration of its anodic ionisation in the pit. The situation is still further complicated by the formation of powerful

macrocells, with the pits as anodes, as a result of the different conditions of access of the electrolyte to a pit, representing a relatively enclosed region, and to the rest of the surface, to which the electrolyte has free access. Owing to hydrolysis of the products of the anodic reaction, the functioning of such cells is accompanied by strong acidification of the medium in the pit with intensified attack on the metal in the latter. Thus from its very birth a pit represents a kind of crevice within which, because of insufficient access of passivator, favourable conditions are created for the rapid development of predominantly anodic processes.

It is obvious that, if pitting represents a special form of crevice corrosion, in which the peculiarities of the electrochemical behaviour of the metal are caused solely by a difference in access of corrosion medium and removal of corrosion products, as has been demonstrated, pitting should cease when identical access of electrolyte to the pits and to the rest of the surface is ensured. Experiments have supported this hypothesis. If the coating is removed from pits which form on a metal surface, and free access of electrolyte to them is thereby ensured, they stop growing. However, in closed pits, to which access of electrolyte, and hence of passivator, is difficult, corrosion continues to penetrate deep into the metal (Fig. 13, curves *1* and *2*).

Interesting results have been obtained also from a study of the number of points at which activation of the alloy with formation of a pit can occur. It is usually supposed that the surface of a stainless steel contains a limited number of points, governed by the structural peculiarities of the alloy, at which pitting can occur[38]. Experiments have shown, however, that this is not altogether the case: the number of pits increases continuously as previously formed pits are opened up (Fig. 14). This is explained by regarding each initially formed covered pit as a point protector, which greatly diminishes the probability of pits being formed at other points on the surface. If, however, the initially formed pits are uncovered, and their growth is thereby terminated, the protective effect disappears, and an ever increasing number of pits appear on the surface (Fig. 14, curves *2–4*). Consequently, doubt should be cast on the assumption that the metal surface contains some limited number of centres which are sensitive to pitting corrosion. In fact there are very many of them, and the formation of new pits is prevented only by the protective effect of previously formed pits.

The experimental work discussed above provides convincing support for the idea that pitting develops by the mechanism of crevice corrosion.

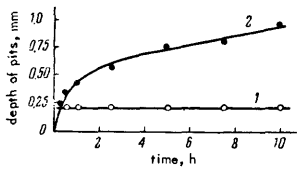


Fig. 13. Penetration of corrosion into stainless steel 1Kh18N9T in 2% $NH_4Fe(SO_4)_2.12H_2O$ + + 3% NH_4Cl: 1) open pits; 2) closed pits.

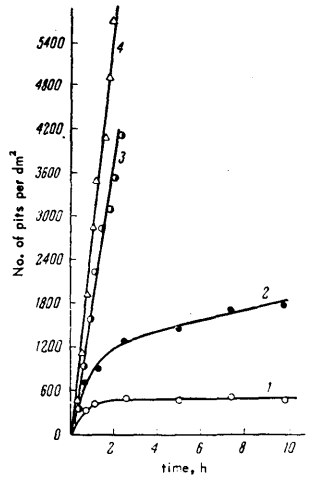


Fig. 14. Pitting of stainless steel 1Kh18N9T in 2% $NH_4Fe(SO_4)_2.12H_2O$ + 3% NH_4Cl: 1) initial pits not uncovered; 2) pits uncovered after 0.5, 1, 2.5, 5, 7.5, and 10 h; 3) pits uncovered every 15 min; 4) as 3) but in electrolyte containing (per litre) 11.5 g $FeCl_3$ + + 25.5 g NaCl.

In conclusion it must be noted that the above phenomena obviously play a decisive role in the corrosion cracking of engineering structures, which usually begins with the appearance of extremely fine cracks in the metal, in which, owing to the insufficient access of electrolyte, anodic processes should develop preferentially.

It is remarkable that research on the above processes, which was initially cognitive in character and aimed at finding methods for slowing them down in order to prevent dangerous forms of breakdown in chemical equipment, has recently had an unexpected outcome in practice in an exactly opposite field — the chemical working of metals and alloys — which requires the rapid occurrence of electrochemical reactions. It has been found that the enhanced etchability of metals in narrow gaps and crevices can be very successfully utilised for the chemical milling, drilling, and cutting of especially hard and strong alloys which are difficult to machine.

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