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Test techniques for pitting and crevice corrosion resistance of stainless steels and nickel-base alloys in chloride-containing environments

J. W. Oldfield

Test methods currently available for determining the resistance of stainless steels and related alloys to pitting and crevice corrosion in chloride environments are assessed. The present understanding of the mechanisms of pitting and crevice corrosion are examined, and the major factors affecting the processes are noted. Accelerated and exposure test techniques are considered in relation to their ability both to provide an accurate ranking of materials and to relate to service conditions. All tests reviewed had some drawbacks. IMR/169

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INTRODUCTION

The successful use of stainless steels and nickel-base alloys in chloride-containing environments, including sea water, depends on their ability to resist localized attack. The term 'localized attack' is generally taken to include pitting corrosion, crevice corrosion, stress corrosion cracking, and intergranular corrosion. This review is concerned with assessing methods currently available to test an alloy's resistance to pitting and crevice corrosion attack. Tables 1 and 2 give the compositions of some of the standard and special stainless steels referred to in this review.

The usual reasons for testing a material are to determine whether or not it will perform satisfactorily in a given environment and to see how it compares with other materials in this respect. In other words, the aim is to obtain information that will allow the selection of the optimum material, in terms of properties and economics, to be made.

In order to assess the validity of a particular test for predicting performance in a given environment, the following facts must be known and understood:

(i) the detailed mechanism by which pitting and crevice corrosion occur
(ii) whether the test relates to resistance to initiation or propagation of attack, or both
(iii) whether the test, its environment, and sample assembly correspond to the practical situation to which it is being related.

Tests themselves fall into two broad categories: accelerated tests and natural exposure tests. Within each category there is a range of tests for both pitting and crevice corrosion.

In this paper the current understanding of pitting and crevice corrosion is reviewed, the factors affecting these processes are examined, and then the individual test techniques which are currently available are assessed in terms of their ability to predict performance in chloride environments.

CURRENT UNDERSTANDING OF PITTING AND CREVICE CORROSION

PIT INITIATION

Kruger and Rhyne[1] have recently reviewed pitting and crevice corrosion, and list the following characteristics as usually being considered necessary for the initiation of localized attack by pitting:

(i) a critical potential E_{np}, usually called the pit nucleation or breakdown potential, must be exceeded; there also exists a critical protection potential E_{cp}, which is more active than E_{np}. Corrosion, once initiated, cannot be stopped at potentials more noble than E_{cp}
(ii) aggressive species, particularly the chloride ion
(iii) an induction period separating the initiation of the breakdown processes, by the introduction of conditions conducive to breakdown, and the completion of the process when pitting commences
(iv) breakdown at localized sites.

Many models have been proposed which satisfy the above requirements. They can be grouped into three general models, and while it is not the purpose of this paper to review these in detail, it is nevertheless worthwhile mentioning them briefly.

Absorbed ion displacement models[2–5]

In these models anionic species such as Cl^- ions are absorbed on to the passive film, either singly or in groups, and compete with oxygen in the film. In this way the protective nature of the film is reduced by reducing the metal ion–metal lattice bond strength.

Ion migration or penetration models[6–8]

These models assume that anions penetrate the passive film, breakdown being complete when the anion reaches the metal/film interface. These models range from those which assume the existence of pores in the passive film to those which assume penetration by migration through a pore-free film.

Table 1 Composition of some standard stainless steels,* wt-%

Structure	AISI grade	C (max.)	Mn (max.)	S (max.)	Cr	Mo	Ni
Austenitic	304	0·08	2	0·03	18–20	...	8–10·5
Austenitic	304L	0·03	2	0·03	18–20	...	8–12
Austenitic	316	0·08	2	0·03	16–18	2–3	10–14
Austenitic	316L	0·03	2	0·03	16–18	2–3	10–14
Austenitic	317	0·08	2	0·03	18–20	3–4	11–15
Austenitic	317L	0·03	2	0·03	18–20	3–4	11–15
Austenitic	321†	0·08	2	0·03	17–19	...	9–12
Austenitic	347‡	0·08	2	0·03	17–19	...	9–13
Duplex	329	0·1	2	0·03	25–30	1–2	3–6
Ferritic	430	0·12	1	0·03	16–18	...	...

*Si and P levels not included.
†Ti: 5 × C (min).
‡Nb + Ta: 10 × C (min).

Breakdown–repair models[9–12]

Models in this group are based on chemically induced mechanical disruption of the passive film. Included in this set are the local acidification model, breakdown occurring via mechanical or electrochemical means followed by hydrolysis of metal ions to give a reduction in pH, and the salt film model, where a non-protective salt film is formed where the film breaks down.

In addition to models which attempt to explain the cause of breakdown of the passive film and the onset of pitting corrosion, recent work has been carried out to investigate the probabilistic nature of pit initiation assuming the process to be stochastic.[13,14] In such work pit initiation is treated as a random event, which in some cases leads to a stable pit being established. This modelling explains many of the observed phenomena, although there is, as yet, no single model which links the stochastic approach to the fundamental modelling outlined above.

PIT PROPAGATION

The nature of propagation is such that theories describing it are concerned mainly with geometry, mass transfer, and reaction kinetics. Propagation models can be divided into three groups.

Metal dissolution hydrolysis[11,15,16]

In this approach the dissolution and hydrolysis of metal ions are considered as a function of pH and potential, and compared with the hydrogen evolution reaction. In Galvele's model[11] a potential is defined at which the rate of production of hydrogen ions via hydrolysis is equal to their rate of consumption via hydrogen evolution. Below this potential passivation is maintained; above it repassivation does not occur.

Table 2 Composition of some special austenitic stainless steels and nickel-base alloys, wt-%

Designation	Cr	Mo	Ni	Cu	Others	Fe
UNS N08904	20	4·5	25	1·5	...	Bal.
Incoloy alloy 825*	21·5	3·0	42	2·2	1·0 Ti	30
Allegheny 6X*	20	6·5	24	...	...	Bal.
UNS S31254	20	6	18	0·8	0·2 N	Bal.
Sanicro 28*	27	3·5	31	1·0	...	Bal.
Alloy 20	20	2·2	34	3·3	Nb	Bal.
Alloy G	22	7·0	46	2·0	2·0 (Nb+Ta)	19
Inconel alloy 625*	21·5	9·0	61	...	3·7 (Nb+Ta)	2·5

*Trademark: proprietary alloys.

Salt layer formation[12,17,18]

In this approach it is assumed that a highly resistive film, probably a salt film, exists on a growing pit's surface. Vetter and Strehblow[12] consider this film to be formed by the cations of the metal and the aggressive ion. The film is considered dense and poreless; the rate of pit growth is equivalent to the rate of salt film dissolution.

Mass transfer control[19,20]

In this group of models the mass transfer of species in and out of the pit are assumed to be the corrosion-controlling reactions. Although mass transfer by migration can occur, the assumption is usually made that it is by diffusion only.

CREVICE CORROSION INITIATION

Crevice corrosion differs from pitting corrosion by virtue of the different geometries involved: a crevice results in the restriction of mass transfer of species in and out of the crevice region, whereas pitting is concerned with an open surface. Nevertheless, the possible mechanisms by which the film breaks down are those of pit initiation described in the previous section, the difference being that the environment becomes more aggressive with time for crevice corrosion.

Assuming a stainless steel crevice in a neutral saline solution, it is generally agreed that the initiation stage of crevice corrosion can be divided into three stages.[1,21,22]

During the first stage, reactions initially take place on both the uncreviced area and the area within the crevice. In simple terms these can be written as follows:

$$\text{Anodic reaction: } Me \rightarrow Me^{2+} + 2e^-$$
$$\text{Cathodic reaction: } H_2O + \tfrac{1}{2}O_2 + 2e \rightarrow 2OH^-$$
$$\text{Overall reaction: } 2Me + O_2 + 2H_2O \rightarrow 2Me(OH)_2$$

This reaction leads to thickening of the passive film. Diffusion of oxygen into the crevice is severely limited, and consequently the solution inside the crevice becomes depleted of oxygen.

In the second stage, after depletion of oxygen inside the crevice, an electrochemical cell is set up with the anodic reaction occurring inside the crevice and the cathodic reaction outside. This results in an increase in metal ions in the solution inside the crevice; these ions then hydrolyse and reduce the pH of the crevice solution:

$$Me^{2+} + 2H_2O \rightarrow Me(OH)_2 + 2H^+$$

At the same time migration of anions from the bulk solution occurs to maintain electrical neutrality; the result is a build up of Cl^- within the crevice. Thus, during this stage the pH falls and the chloride level increases within the crevice.

The third stage is the point in the process when the solution in the crevice is able to break down the protective passive film on the stainless steel. The composition of this solution is defined by a pH and a

Cl^- level and is termed the critical crevice solution (CCS). This signals the end of the initiation stage and the start of the propagation stage.

This mechanism of crevice corrosion initiation has been modelled, taking account of a whole range of factors including crevice geometry, bulk environment, and CCS values.[21,23] It has also been adapted and is used as a test method for predicting resistance to crevice corrosion initiation.[24]

CREVICE CORROSION PROPAGATION

Once the breakdown of passivity has occurred within the crevice, rapid dissolution takes place. This reaction is balanced by the cathodic reduction of oxygen outside the crevice and, if the pH is low enough, hydrogen evolution inside the crevice. As with pitting corrosion the rate of propagation is mainly concerned with geometry, mass transfer, and reaction kinetics, and no complete model of the process has yet been developed, although attempts have been made to do so.[25,26]

FACTORS AFFECTING PITTING AND CREVICE CORROSION

It is not the purpose of this review to go into great detail on the influence of individual factors on the pitting and crevice corrosion of stainless steels. Nevertheless, it is worthwhile to consider these briefly since many of them play an important part in the test techniques discussed below.

ALLOY COMPOSITION

The main effect of alloy composition is that it controls the stability of the protective passive film, and this is dealt with below. However, there are other effects. For example, if the passive current is assumed to comprise metal ions in the ratio in which they are present in the alloy, then, in a crevice during the initiation stage, this will affect the rate of fall of pH, i.e. the more chromium there is in the alloy, the faster the pH will fall for a given passive current.[21] Also, once propagation commences it is the alloy composition and its dissolution characteristics which determine the maximum rate of corrosion. For example, the maximum possible corrosion rate of a super ferritic stainless steel is much higher than that for a high-alloy austenitic material.[27]

PASSIVE FILM CHARACTERISTICS

The passive current and the film stability determine an alloy's inherent resistance to pitting and crevice corrosion initiation. These characteristics, however, can be affected by surface finish,[28] surface preparation,[28] heat treatment, and cold working,[29] and therefore all these factors need to be considered when studying pitting and crevice corrosion.

ELECTROCHEMICAL REACTIONS

As noted above, the active metal dissolution rate defines the maximum possible corrosion propagation rate at a given potential. However, in practice, this rate is not often reached, but is modified to some extent by the rate of oxygen reduction on the area surrounding the corroding metal and the rate of hydrogen evolution on the corroding area, if the pH of the solution in this region is low enough.[27,30] These reactions can be major factors in influencing propagation and can hide large differences in corrosion resistance between different alloys. The addition of alternative oxidizing species such as chlorine or ferric ions can alter dramatically a given alloy/environment state, and great care must always be taken in assessing such situations.[31]

MASS TRANSPORT

Mass transport occurs via migration, diffusion, and convection and all three modes are extremely important in both crevice and pitting corrosion. Note must be taken of all three in any given situation; for example, while diffusion and migration control the build up of an aggressive solution in a crevice,[21] the flowrate of the bulk solution controls the rate of oxygen reduction, which may control the overall corrosion rate.[27] Mass transport effects are very difficult to quantify; nevertheless, it is important that attempts are made to do so.

BULK SOLUTION ENVIRONMENT

The bulk solution environment covers the temperature, flowrate, and volume of the solution: all three are important. Temperature effects can be both dramatic and unexpected. Increases in temperature can sometimes increase corrosion rates and at other times reduce them.[32,33] Flowrate effects have been mentioned under mass transport. Volume effects are important, particularly from the point of view of scaling a corrosion test: the ratio of solution volume to metal area should be kept constant.[34]

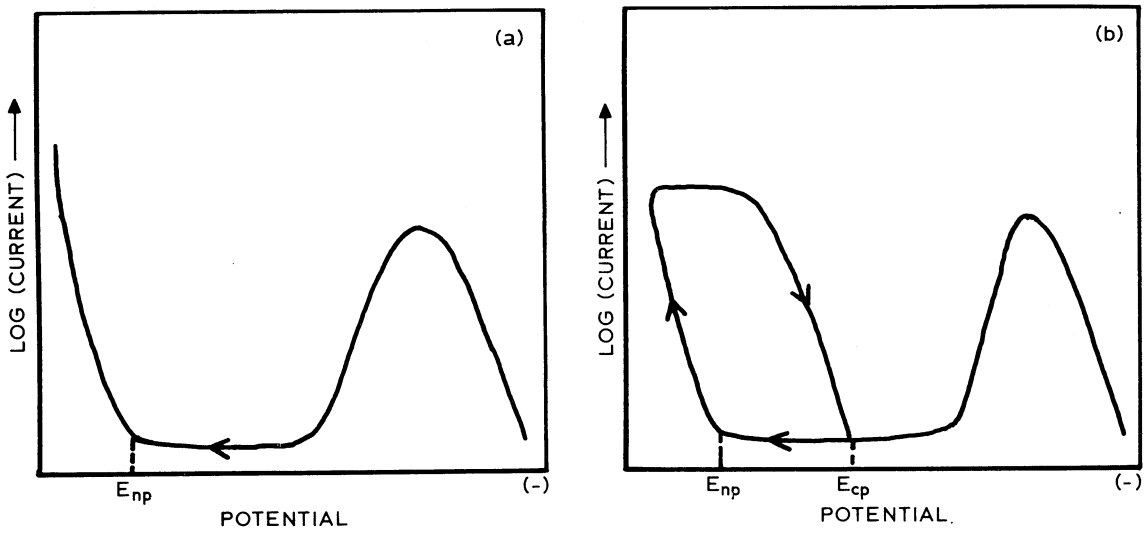
BULK SOLUTION COMPOSITION

The ingredients of the bulk solution, such as the Cl^- level, pH, pollutants, oxygen level, and so on, determine its basic corrosivity. Care should always be taken in using simulated or synthetic environments and relating results directly to the 'real' environment.[27,30]

GEOMETRY

Geometry affects crevice corrosion rather than pitting corrosion. It is now well established that the 'tighter' a crevice, the more 'severe' it is.[33] What is not well established is how crevices, such as flanges, fasteners, and so on, relate to test assemblies and to actual crevice gap dimensions. Tightness is controlled by the crevice type, e.g. metal/metal or metal/non-metal, and the force with which the two faces are held together. Tightness controls the volume of solution between the two crevice faces. The smaller the volume, the more severe is the crevice; thus, surface finish and material properties, particularly in metal/non-metal crevices, play an important role.

The depth of a crevice is important: it is thought that a deeper crevice is more severe than a shallow one.[21,33] The number of crevices on an assembly is important: if one starts to propagate, it may cathodically protect others. The crevice/non-crevice area



a potential sweep in anodic direction only; *b* anodic potential sweep followed by the reverse sweep

1 Schematic representation of anodic polarization curves obtained using all three potentiokinetic methods

ratio is very important, since this affects the available cathodic reaction current and can be the factor limiting the propagation rate.[30] Thus, geometry in all respects is an important factor in crevice corrosion. Some aspects of geometry are also important in pitting corrosion; for example, a propagating pit may cathodically protect a significant area around it and thereby prevent further pit initiation.

ACCELERATED PITTING CORROSION TESTS

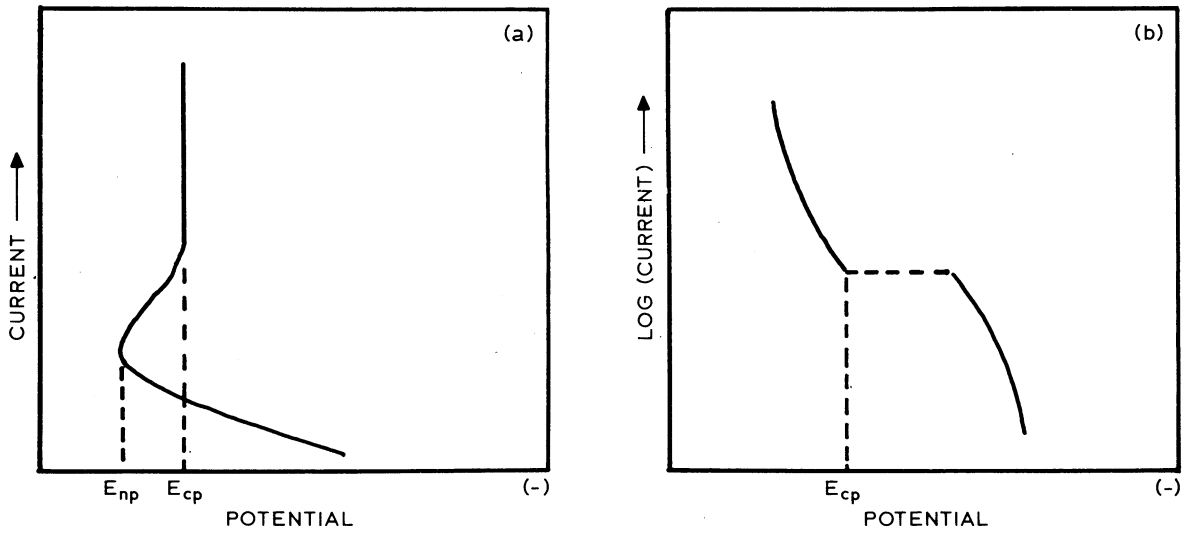
Accelerated tests fall into two broad groups: electrochemical and chemical. The various techniques currently in use are described and discussed below, together with emerging techniques based on the stochastic theory of pitting corrosion.

ELECTROCHEMICAL TESTS

The majority of electrochemical tests for pitting corrosion revolve around the determination of a pitting potential.[35] There are in fact two potentials which are frequently referred to:[36] the pit nucleation or breakdown potential E_{np} and the critical pitting, protection, or repassivation potential E_{cp}. These can be defined as follows:

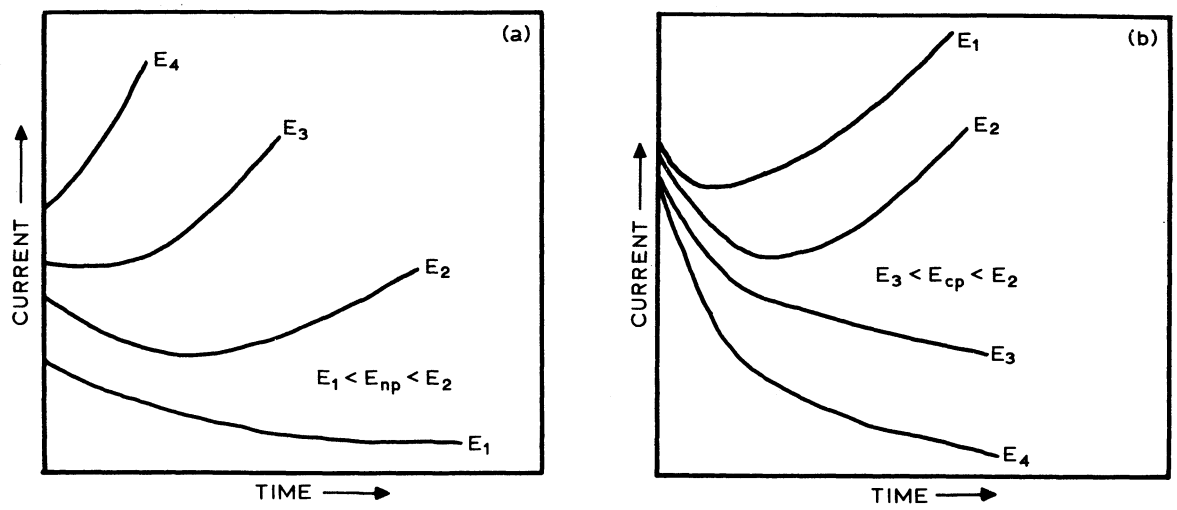
$E \geqslant E_{np}$ stable pits initiate and propagate
$E \leqslant E_{cp}$ no initiation or propagation of pits; pits formed above E_{np} will eventually repassivate below E_{cp}.

It is worth noting here that, in the mechanism of pitting, E_{np} refers to the kinetics of nucleation (defined here as the formation of a stable pit), whereas E_{cp}, the critical potential, is a measure of the kinetics of



a galvanodynamic and quasi-stationary methods; *b* stationary methods

2 Schematic representation of anodic polarization curves obtained using galvanokinetic methods



a determination of E_{np}; *b* determination of E_{cp}

3 Schematic representation of current *v.* time curves obtained using potentiostatic methods

repassivation. As such, neither of the potentials relate to the length of the induction period or to the kinetics of propagation once initiation has occurred. This is a major drawback in the present system used to characterize pitting corrosion. Nevertheless, these potentials do provide a useful method for characterizing, on a relative basis, the susceptibility of a material in a given environment to pit nucleation and repassivation; they have no use other than this. Actual methods for determining these potentials are given below.

Potentiokinetic methods

Potentiokinetic techniques as a group determine current as a function of potential ($I = f(E)$), as illustrated schematically in Fig. 1. There are three methods by which this relationship can be obtained:

(i) the potentiodynamic method, where there is a continuous change in potential at a fixed rate
(ii) the quasi-stationary method, where there is a stepwise change of potential at a certain rate
(iii) the stationary method, where there is a stepwise change of potential which is maintained until a stable current is established.

These methods are the ones most commonly used in determining pitting potentials; both E_{np} and E_{cp} can be determined in a single experiment, as shown in Fig. 1*b*. However, values of E_{np} and E_{cp} are dependent on scanning rate; usually the higher the scanning rate, the more noble is E_{np}. This is because there is an induction period associated with each potential; the higher the potential, the shorter is this period. When the scan rate is high, pit nucleation only occurs at potentials where the induction period is very short. There are, however, exceptions to this rule; if the scan rate is reduced, then the passive film has a longer time to develop, thereby increasing the resistance of the metal or alloy to pitting corrosion. The most reliable and consistent method is (iii); however, this is also the most time-consuming.

A detailed standard procedure for carrying out method (i) is laid down in ASTM Standard G61 (Ref. 37), which recommends a scan rate of $0{\cdot}6\,V\,h^{-1}$ ($10\,mV\,min^{-1}$). Alternatives to this practice have been used: one example of this is the rapid scan method which involves scan rates of up to $50\,V\,h^{-1}$ (Refs. 38, 39); another uses an intermediate rate of $1\,mV\,s^{-1}$ (Ref. 40).

Galvanokinetic methods

Galvanokinetic techniques as a group determine potential as a function of current ($E = f(I)$), as illustrated schematically in Fig. 2. As with the potentiokinetic methods, there are three methods by which this relationship can be obtained:

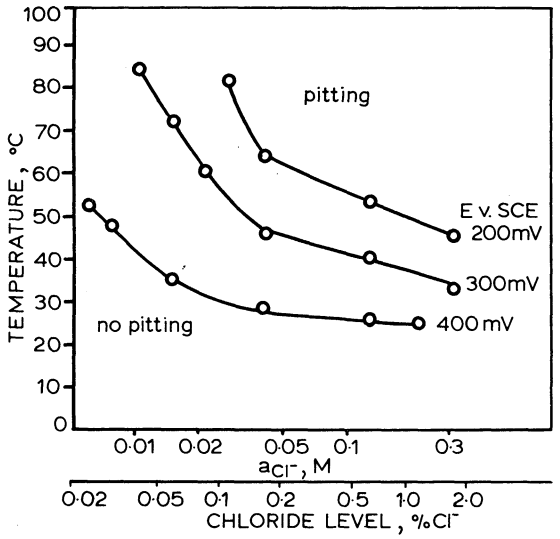
(i) the galvanodynamic method, where there is a continuous change in current at a fixed rate
(ii) the quasi-stationary method, where there is a stepwise change in current at a certain rate
(iii) the stationary method, where there is a stepwise change in current which is maintained until a stable potential is established.

Method (i) is supposed to give both E_{np} and E_{cp} in one experiment,[41] as shown in Fig. 2*a*; however, the technique is not very reliable.[36] The results depend very much on the experimental procedure adopted, particularly on the current density at which the measurements start and on the current sweep rate. Some results have been obtained which show that method (ii) gives quite good reproducibility, with results corresponding well with values obtained by the slowest potentiokinetic methods.[41] Method (iii) gives a single potential supposed by some authors to be E_{cp} and by others to be E_{np} (Ref. 41). The present author considers E_{np} to be the potential determined by this method.

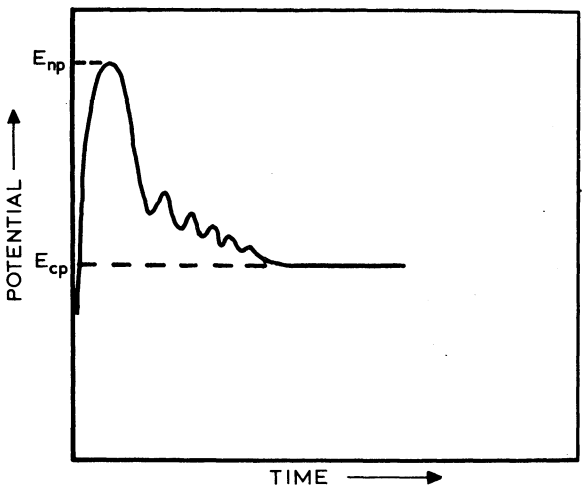
In general these methods are not widely used in connection with pitting potential determinations.

Potentiostatic methods

Potentiostatic techniques as a group determine current as a function of time at constant potential (E = constant, $I = f(t)$), as illustrated in Fig. 3. There are two general methods: one to determine E_{np} and one to determine E_{cp}. These are:



4 Critical pitting temperature of AISI 316 as a function of chloride level in neutral solutions obtained at three potentials using a Santron CTD-400 instrument (Ref. 43)



5 Schematic representation of potential time curve obtained using galvanostatic method

(i) the determination of E_{np} by recording I versus t curves at different constant potentials using a new passive specimen for each potential
(ii) the determination of E_{cp} by recording I versus t curves at different constant potentials using electrodes on which active pits have been initiated.

These are perhaps the most reliable methods of determining E_{np} and E_{cp}, and they have been used extensively.[36,42] In general, they give values more active than the potentiokinetic and galvanokinetic methods. (This in itself casts doubts on any absolute significance of E_{np} and E_{cp}.)

Method (i) has been turned into an automatic technique by Bernhardsson *et al.*[43,44] However, with this technique a series of I versus t curves are obtained at a constant potential but at increasing temperatures until breakdown, signified by an increase in current, is observed; in this way the temperature is obtained at which the constant potential is equal to E_{np}. By doing a series of runs at different constant potentials, E_{np} can be obtained as a function of temperature. These data are then viewed with the temperature, rather than the potential, as the ranking parameter, and the term 'critical pitting temperature' (CPT) has been coined for that temperature which gives rise to pitting at a given potential. An example of this is shown in Fig. 4, where the CPT is shown as a function of Cl^- level at three different potentials for AISI 316 stainless steel.

In method (ii) the active pits can be initiated at potentials more noble than the pitting potential. However, an alternative method is to remove the passive film in a controlled way by scratching. This technique, known as the scratch method, has been used extensively by a number of authors.[45–47]

Galvanostatic methods

Galvanostatic techniques determine the potential as a function of time at constant current (I = constant, $E = f(t)$), as illustrated in Fig. 5. There are two general methods: one that determines both E_{np} and E_{cp} and one that determines E_{cp} only.[36] These are:

(i) the determination of E_{np} and E_{cp} by recording E versus t curves at constant current starting from the corrosion potential
(ii) the determination of E_{cp} by recording E versus t curves at constant current starting from a fixed potential.

Neither of these techniques is in general use, and there is some doubt as to whether method (i) gives an accurate value of E_{np}.

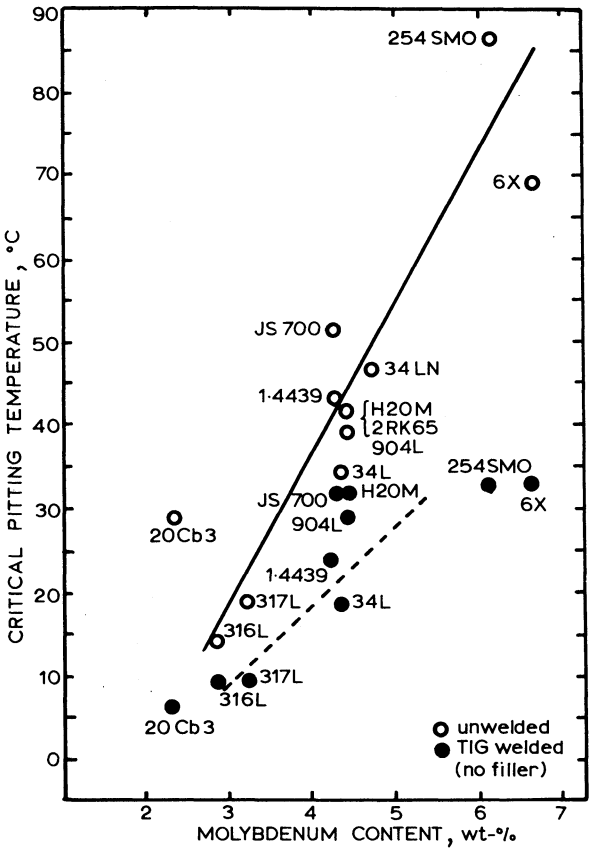
CHEMICAL TESTS

Chemical methods used for assessing resistance to pitting corrosion are based on solutions containing an activator, which is usually Cl^- and an oxidizing agent, in definite concentrations. For this reason such methods cannot be used to predict pitting corrosion resistance in natural environments, but can only be used to provide a ranking. Such methods, however, are usually simple and need no complicated electronic apparatus, so that the tests do not need to be performed by 'experts'.[48] The most common chemical used is ferric chloride; nevertheless, other chemicals are also used and these will be mentioned.

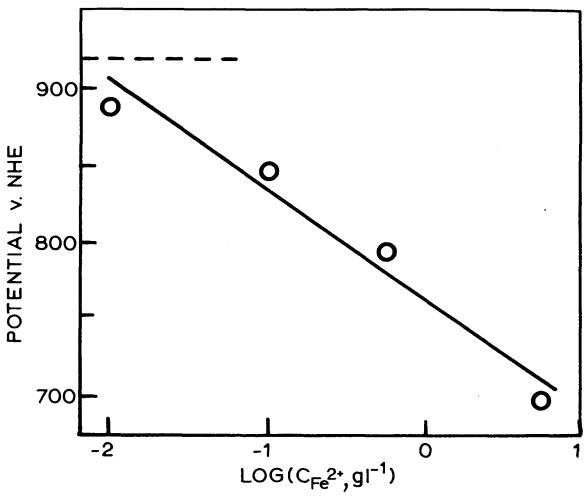
Ferric chloride

The best known test using ferric chloride as the chemical is ASTM Standard G48 (Ref. 49). The test is straightforward, involving the immersion of the test specimen in a 6%$FeCl_3$ solution for a reasonable length of time, say 72 h, and measuring the weight loss. Variations on the test in terms of the concentration of $FeCl_3$ and additions of NaCl and HCl are frequently used. Sometimes weight loss is determined as a function of time, say after 24, 96, and 168 h. In all these variations the assessment of corrosion is based on whether or not it has occurred; if it has, then weight loss is used as a ranking parameter.

An alternative use of the ferric chloride test, whereby temperature is used as the ranking parameter, was pioneered by Brigham.[50] He defined the CPT



6 Critical pitting temperature *v.* Mo content of commercial austenitic stainless steels after testing in 10% $FeCl_3$; CPT increases with Mo content and decreases after autogenous welding (Ref. 51); Table 3 gives compositions of alloys tested



7 Redox potential of 10% $FeCl_3.6H_2O$ solution *v.* concentration of Fe^{2+} ions; broken line, solution without added Fe^{2+} (Ref. 48)

as the minimum temperature at which pitting occurred on a sample exposed for 24 h in 10%$FeCl_3$ (any edge or end grain attack which may occur below the CPT is not considered in deciding whether or not pitting has occurred). This technique is now widely used, and Brigham claims excellent correlation between the CPT determined in this way and the temperature at which a break in the pitting potential *v.* temperature curve occurs for potentiodynamic anodic polarizations in acidified 0·6 M NaCl solution. He notes, however, that it is essential, when testing below room temperature, that samples be prechilled to the testing temperature before immersion. Figure 6 shows an example of results from this form of testing; Table 3 gives the compositions of the alloys tested.

The significance of the results from ferric chloride immersion tests in relation to pitting resistance in practical situations is somewhat dubious. The redox potential of a 6%$FeCl_3$ solution as a function of Fe^{2+} concentration is shown in Fig. 7. On initial immersion in $FeCl_3$, when no significant Fe^{2+} is present, the potential experienced by the sample is +900 mV versus NHE (i.e. +658 mV versus SCE). If the breakdown potential E_{np} of the sample in the test solution is above this value, no pitting will occur; if it is below this, then pitting will occur. It is difficult to see how this relates to the majority of practical situations, where the potential is appreciably lower than in ferric chloride.

Redox couples

Other chemical accelerated tests involve controlling the potential by means of a redox couple; many redox couples have been used in this way. Perhaps the best known is $[Fe(CN)_6]^{3+}/[Fe(CN)_6]^{2+}$ which has been used with additions of NaCl to give a redox potential of +700 mV versus NHE in neutral and alkaline solutions.[52] In this test, pit nuclei are clearly visible because the Fe^{2+} corrosion product forms a patch of 'Prussian blue' at the pit site. This test tells us whether

Table 3 Chemical analyses of laboratory-tested commercial stainless steels referred to in Fig. 6 (Ref. 51), wt-%

Alloy	C	Si	Mn	P	S	Cr	Mo	Ni	N	Others
316L	0·03	0·5	1·6	0·021	0·012	16	2·8	13	...	...
317L	0·02	0·5	1·9	0·029	0·009	18	3·2	14	0·07	...
Eastern SS 317LM	0·02	0·7	1·2	0·029	0·008	18	4·0	14	...	...
Uddeholm 34L	0·03	...	...	...	...	17	4·3	14	...	...
Uddeholm 34LN	0·03	0·6	1·4	...	...	18	4·7	14	0·15	...
1·4439	0·03	0·5	1·5	...	...	18	4·3	14	0·13	...
Uddeholm 904L	0·02	0·4	1·8	0·025	0·004	20	4·2	25	...	1·45Cu
Jessop JS700	0·03	0·5	1·7	...	...	21	4·5	25	...	0·3Nb
Haynes H20M	0·03	0·6	0·8	0·013	0·010	22	4·2	26	...	0·36Ti
AL-6X	0·02	0·3	1·7	0·021	0·001	20	6·6	24	...	0·05Al, 0·07Ce
Avesta 254 SMO	0·02	0·5	0·5	0·015	0·002	20	6·1	18	0·21	0·69Cu
Carpenter 20 Cb 3	0·04	0·4	0·3	0·015	0·005	20	2·4	33	...	3·38Cu, 0·83(Nb+Ta)

the material under test is being subjected to pitting corrosion and gives an indication of the induction period. In principle this method has advantages over the ferric chloride test since the pH and Cl^- levels can be varied independently over a wide range of values.

Chemical etchants

Another chemical test which has been developed involves the use of a series of chemical etchants.[53] The etchants are glycerol–ethanolic solutions of $FeCl_3 + AlCl_3 + LiCl$. Using these solutions it is possible to change the characteristics of attack by varying the concentration of the components of the solution; it is claimed that tests performed with chemical etchants reflect the pitting susceptibility of a metal more closely than potentiostatic tests since the latter do not take into account the cathodic characteristics of the metal.

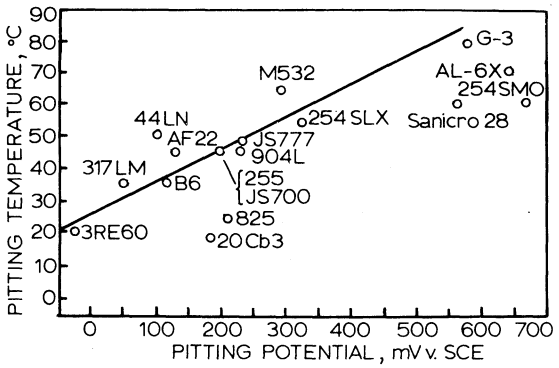
TESTS BASED ON STOCHASTIC THEORY OF PITTING

The probabilistic approach to pitting has been referred to in the section 'Pit initiation' above.[13,14] This approach to pitting has led to a number of attempts by various authors to develop a new technique for assessing pitting corrosion.[54–57]

A number of techniques can be used to characterize electrochemical noise attributed to the stochastic nature of pitting. Bertocci[54] has used a spectrum analyser and studied signals in the frequency domain. Hladky and Dawson have used the same technique to measure low-frequency $1/f$ noise,[56] and have also attempted to characterize different types of localized attack by the noise output as a function of time.[55] Williams and Westcott[57] describe in detail a specific technique for evaluation of susceptibility to pitting corrosion based on an interrupted potentiodynamic sweep. 'Events' are classified as trigger events or breakdown events: the former are unstable pits and the latter propagating pits. The problem of evaluating susceptibility to pitting corrosion is framed as the evaluation of the probability of initiation of a propagating pit. There are three experimental parameters associated with the technique.

(i) the potential scan rate: the electrode potential is increased at a constant rate until the current exceeds a predefined trigger level. This is assumed to be caused by the nucleation of a pit
(ii) the trigger current level: when the current rises above this level, the potential scan is halted and the potential held constant for a predetermined time
(iii) the hold time: if, at the end of the hold time, the current has fallen back below the trigger level, then the pit is unstable, so the potential scan is restarted. If the current has stayed above the trigger level, then a propagating pit is present.

The experiment is performed on a number of nominally identical specimens, and the results displayed as a cumulative distribution of potentials at which trigger events are observed and a distribution of potentials at which stable pitting is established.



8 Pitting temperature as function of pitting potential for 17 commercial stainless steels; immersion tests carried out in 4%NaCl + 0·01 M HCl + 0·1%$Fe_2(SO_4)_3$; potentiodynamic slow scan pitting potentials obtained in 4%NaCl + 0·01 M HCl (Ref. 61); Table 4 gives compositions of alloys tested

To obtain the critical potential at which the initiation frequency falls to zero, extreme value analysis of the distribution is carried out. This potential, however, is not only dependent on the alloy and the solution but also on hydrodynamic conditions, buffer capacity, solution conductivity, and surface preparation.

Although there is much interest in the development of stochastic theories of pitting corrosion and the measurement of 'events' to explore the corrosion processes, the approach has not yet produced any widely accepted test techniques. Williams and Westcott's work[57] goes furthest in this direction; there is little doubt that with the continued interest in this field improved test techniques will emerge.

COMPARISON OF ACCELERATED PITTING CORROSION TESTS

From the review of the techniques above, it can be concluded that the most widely used accelerated tests for pitting corrosion are potentiokinetic methods, potentiostatic methods, and ferric chloride tests.

Various comparisons between the above types of test have been published.[58–61] Degerbeck[58] compared field tests with potentiodynamic pitting potentials and chemical pitting in various solutions. Degerbeck's conclusions are most interesting and relevant to this review, and can be summarized as follows:

(i) the effect of minor deviations in alloy content in stainless steels on the resistance to localized corrosion in calm natural sea water cannot be evaluated with any degree of certainty by means of the accelerated electrochemical or chemical tests that he performed
(ii) the agreement between tests is not acceptable unless the difference in steel composition is at least as great as that between the following stainless steels: Cr–9Ni, 18Cr–13Ni–3Mo, 17Cr–15Ni–4·5Mo, and 18Cr–20Ni–4·5Mo–N
(iii) the poor correlation between most of the tests makes it difficult to predict sea water corrosion resistance on the basis of just one accelerated test or to relate different tests to each other.

Table 4 Chemical analyses of alloys referred to in Fig. 8 (Ref. 61), wt-%

	Element															
	C	Ce	Co	Cr	Cu	Fe	Mn	Mo	N	Nb	Ni	P	S	Si	Ti	V
Duplex alloys																
3RE60	0·024	...	0·12	18·77	0·24	70·11	1·60	2·73	0·078	...	4·92	0·026	0·003	1·53	...	...
AF22	0·020	...	...	21·62	0·04	67·20	1·52	2·82	0·120	...	5·20	0·021	0·004	0·62	...	...
44LN	0·027	...	...	24·53	0·01	65·83	1·69	1·51	0·169	...	6·03	0·007	0·007	0·52	...	...
Ferralium* alloy 255	0·020	...	0·16	25·63	1·70	62·07	0·83	3·28	0·190	...	5·57	0·018	0·004	0·27	...	...
20 Type alloys																
Jessop 700	0·020	0·23	...	20·88	0·18	48·25	1·48	4·68	0·035	0·25	23·76	0·021	0·012	0·32	...	0·05
Hastelloy† alloy M-532	0·004	0·57	...	21·81	0·08	44·95	0·94	4·98	0·026	...	25·61	0·021	0·008	0·58	0·35	0·04
AL-6X	0·019	0·48	...	20·21	0·13	45·98	0·62	6·41	0·021	0·06	24·95	0·022	0·002	0·34	...	0·08
254 SMO	0·020	0·18	...	19·45	0·86	54·31	0·39	6·12	0·20	...	17·80	0·018	0·002	0·54	...	0·04
20 CB 3‡ alloy	0·020	0·35	...	19·65	3·19	39·48	0·34	2·08	0·018	...	34·13	0·016	0·002	0·39	0·01	0·06
254 SLX	0·020	0·35	...	19·65	1·81	46·69	1·39	4·82	0·040	...	24·53	0·020	0·002	0·48	...	0·06
Uranus B6	0·009	0·16	...	19·92	1·55	47·01	1·67	4·57	0·015	...	24·72	0·031	0·002	0·27	...	0·04
Jessop 777	0·030	0·26	...	20·87	2·31	44·41	1·31	4·86	0·030	0·25	24·91	0·023	0·012	0·42	...	0·07
904L	0·024	0·25	...	20·29	1·78	45·54	2·96	4·61	0·044	...	26·54	0·021	0·009	0·38	...	0·05
Other alloys																
317 LM	0·016	...	...	17·92	0·11	61·16	0·90	3·84	0·047	...	14·58	0·021	0·020	0·54	...	...
Sanicro§ 28 alloy	0·020	0·04	...	26·41	1·18	36·02	1·22	2·98	0·046	0·06	31·38	0·004	0·002	0·06	...	...
825	0·012	NA	...	22·17	1·83	30·00	0·27	2·72	NA	NA	41·64	0·018	0·004	0·06	0·87	0·04
Hastelloy† alloy G-3	0·006	3·00	...	22·71	1·84	18·20	0·86	6·95	0·050	0·15	45·08	0·014	0·004	0·39	...	...
Hastelloy† alloy G	0·030	1·82	...	22·10	1·78	19·03	1·35	6·52	0·050	2·09	42·99	0·026	0·007	0·30	...	...

NA: not analysed.
*Registered trademark of Bonar Langley Alloys Ltd.
†Registered trademark of Cabot Corporation.
‡Registered trademark of Carpenter Technology Corporation.
§Registered trademark of Sandvikens Jernverks AB.

France and Green[59] in their work compared chemically and electrolytically induced pitting on stainless steel in identical solutions and found no correlation. For example, on AISI 430 stainless steel in neutral NaCl, corrosion rates of 9·92 mm/year were observed in controlled potential tests compared with 0·13 mm/year in conventional immersion tests. The potential of the specimen was the same in both cases.

Manning[61] compared slow scan potentiodynamic pitting tests with immersion pitting tests in acid chloride solutions with ferric sulphate as an oxidizing agent. Figure 8 shows the correlation he obtained; Table 4 gives the compositions of the alloys tested. He concludes that the correlation is reasonably good and that the immersion pitting temperature test is the best, from the techniques he examined, in correlating with service performance. However, no quantitative comparison was made with service performance.

Manning's data in Fig. 8 does show some correlation, but from a realistic point of view it is poor, and a much more accurate conclusion would be similar to the one drawn by Degerbeck and given above, namely that agreement between tests is not acceptable unless there are significant differences in steel composition. In other words, these accelerated tests are unable to rank accurately stainless steels whose service performances do not differ by a great amount.

Thus, the conclusions to be drawn concerning the various accelerated pitting tests are as follows:

(i) none of the tests examined relate directly to service experience and therefore they simply provide a ranking order
(ii) correlation between techniques, when studying alloys of similar corrosion resistance, is poor and therefore the ranking order obtained depends to a large extent on the test selected
(iii) of the widely used tests, the potentiostatic methods, carried out in environments relating to service, are probably the best while ferric chloride tests are the worst.

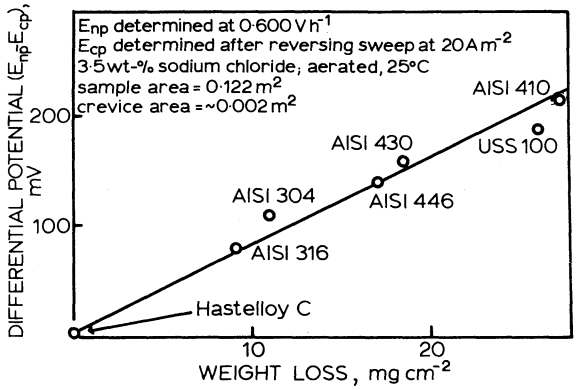
EXPOSURE TESTS FOR PITTING CORROSION

The natural exposure of a metal or alloy to a given environment is obviously the most reliable way to determine how it will react under those conditions. However, such tests have the inherent drawback that they take a long time to carry out.

The tests are normally either the exposure of single specimens at specific test sites[62] or the exposure of a range of different specimens in one test *in situ*. This latter test, normally referred to as a 'spool test',[63] is used when a range of alloys are to be tested in a given environment, say for use at a particular stage of a chemical process. Test discs are mounted on a central rod and separated from one another by an insulating spacer; the spacer forms a crevice which means that some appreciation of susceptibility to crevice corrosion will be obtained, as well as susceptibility to pitting corrosion. The entire assembly is then placed in the relevant part of the plant for the duration of the test.

The analysis of these tests usually consists of weight loss measurements coupled with measurement of the maximum depth of attack. Interpretation of these data is very difficult since the induction period to the start of pitting is not known and therefore a true average rate of weight loss cannot be determined. Even if the induction period were known, the significance of the average weight loss is dubious since it is unlikely to remain constant and it is the variation of this rate with time which is required 'to complete the picture'.

Thus, although natural exposure tests to determine pitting susceptibility are important, the interpretation of the results of these tests is limited, not least because it is difficult to avoid the presence of crevices, which



9 Correlation between $E_{np} - E_{cp}$ and corrosion weight loss of stainless steels with crevice exposed in sea water for 4·25 years (Ref. 66); USS 100 is 12%Cr stainless steel; Hastelloy C is 15·5Cr–13·5Mo–Ni-base alloy

additionally confuse the interpretation of the results. In view of this, exposure tests specifically aimed at assessing pitting resistance are very rarely undertaken. However, this is certainly not the case when assessing crevice corrosion, as will be seen in the section 'Exposure tests for crevice corrosion' below.

ACCELERATED CREVICE CORROSION TESTS

As already noted in this review, it is virtually impossible to eliminate all crevices from a structure and, since crevice corrosion occurs more readily than pitting corrosion, it is resistance to crevice corrosion which is the more important from a practical point of view.

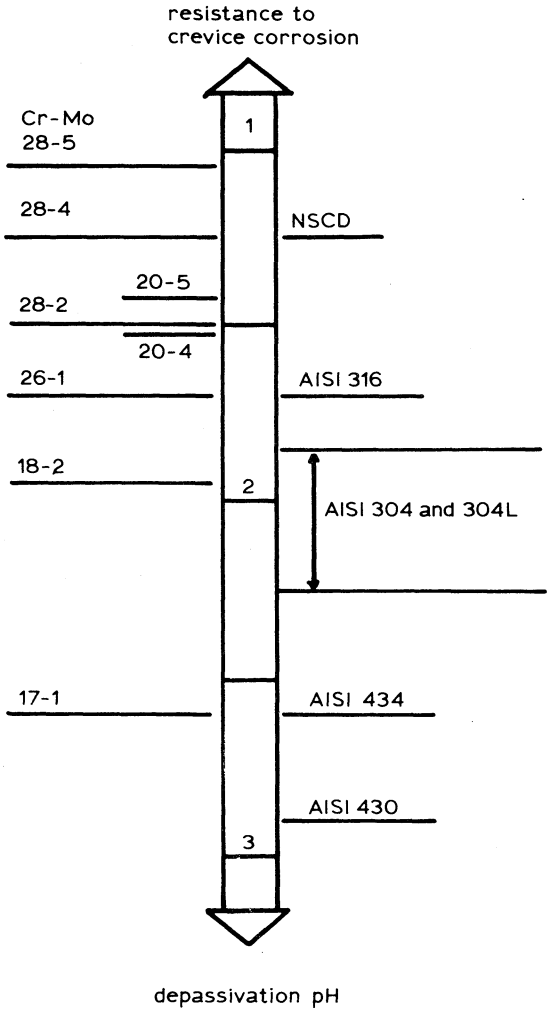
As with pitting corrosion there are electrochemical and chemical tests. These tests are discussed below.

ELECTROCHEMICAL TESTS

The electrochemical tests used for assessing crevice corrosion resistance have been admirably reviewed by Ijsseling;[64] they are not so well established as those described above in the section 'Electrochemical tests' for pitting corrosion. They essentially fall into two groups, potentiodynamic and potentiostatic, and these are discussed below.

Potentiodynamic methods

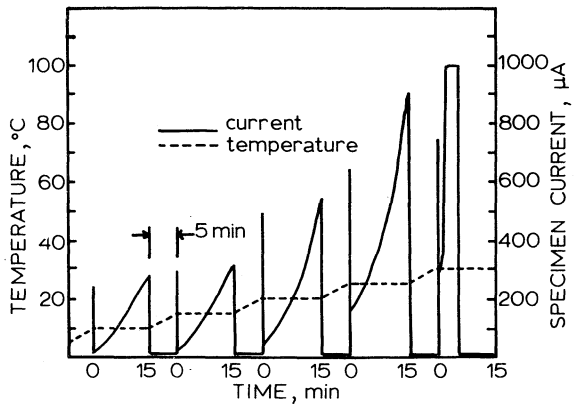
The first potentiodynamic method used for studying crevice corrosion was that put forward by Wilde and Williams[65] and Wilde.[66] On the basis of the assumption that a propagating pit is a special form of crevice growing by the same mechanism, they proposed that, for given experimental conditions, $E_{np} - E_{cp}$ would provide a measure of an alloy's resistance to crevice corrosion propagation. A linear relationship was obtained between this potential difference and the absolute crevice corrosion rate of alloys, immersed for 4·25 years in sea water, based on weight loss. These data are shown in Fig. 9. Although good agreement is shown in Fig. 9, the interpretation of the results is not obvious, and Postlethwaite[35] concludes that further work needs to be done if the technique is to be used successfully.



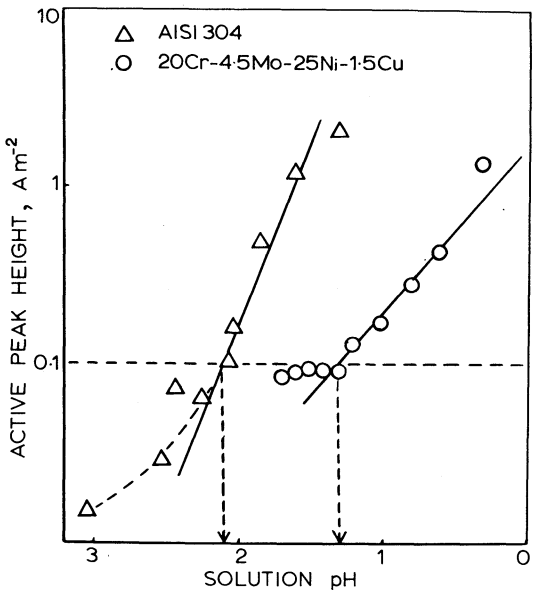
10 Depassivation pH of series of standard commercial stainless steels compared with series of experimental Cr–Mo ferritic stainless steels (Ref. 70); NSCD is an alloy with 17·5Cr–16Ni–6Mo–2·5Cu

A modification of this technique has been used by Fukumoto *et al.*,[67] who measured repassivation potentials on creviced assemblies to study the influence of gasket materials and packing shapes on the corrosion resistance of AISI 304 stainless steel. This approach has also been used by other authors.[68,69]

The second potentiodynamic technique was developed and first published by Crolet *et al.*[70] This is based on determining a 'depassivation pH', that is, a pH at which the passive film no longer offers protection against corrosion. This value is obtained by constructing polarization curves in a deaerated 2 M NaCl solution at a series of pH values; the height of the active anodic peak, corrected for any hydrogen evolution reaction, is then plotted as a function of pH. The pH at which the active peak reaches the nominal figure of 0·1 A m^{-2} is taken as the 'depassivation pH'. Figure 10 shows an example of a ranking based on depassivation pH values;[70] the technique is now used quite regularly, particularly in France.[71] The basis of the technique is that the pH fall that develops in a



11 Effect of temperature on crevice corrosion of AISI 304 stainless steel at constant potential in synthetic sea water obtained using a Santron CTD-400 potentiostat at applied potential of 60 mV versus SCE with critical current of 0·3 A m^{-2} (Ref. 72)



12 Effect of solution pH on height of active anodic current peak used to determine CCS values (Ref. 26)

crevice will eventually lead to breakdown of the passive film (i.e. depassivation). The higher the pH at which this occurs, the less resistance it has to crevice corrosion in practice. Thus, the interpretation of the results produced by this method is simple, namely they show resistance to crevice corrosion initiation.

Potentiostatic methods

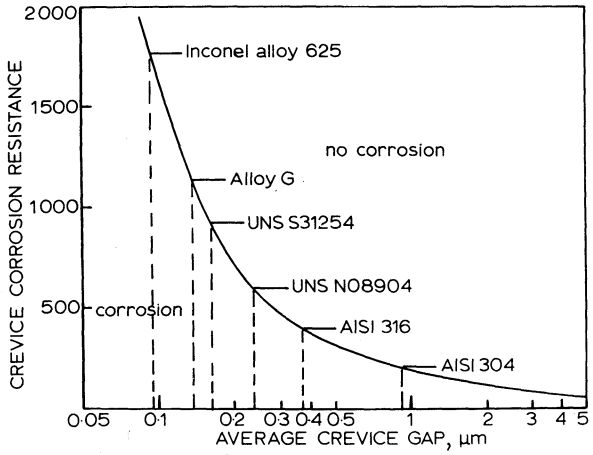
The potentiostatic methods described above for determining the breakdown potential on a material[43,44] have been used as a test for crevice corrosion.[72] In this test a preselected, constant anodic potential is applied to a crevice specimen and the current monitored for a preselected time at each test temperature. The temperature at which the current exceeds a preset critical level, supposedly corresponding to the initiation of crevice attack, is defined as the crevice corrosion temperature. An instrument has been specifically designed by Bernhardsson *et al.*[43] to carry out this test. This allows the preselection of a number of experimental parameters, such as applied potential, time at each temperature, critical current level, and starting temperature; it also provides automatic control of test temperature and interval between temperatures.

This technique is being used quite extensively. The theoretical significance of the rankings obtained using this approach is not at all clear. In particular, although the results are supposed to represent resistance to crevice corrosion initiation, the critical currents used are typically 10 A m^{-2} (Ref. 72). This current value corresponds to a rapid propagation rate (~10 mm/year) compared with the value for initiation of corrosion used by Crolet *et al.*[70] of 0·1 A m^{-2} when using the depassivation approach. In addition, the same sample is used at progressively increased temperatures; at each temperature, changes will occur in the crevice solutions, and it may well be that initiation actually occurs at a lower temperature than the critical crevice temperature (CCT), since it will take some time for the propagation rate to reach 10 A m^{-2}. This point is demonstrated in Fig. 11, where, for AISI 304, even at 10°C the corrosion current is increasing, indicating initiation has occurred, and yet the final CPT is determined at 30°C. Thus, while rankings can be produced quite readily using this technique, it would appear that they correspond to a mix of resistance to crevice corrosion initiation, crevice corrosion propagation, pit initiation, and pit propagation; they should therefore be interpreted with care, particularly when applying them to practical situations.

A technique has been developed by Drugli and co-workers[73,74] based on the potentiostatic determination of cathodic and anodic polarization curves on separate cathode (free surface) and anode (crevice) specimens, respectively. A crevice corrosion initiation potential is defined and, from the anodic polarization curves, this is found to be a function of crevice geometry. A protection potential is also defined and this is found to be independent of crevice geometry. The compilation of anodic and cathodic polarization curves, together with information on initiation and protection potentials, allows this technique to be used to give predictions on both initiation and propagation of crevice corrosion, and reasonable agreement with long-term exposure data has been observed.[73]

Mathematical modelling method

Oldfield and Sutton[21,23,24] have developed a technique based on a mathematical model of the crevice corrosion process. This process is divided into four stages, *see* the section 'Current understanding of pit and crevice corrosion' above: the depletion of oxygen within the crevice; the fall in pH and increase in chloride level in the crevice solution; the eventual breakdown of passivity when a CCS is reached; and finally propagation. The model requires various parameters as input, such as alloy composition, crevice geometry, chloride level of the bulk solution, and so on. However, the model also requires two



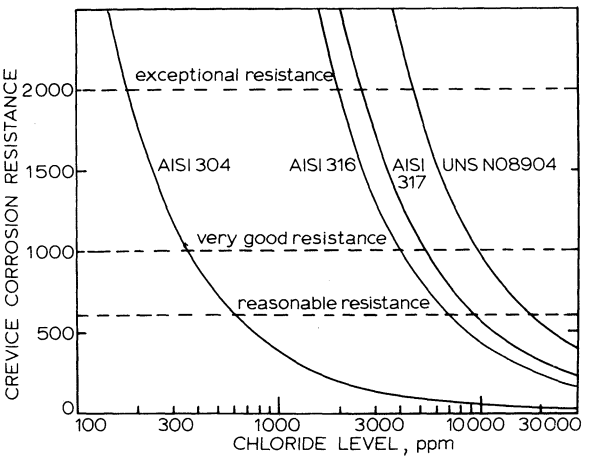
13 Prediction of whether or not crevice corrosion will occur in 5 mm deep crevice in ambient temperature sea water as function of crevice gap (Ref. 75); Tables 1 and 2 give compositions of alloys referred to

inputs which have to be determined electrochemically; the CCS and the passive current.

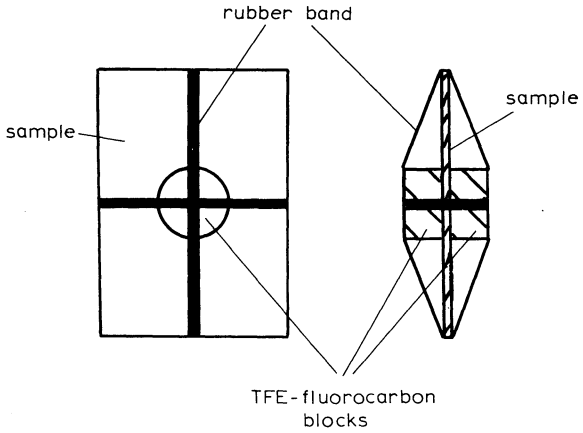
The CCS is determined by slightly modifying Crolet's depassivation pH method. In this case the chloride level in the test solution is increased as the pH is reduced, as would happen in a real crevice; polarization curves are determined in increasingly aggressive solutions, and the CCS is defined as that in which the anodic active peak height reaches 0·1 A m^{-2}. Figure 12 shows an example of such a determination.

Passive current determinations are reported by Oldfield and Sutton;[24] they used a value of 1 mA m^{-2} for all the stainless steels and nickel-base materials that they have tested, on the grounds that they have been unable to distinguish values for these materials.

This technique, which relates to crevice corrosion initiation, has been used both to make absolute predictions of times to the initiation of corrosion and to provide rankings of materials.[26] The technique has been improved recently to provide information on



14 Predicted resistance to crevice corrosion initiation of range of stainless steels in waters of varying chloride content (Ref. 75); Tables 1 and 2 give compositions of alloys referred to



15 Schematic diagram of ASTM G48 recommended assembly for crevice corrosion testing in ferric chloride solution

whether or not corrosion will occur in a given environment (Fig. 13) and on what chloride level can safely be used for a given stainless steel (Fig. 14).[35,75]

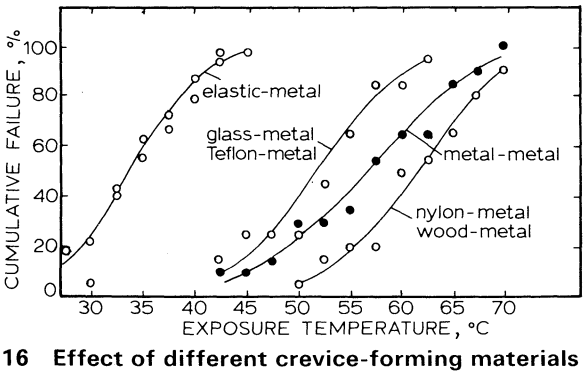
CHEMICAL TESTS

As with pitting corrosion, chemical tests for assessing crevice corrosion resistance are based on solutions containing an activator, which is usually Cl^- and an oxidizing agent, in definite concentrations. The various methods that have been developed in this category are described below.

Ferric chloride

The best known test using ferric chloride as the chemical is, as mentioned above, ASTM G48 (Ref. 49). The test involves immersing rectangular specimens, each with a cylindrical TFE–fluorocarbon block on either side held in place by fluorinated elastomer O-rings or rubber bands. A reasonable test time is 72 h. Besides weight loss and depth of attack measurements, the number of crevices which have corroded (there are six in all) is frequently reported. Figure 15 shows a schematic representation of this assembly.

As with pitting corrosion an alternative use of the ferric chloride test was developed by Brigham.[50] In his work three crevice geometries, metal to metal, Teflon



16 Effect of different crevice-forming materials on variation of crevice corrosion temperature in 10%$FeCl_3$ solution for Mn-substituted austenitic stainless steel, 0·03C–5·9Mn–22·1Cr–3·9Mo–12·7Ni–0·41N (Ref. 76)

to metal, and rubber to metal were used to ensure that a very severe crevice geometry had been employed. Typically $20 \times 30 \times 2{\cdot}5$ mm metal coupons were used in the tests and a temperature, defined as the crevice corrosion temperature, was found, below which no corrosion of any type was found on visual examination after 24 h in 10% $FeCl_3$. The crevice geometry in these tests is extremely important as was shown by Brigham in more recent work.[76] Figure 16 illustrates this point extremely well.

Accelerated test using activated carbon

A test has been developed whereby activated carbon is introduced into the test solution to catalyse the oxygen reduction reaction and thereby move the potential of the 'system' to more noble values.[77–80]

The technique consists of immersing a crevice test specimen in an aerated solution of 3%NaCl + 0·05 M Na_2SO_4 + activated carbon. Activated carbon is mixed into the solution with a weight ratio of 2 parts of activated carbon to 5 parts of solution. The test allows evaluations to be made in a short period of time. The proposed mechanism[79] by which both the initiation and propagation of corrosion are accelerated is illustrated in Fig. 17. The catalysis of the oxygen reduction reaction causes initiation via pitting, which occurs preferentially within the crevice as a result of the more noble corrosion potential. The propagation is accelerated as a result of the increased oxygen reduction current.

Good correlation is claimed between test results and field exposure tests in sea water.[79] However, this is based on weight loss rather than depth of attack, which is the more important parameter from a practical point of view. Nevertheless, the test has many advantages over the ferric chloride test, which, according to Nagano,[79] does not correlate with field tests.

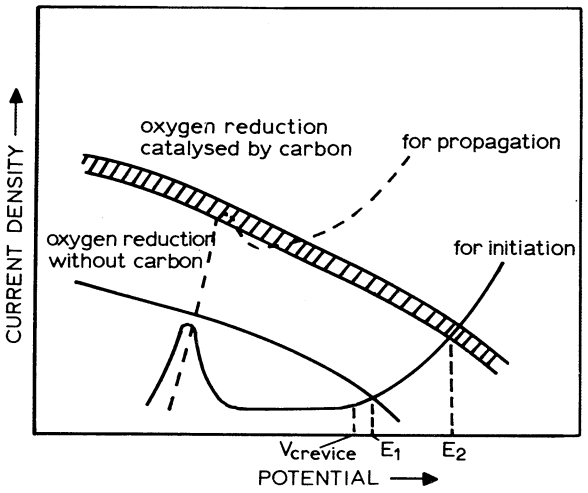
Compartmentalized cell

In the compartmentalized cell test two metal samples are physically separated but electrically connected.[81,82] The two specimens are exposed in separate environmental compartments, which are connected by an ion conducting bridge. The large cathode specimen is exposed in one compartment containing the bulk environment of interest. The small anode specimen does not have a physical crevice but, rather, is exposed in a deaerated acid chloride solution. The composition of this acid chloride solution simulates the crevice environment conditions.

This approach permits the study of crevice corrosion propagation as a function of crevice solution[82] without having to be concerned with initiation. However, to date, there has been no attempt to use this method to rank materials or to compare results with field test data.

COMPARISON OF ACCELERATED CREVICE CORROSION TESTS

rhaps helpful to list the tests which have been referred to above (the type of specimen used is also indicated):



17 Mechanism of crevice corrosion of stainless steel accelerated by activated carbon: E_1 and E_2 are corrosion potentials without and with carbon, respectively; $V_{crevice}$ is initial potential above which crevice corrosion will initiate (Ref. 79)

Potentiodynamic	– noble hysteresis loop, plain specimen
	– repassivation potential, crevice specimen
	– depassivation pH, plain specimen
Potentiostatic	– crevice corrosion temperature, crevice specimen
	– anodic and cathodic polarization curves, crevice specimen
Mathematical modelling	– plain specimen
Ferric chloride	– ASTM G48, crevice specimen
	– crevice corrosion temperature, crevice specimen
Activated carbon	– crevice specimen
Compartmentalized cell	– plain specimen

Of the ten methods listed, six use a crevice specimen and four a plain specimen. The effect of crevice geometry has already been mentioned in general terms in this review, and its effect on the initiation of crevice corrosion is well documented[33,76] (*see* Fig. 15). Thus, in any test which requires a crevice specimen, the crevice geometry must be very carefully controlled. This is not easy to do, and care must therefore be taken when interpreting and comparing results using such specimens.

All the techniques can be used to give a ranking of materials. However, it is whether or not the ranking has any significance to practical situations that is important. In other words, can the ranking either be interpreted in a useful way or be converted into a prediction regarding corrosion?

Results from the hysteresis loop technique and the repassivation potential method are difficult to interpret. The former involves pit initiation and repassivation and, perhaps, crevice corrosion propagation; the latter relates to pit repassivation and crevice

to metal, and rubber to metal were used to ensure that a very severe crevice geometry had been employed. Typically $20 \times 30 \times 2{\cdot}5$ mm metal coupons were used in the tests and a temperature, defined as the crevice corrosion temperature, was found, below which no corrosion of any type was found on visual examination after 24 h in 10% $FeCl_3$. The crevice geometry in these tests is extremely important as was shown by Brigham in more recent work.[76] Figure 16 illustrates this point extremely well.

Accelerated test using activated carbon

A test has been developed whereby activated carbon is introduced into the test solution to catalyse the oxygen reduction reaction and thereby move the potential of the 'system' to more noble values.[77–80]

The technique consists of immersing a crevice test specimen in an aerated solution of 3%NaCl + 0·05 M Na_2SO_4 + activated carbon. Activated carbon is mixed into the solution with a weight ratio of 2 parts of activated carbon to 5 parts of solution. The test allows evaluations to be made in a short period of time. The proposed mechanism[79] by which both the initiation and propagation of corrosion are accelerated is illustrated in Fig. 17. The catalysis of the oxygen reduction reaction causes initiation via pitting, which occurs preferentially within the crevice as a result of the more noble corrosion potential. The propagation is accelerated as a result of the increased oxygen reduction current.

Good correlation is claimed between test results and field exposure tests in sea water.[79] However, this is based on weight loss rather than depth of attack, which is the more important parameter from a practical point of view. Nevertheless, the test has many advantages over the ferric chloride test, which, according to Nagano,[79] does not correlate with field tests.

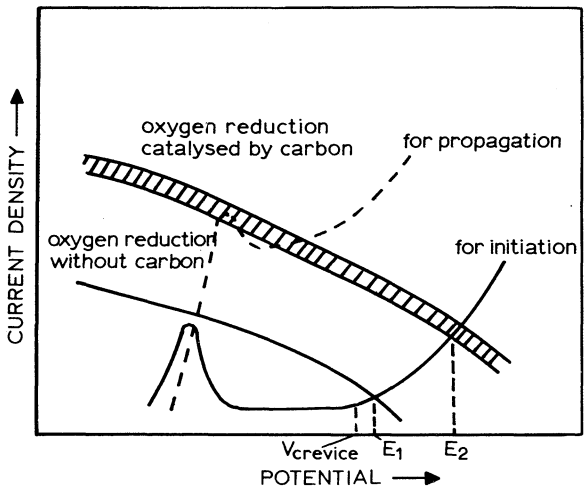
Compartmentalized cell

In the compartmentalized cell test two metal samples are physically separated but electrically connected.[81,82] The two specimens are exposed in separate environmental compartments, which are connected by an ion conducting bridge. The large cathode specimen is exposed in one compartment containing the bulk environment of interest. The small anode specimen does not have a physical crevice but, rather, is exposed in a deaerated acid chloride solution. The composition of this acid chloride solution simulates the crevice environment conditions.

This approach permits the study of crevice corrosion propagation as a function of crevice solution[82] without having to be concerned with initiation. However, to date, there has been no attempt to use this method to rank materials or to compare results with field test data.

COMPARISON OF ACCELERATED CREVICE CORROSION TESTS

rhaps helpful to list the tests which have been referred to above (the type of specimen used is also indicated):



17 Mechanism of crevice corrosion of stainless steel accelerated by activated carbon: E_1 and E_2 are corrosion potentials without and with carbon, respectively; $V_{crevice}$ is initial potential above which crevice corrosion will initiate (Ref. 79)

Potentiodynamic	– noble hysteresis loop, plain specimen
	– repassivation potential, crevice specimen
	– depassivation pH, plain specimen
Potentiostatic	– crevice corrosion temperature, crevice specimen
	– anodic and cathodic polarization curves, crevice specimen
Mathematical modelling	– plain specimen
Ferric chloride	– ASTM G48, crevice specimen
	– crevice corrosion temperature, crevice specimen
Activated carbon	– crevice specimen
Compartmentalized cell	– plain specimen

Of the ten methods listed, six use a crevice specimen and four a plain specimen. The effect of crevice geometry has already been mentioned in general terms in this review, and its effect on the initiation of crevice corrosion is well documented[33,76] (*see* Fig. 15). Thus, in any test which requires a crevice specimen, the crevice geometry must be very carefully controlled. This is not easy to do, and care must therefore be taken when interpreting and comparing results using such specimens.

All the techniques can be used to give a ranking of materials. However, it is whether or not the ranking has any significance to practical situations that is important. In other words, can the ranking either be interpreted in a useful way or be converted into a prediction regarding corrosion?

Results from the hysteresis loop technique and the repassivation potential method are difficult to interpret. The former involves pit initiation and repassivation and, perhaps, crevice corrosion propagation; the latter relates to pit repassivation and crevice

corrosion propagation. As a result neither of these techniques is considered particularly reliable.

The tests using ferric chloride are not easy to interpret and do not relate to the majority of practical situations. The limitations of these tests are frequently noted,[50,72] yet they continue to be used. The results from these tests do, in fact, relate to strongly oxidizing, low pH, chloride-containing environments. However, the rankings are most frequently used give a guide to performance in neutral chloride-containing environments with oxygen present. This is not recommended.

The remaining six tests have varying degrees of merit. The potentiostatic crevice corrosion temperature method is a well controlled technique which relates to a mixture of crevice corrosion initiation and propagation usually by a pitting mechanism since the potential is normally held at noble values. Consequently intepretation of results is not straightforward.

The activated carbon technique accelerates crevice corrosion by effectively providing a large cathode area and plenty of oxygen. It provides weight loss data which correlate well with sea water exposure tests; however, it is depth of attack which is the most important parameter. No indication is given as to the correlation of depth of attack data between this test and exposure tests.

The compartmentalized cell technique is a controlled method of measuring propagation rates under a given set of conditions. It could well develop into a useful technique, but at present it is not used to any great extent.

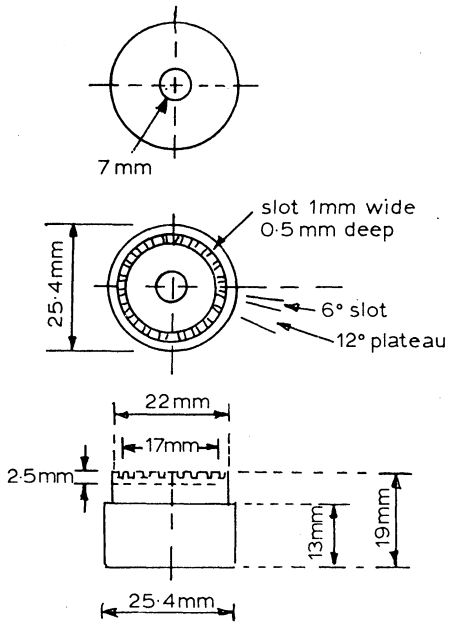
The potentiodynamic depassivation pH technique is well established and easy to interpret; it relates simply to crevice corrosion initiation and is extremely useful in providing rankings for this. The mathematical modelling technique takes this a stage further, first, by obtaining the depassivation pH in solutions containing high chloride levels linked to the pH value, and second, by using this as one of a number of inputs to a mathematical model of crevice corrosion. The technique relates to crevice corrosion initiation; it can be used to make predictions of whether or not corrosion will occur in a given situation as well as providing rankings. Some progress has been made in extending the technique to cover crevice corrosion propagation.[26]

Finally, the potentiostatic technique involving the determination of anodic and cathodic polarization curves is a useful one. Compiling such curves gives information on both initiation and propagation of corrosion in practical situations; it also allows a protection potential to be defined.

Thus, of the tests considered the most useful methods are the depassivation pH, the mathematical modelling approach, and the compilation of anodic and cathodic polarization curves.

EXPOSURE TESTS FOR CREVICE CORROSION

While there is little interest in carrying out natural exposure tests for pitting corrosion, except perhaps where decorative appearance is of prime importance,



18 Schematic diagram of multiple crevice assembly washer

this is not the case for crevice corrosion. There have been a number of developments aimed at generating reliable, reproducible results, and these are discussed below. As a result of problems encountered in some of these developments, ASTM standard G78 (Ref. 83) has been issued. This standard, published in 1983, gives a good overview of the assemblies that are used and how best to overcome problems associated with them.

SPOOL TEST

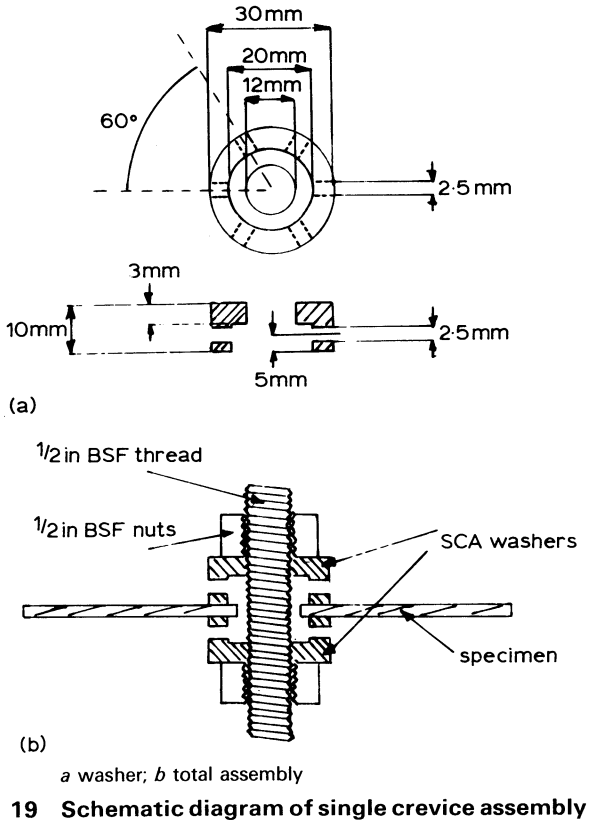
The spool test has already been described above in the section 'Exposure tests for pitting corrosion'. It involves the exposure of a range of different specimens in one test. The specimens are discs, mounted on a central rod and separated from one another by an insulating spacer which also serves to form a crevice. The entire spool is placed in the test environment.

Although such tests can generate a lot of data, the interpretation is difficult, particularly in view of the fact that the crevices are not controlled in any quantitative manner.

MULTIPLE CREVICE ASSEMBLY (MCA)

The first attempt to introduce a 'standard' crevice capable of providing consistent and reproducible data was developed by Anderson.[84] The criteria used in the development can be summarized as follows:

(i) the required test period must be reasonably short, e.g. 1 month
(ii) the test must be capable of differentiating between alloys with known, different capabilities, e.g. AISI 304 and 316
(iii) the test must be capable of providing a clear assessment of the merits of alloys that are highly corrosion resistant



a washer; *b* total assembly

19 Schematic diagram of single crevice assembly

(iv) the test must be adaptable to specimens of various thicknesses, shapes, and surface conditions, and not necessarily entail destruction of as-received surfaces

(v) the test should not require electrochemical stimulation or chemical alteration of the environment.

The resultant test involves flat panel specimens, nominally 150 × 100 mm with multiple crevices formed by two grooved, non-metallic washers as shown in Fig. 18. Assemblies fabricated in acetal resin, e.g. Delrin* and PTFE–fluorocarbon, have been shown to be suitable for sea water exposures. Although various designs have been used, the most popular one has 20 separate crevice sites on each side of the specimen.

Because crevice geometry is important, the two washers are bolted to a test panel using a torque wrench to provide a consistent degree of initial tightness.[85] The method gives information on resistance to initiation of attack via the number of crevice sites that break down, and on resistance to propagation via the depths of attack.

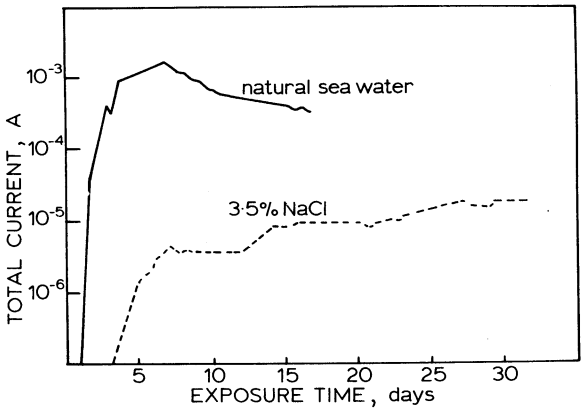
SINGLE CREVICE ASSEMBLY (SCA)

The MCA was developed in the early 1970s and is still used extensively. However, the increased understanding of crevice corrosion raises two question marks over its use.

(i) the individual plateaus are relatively small compared with 'practical' crevices and it is known that crevice geometry, both gap and depth, are important: so, does this small crevice give results which can be related to practical situations?

(ii) once one or two crevice sites begin to corrode, is it possible for them to protect the remaining sites cathodically?

*Trademark.



20 Variation in current measurements for remote crevice assemblies of UNS N08904 stainless steel exposed to natural and synthetic sea water (Ref. 88)

In view of these questions a single crevice former was developed with the same criteria listed in the previous section[76] and shown in Fig. 19. This assembly, constructed in Perspex,* has been used in an attempt to quantify the effect of crevice gap and depth, and has gone some way towards doing this.[33]

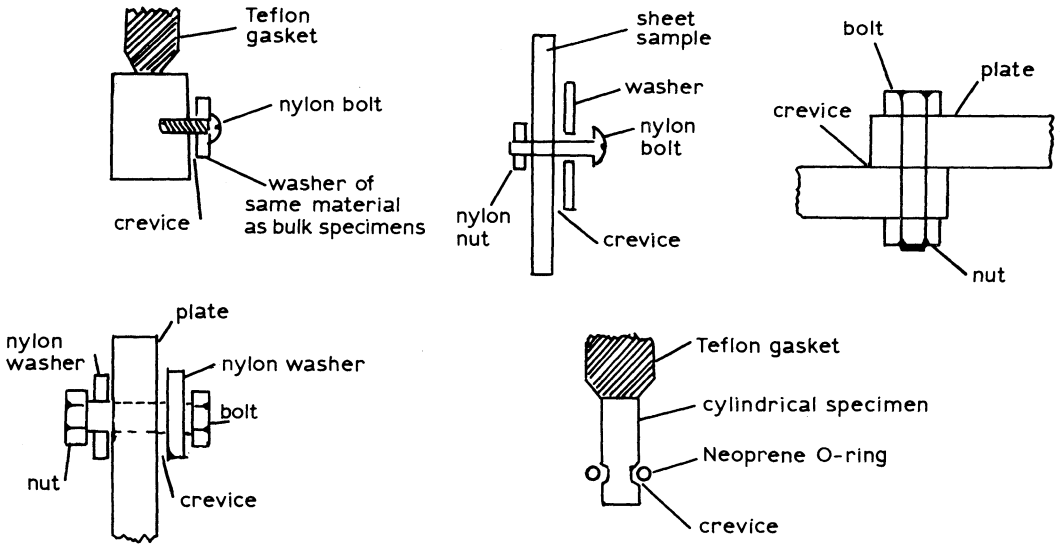
As with the MCA, the SCA is bolted to a test panel to provide a consistent degree of initial tightness. The method gives information on resistance to both initiation and propagation of attack. When constructed of a transparent material such as Perspex, the site of initiation can be identified during the test.

REMOTE CREVICE ASSEMBLY (RCA)

This test was developed so that the anode and cathode processes could be studied individually during an exposure test.[86,87] The anode and cathode are physically separated but electrically connected; the crevice is formed by sandwiching the specimen between two acrylic plates. Both the creviced anode and the uncreviced cathode are exposed in the environment of interest.

Using this assembly the measurement of current between the anode and cathode, with a zero-resistance ammeter, provides an indication of time to initiation of crevice corrosion, as reflected by a rapid increase in current. It also allows measurement of the rate of propagation of corrosion in the crevice as indicated by the magnitude of the current. The corrosion potential of the assembly can be measured, together with the mass loss and depth of attack on the anode specimen, once the test is terminated.

This method gives quantitative information on times to initiation of crevice corrosion, propagation rates, and the variation of potential with time. An example of the information that can be obtained is shown in Fig. 20, where crevice corrosion current as a



21 Schematic representation of various forms of crevice assembly (Ref. 66)

function of time is compared in natural and synthetic sea water.[88]

OTHER CREVICE ASSEMBLIES

There are innumerable ways in which a crevice can be formed. Figure 21 illustrates five that were used by Wilde in his studies.[66] A rather novel technique for giving a reproducible crevice was suggested by Degerbeck and Gille.[89] This involves using a felt tip pen and applying the plastic 'paint' from such a pen on to the steel surface. The paint dries to form a well defined adhesive layer in the form of stripes, bands, or whatever is desired. Rankings produced with this test have been in good agreement with practical operational experience.

Although the many available assemblies do result in crevice corrosion of stainless steels, the majority of them do lack control of crevice geometry. In addition none of them has been used consistently by different groups of workers, and therefore there is no 'data bank' of information on any one of the assemblies by which results can be compared. Thus, at present the only techniques which offer these advantages are the MCA, the SCA, and the RCA.

CREVICE CORROSION MONITORING

Crevice corrosion monitoring does not form part of this review. Nevertheless, it should be pointed out that the continued increase in our understanding of the crevice corrosion process, which has led to improved exposure testing techniques, is also leading to the development of test cells which can be used for on-line monitoring of crevice corrosion in chemical process systems.[90,91] It is only a matter of time before such cells come into common use.

Table 5 Average times to initiation of corrosion at 16 and 30°C using a single crevice assembly (Ref. 33)

	16°C		30°C	
Steel	Data points	Time, *h	Data points	Time, *h
AISI 316	5	566 ± 104	39	136 ± 91
UNS N08904	3	528 ± 85	35	141 ± 112

*± one standard deviation.

COMPARISON OF EXPOSURE TESTS FOR CREVICE CORROSION

The criteria laid down by Anderson[84] in his development of the MCA represented a significant step forward in our understanding of what is required for a reliable and meaningful crevice corrosion exposure test. However, in the light of our present understanding of the corrosion process, an additional requirement should be added, namely that the crevice gap and depth should be both reproducible and controllable. Figure 13 shows how small changes in gap can override quite significant changes in alloy composition, thereby necessitating good reproducibility. Data in Table 5 demonstrate that severe crevice gaps result in similar times to breakdown for materials with known differences in corrosion resistance. This means that different crevice gaps are required to differentiate between materials within different classes of corrosion resistance; for example, testing of AISI 316 and 904L ideally requires a gap which is wider than one required for materials such as AL-6X and Avesta 254 SMO. Thus, the ability to vary the gap is extremely important. Crevice depth is an important parameter and any test assembly should be able to handle different depths.

Of the test assemblies discussed the spool test and the other assemblies have not so far been used with the degree of control necessary for them to be reliable for assessing crevice corrosion resistance. The three assemblies which have been used in a controlled way are the MCA, the SCA, and the RCA.

The possible drawbacks of each of these tests is as follows:

(i) the MCA, with its large number of crevice sites, is unlikely to have the same crevice gap at each one. This can cause difficulty in interpreting

correctly the significance of the number of sites attacked. In addition, as already mentioned, there is the possibility of the corrosion reaction at one or two crevices affording cathodic protection to other crevice sites, and there is the fact that the individual crevice depth is small compared with the majority of practical crevices

(ii) the SCA and RCA with their large crevice area, require the specimen to be flat over this area if a constant crevice gap is to be obtained

(iii) the method used to provide variability in gap is to vary the torque used to tighten the assemblies[82] in conjunction with the use of soft inserts in the crevice which mould to the shape of the metal surface.[26] This technique does work to some extent, but in general the torque method of applying a force is not a good one. The assembly is almost certain to 'relax' so that the crevice gap will also relax with time.

These points notwithstanding all three methods have their place and all have been used to generate useful information in the past. Nevertheless, there is clearly room for an improved assembly with better and more quantitative control of crevice geometry.

SUMMARY AND CONCLUSIONS

Test methods currently available for determining the resistance of stainless steels and related alloys to pitting and crevice corrosion in chloride environments have been assessed. The present understanding of the mechanisms of pitting and crevice corrosion are examined and the major factors affecting the processes are noted. The need for a test to relate clearly to either the initiation or propagation stage of either pitting or crevice corrosion is highlighted together with the fact that in practice it is crevice corrosion rather than pitting corrosion that occurs.

Tests are reviewed under the following headings:

Accelerated pitting corrosion tests	– electrochemical tests – chemical tests – stochastic theory based tests
Exposure tests for pitting corrosion	
Accelerated crevice corrosion tests	– electrochemical tests – chemical tests
Exposure tests for crevice corrosion	

The conclusions reached concerning the accelerated pitting corrosion tests are as follows:

1. The most widely used tests are potentiokinetic methods, potentiostatic methods, and ferric chloride immersion tests.

2. None of the tests examined related directly to service experience; they simply provide an alloy ranking.

3. Correlation between techniques, when studying alloys of similar corrosion resistance, is poor, and the ranking order obtained therefore depends on the test selected.

Exposure tests for pitting corrosion are not often performed, since any assembly will contain some form of crevice where preferential attack is likely. Ten accelerated crevice corrosion tests are reviewed and the following conclusions have been reached concerning these:

1. Six of the ten techniques use a crevice specimen. Crevice geometry has a marked effect on the initiation of corrosion, and difficulty in controlling this geometry is likely to cause problems when comparing results.

2. Tests using ferric chloride solutions do not give results which can be related to the majority of practical situations.

3. Two methods are available that can predict performance as well as provide meaningful rankings. One is based on the compilation of anodic and cathodic polarization curves, the other on a mathematical model of crevice corrosion using electrochemical data as part of the input.

Exposure tests for crevice corrosion are used extensively. Three types of assembly are used where an attempt is made to control the crevice geometry: the multiple crevice assembly (MCA), the single crevice assembly (SCA), and the remote crevice assembly (RCA). The conclusions reached concerning these assemblies are as follows:

1. The MCA is a useful test which is easy to administer. A constant torque can be applied in an attempt to give reproducible geometry. Interpretation of results is not straightforward.

2. The SCA provides larger crevice depths than the MCA; if constructed in transparent material, it allows visual observation of initiation sites. Interpretation of results is straightforward.

3. The RCA allows detailed measurements to be made of current and potential variations that occur during the corrosion process. It is therefore a powerful exposure technique.

4. Because of the importance of crevice geometry, particularly crevice gap, and the poor control afforded by initially applying a fixed torque, there is clear scope for the development of an improved assembly with better and more quantitative control of the force maintaining the crevice.

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