
**Corrosion of metals and alloys —
Guidelines for the evaluation of pitting
corrosion**

*Corrosion des métaux et alliages — Lignes directrices pour
l'évaluation de la corrosion par piqûres*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 262, *Metallic and other inorganic coatings, including for corrosion protection and corrosion testing of metals and alloys*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 11463:1995), which has been technically revised. The main changes compared with the previous edition are as follows:

- modern surface analysis and characterization techniques for ex situ examination have been included.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

It is important to be able to determine the extent of pitting and its characteristics, either in a service application, where it is necessary to estimate the remaining life in a metal structure, or in laboratory test programmes that are used to select pitting-resistant materials for a particular service. Corrosion pits can also act as the precursor to other damage modes such as stress corrosion cracking and corrosion fatigue.

The application of the materials to be tested will determine the minimum pit size to be evaluated and whether total area covered, average pit depth, maximum pit depth or another criterion is the most important to measure.

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Corrosion of metals and alloys — Guidelines for the evaluation of pitting corrosion

1 Scope

This document gives guidelines for the selection of procedures that can be used in the identification and examination of corrosion pits and in the evaluation of pitting corrosion and pit growth rate.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

4 Identification and examination of pits

4.1 Preliminary low magnification visual inspection

4.1.1 A visual examination of the corroded metal surface with or without the use of a low-power magnifying glass may be used to determine the extent of corrosion and the apparent location of pits. It is often advisable to photograph the corroded surface so that it can be compared with the clean surface after the removal of corrosion products or with a fresh unused piece of material.

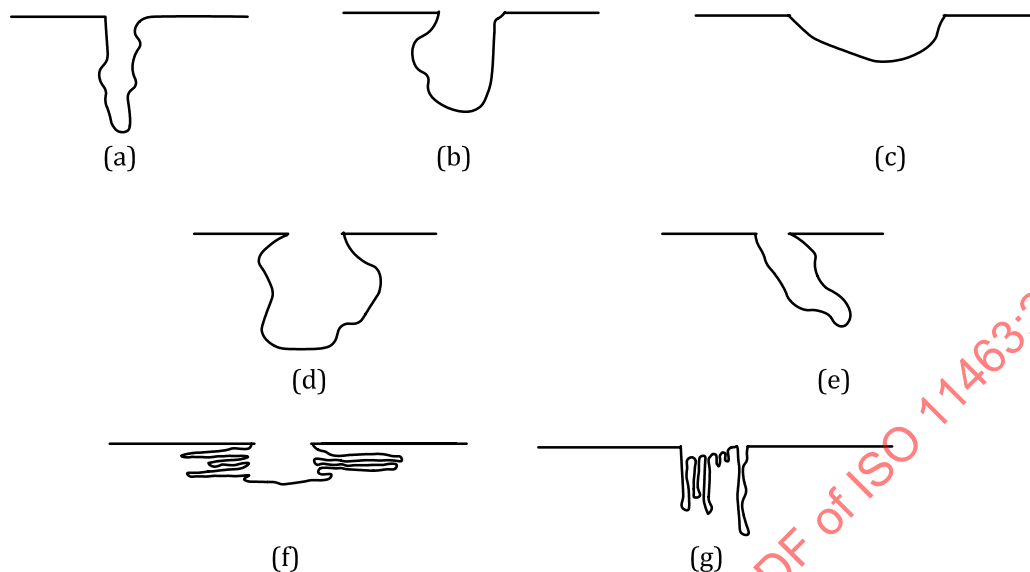
4.1.2 If the metal specimen has been exposed to an unknown environment, the composition of the corrosion products may be of value in determining the cause of corrosion. Recommended procedures for the removal of particulate corrosion products should be followed and the material removed should be preserved for future identification.

4.1.3 To expose the pits fully, it is recommended that cleaning procedures should be used to remove the corrosion products. Rinsing with water followed by light mechanical cleaning can be sufficient for lightly adhered corrosion products. Chemical cleaning is required for more adherent products. ISO 8407^[1] provides a range of chemical cleaning processes. Preliminary testing should be undertaken to ensure that attack of the base metal is avoided.

4.2 Optical microscopic examination of pit size and shape

4.2.1 Examine the cleaned metal surface to determine the approximate size and distribution of pits. Follow this procedure by a more detailed examination through a microscope using a low magnification (approximately $\times 20$). Pits can have various sizes and shapes. A visual examination of the metal surface can show a round, elongated or irregular opening, but it seldom provides an accurate indication of the

extent of corrosion beneath the surface. Thus, it is often necessary to cross-section the pit to determine its actual shape. Several common variations in the cross-sectioned shape of pits are shown in [Figure 1](#).



Key

- | | |
|-------------------|--|
| (a) narrow, deep | (e) undercutting |
| (b) elliptical | (f) microstructural orientation (horizontal) |
| (c) wide, shallow | (g) microstructural orientation (vertical) |
| (d) sub-surface | |

Figure 1 — Variations in the cross-sectional shape of pits

4.2.2 It is difficult to determine pit density by counting pits through a microscope eyepiece, but the task can be made easier by the use of a plastic grid. Place the grid, containing 3 mm to 6 mm squares, on the metal surface. Count and record the number of pits in each square and move across the grid in a systematic manner until all the surface has been covered. This approach minimizes eyestrain because the eyes can be taken from the field of view without fear of losing the area of interest. Enlarged photographs of the area of interest may also be used to reduce eyestrain. An alternative approach is to mount the specimen on an x-y stage and measure both the number and spatial distribution of pits. When coupled with optical depth measurement, where applicable, the number, depth and spatial distribution of pits can be determined.

4.2.3 Advanced optical microscopy techniques, such as infinite focus microscopy and confocal laser microscopy may be used to obtain three-dimensional images of the pit surface, within the constraints of optical observations [most relevant to [Figure 1 a\)](#) to c) but not applicable to undercut]. Such measurements can be used to view the surface features and quantify surface roughness, pit depth, surface profile, etc.

4.2.4 To carry out a metallographic examination, select and cut out a representative portion of the metal surface containing the pits and prepare a metallographic specimen. If corrosion products are to be examined in cross-section, it may be necessary to fix the surface in a mounting compound before cutting. Examine microscopically to determine whether there is a relation between pits and inclusions or microstructure, or whether the cavities are true pits or might have resulted from metal loss caused by intergranular corrosion, dealloying, etc.

4.3 In situ non-destructive inspection

4.3.1 General

Several techniques have been developed to assist in the detection of cracks or cavities in a metal surface without destroying the material (see Reference [2]). These methods are less effective for locating and defining the shape of pits than some of those described previously, but they merit consideration because they are often used in situ, and thus they are more applicable to field applications.

4.3.2 Radiographic

Radiation, such as X-rays, passes through the object. The intensity of the emergent rays decreases with increasing thickness of the material. Imperfections can be detected if they cause a change in the absorption of X-rays. Detectors or films are used to provide an image of interior imperfections. The metal thickness that can be inspected is dependent on the available energy output. Pits must be as large as 0,5 % of the metal thickness to be detected and care should be taken to ensure that pits are not confused with pre-existing pores.

4.3.3 Electromagnetic

4.3.3.1 Eddy currents may be used to detect defects or irregularities in the structure of electrically conductive materials. When a specimen is exposed to a varying magnetic field, produced by connecting an alternating current to a coil, eddy currents are induced in the specimen and they in turn produce a magnetic field of their own. Materials with defects will produce a magnetic field that is different from that of a reference material without defects, and an appropriate detection instrument is required to determine these differences.

4.3.3.2 The induction of a magnetic field in ferromagnetic materials is another approach that is used. Discontinuities that are transverse to the direction of the magnetic field cause a leakage field to form above the surface of the part. Ferromagnetic particles are placed on the surface to detect the leakage field and to outline the size and shape of the discontinuities. Rather small imperfections can be detected by this method. However, the method is limited by the required directionality of defects to the magnetic field, by the possible need for demagnetization of the material, and by the limited shapes of parts that can be examined.

4.3.4 Ultrasonics

In the use of ultrasonics, pulses of sound energy are transmitted through a couplant, such as oil or water, on to the metal surface where waves are generated. The reflected echoes are converted to electrical signals that can be interpreted to show the location of flaws or pits. Both contact and immersion methods are used and various techniques can be applied. The test should be carried out from the non-pitted face. The test is affected by the morphology of the pits, the ultrasonic technique selected and the performance of the probe and flaw detector. Information about the size and location of flaws can be established. However, the capability of the technique for the pitting expected should be assessed and reference standards produced for comparison. Operators should be trained in the application of the technique and the interpretation of the results.

4.3.5 Penetrants

Defects opening to the surface can be detected by the application of a penetrating liquid that subsequently exudes from the surface after the excess penetrant has been removed. Defects are located by spraying the surface with a developer that reacts with a dye in the penetrant, or the penetrant may contain a fluorescent material that is viewed under ultraviolet light. The size of the defect is shown by the intensity of the colour and the rate of bleed-out. This technique provides only an approximation of the depth and size of pits.

4.3.6 Replication

Images of a pitted surface can be created by applying a material to the surface that conforms to the shape of the pits and can be removed without damaging its shape. This method will not work, however, for pits of subsurface or undercut type. The removed material contains a replica of the original surface that, in some cases, is easier to analyse than the original. Replication is particularly useful for the analysis of very small pits.

4.4 Ex situ examination techniques

4.4.1 General

Several sophisticated ex-situ techniques are available for examining the size, shape and distribution of pits in metallic samples. Their application would involve transport of the specimens to a laboratory or dedicated analytical facility. Some of these techniques are described in [4.4.2](#) to [4.4.5](#).

4.4.2 Scanning electron microscopy

Scanning electron microscopy (SEM) can be used to obtain images containing topographic and phase contrast information. It is a very useful technique for obtaining images of pits in surfaces and the technique can be used to determine the dimensions of the pit and any relationships with different phases within the microstructure of the metal. By combining electron-dispersive X-ray spectroscopy (EDS) or wavelength-dispersive X-ray spectroscopy (WDS), elemental composition and distribution of any corrosion products in pits can be determined. However, in deeper pits and where subsurface undercutting of the pit mouth has occurred, electron emission is shielded from the detector and this can limit the effectiveness of the technique for imaging the pit morphology.

4.4.3 X-ray computed tomography

X-ray computed tomography (CT) is a non-destructive technique that, coupled with reconstruction software, can enable 3D imaging of pits. The images are constructed by taking slices through the sample using high intensity X-ray sources, which may be X-ray tubes in conventional laboratories or derived from synchrotron X-ray sources. The thickness of specimen can be limited due to X-ray attenuation. Sectioning parallel to the surface can be required to reduce the thickness. Nevertheless, the technique is a powerful tool for 3D imaging of pits of complex shape.

4.4.4 Image analysis

Image analysis is the technique whereby images that have been taken using a measurement technique such as optical microscopy or X-ray computed tomography are post-processed to extract quantitative information. The technique can be used to automate the analysis or post-processing of images to reduce time and cost. It also permits the analysis of a greater number of images, thereby improving the statistical reliability of the measurements. Image analysis allows micrographs to be processed rapidly and can produce data that are more accurate and statistically robust than manual methods.

4.4.5 Profilometry

Profilometry measures the physical surface geometry or topography of a sample. It may be classed as “contact” or “non-contact”. Contact profilometry involves a stylus, with known tip dimensions, being brought into contact with the sample surface, and then rastered over the surface. The displacement of the stylus tip as it comes into contact with high and low features on the surface is monitored and recorded as a function of its position. From this data, the physical characteristics of the surface, such as roughness, can be measured, and any features of interest, such as pitting, can be identified and quantified.

Non-contact methods record the same type of information, although they usually employ laser-based optical methods, such as an infinite focus microscope, and they do not require direct physical contact with the sample surface. Such techniques develop a 3D surface profile through the accumulation of

images at different optical focal planes, and white-light interferometry, where the phase difference between light reflected from the sample surface and light from a reference mirror are compared, and differences in the path length due to the surface morphology may be recorded. Confocal laser microscopes can give similar information.

The disadvantage of these techniques is that they characterize only what they can detect optically and are applicable mainly to pit types such as [Figure 1 a\) to c\)](#) (see also [4.2.3](#)).

5 Extent of pitting

5.1 Mass loss

Metal mass loss is not ordinarily recommended for use as a measure of the extent of pitting unless general corrosion is slight and pitting is fairly severe. If uniform corrosion is significant, the contribution of pitting to total metal loss is small, and pitting damage cannot be determined accurately from mass loss. In any case, mass loss can only provide information about total metal loss due to pitting but nothing about density of pits and depth of penetration. However, mass loss should not be neglected in every case because it may be of value. For example, mass loss along with a visual comparison of pitted surfaces can be adequate to evaluate the pitting resistance of alloys in laboratory tests. Mass loss may also be useful to detect the existence of subsurface metal loss.

5.2 Pit depth measurement

5.2.1 Metallography

Pit depth may be determined by sectioning vertically through a preselected pit, mounting the cross-sectioned pit metallographically and polishing the surface. A better or alternative way is to section slightly away from the pit and slowly grind until the pit is in the cross-section. Sectioning through a pit can be difficult and the deepest portion can be missed. The depth of the pit is measured on the flat, polished surface using a microscope with a calibrated eyepiece. The method is very accurate, but it requires good operator skill, good judgement in the selection of the pit and good technique in cutting through the pit. Its limitations are that it is time-consuming, the deepest pit may not have been selected and the pit may not have been sectioned at the deepest point of penetration. This technique will result in the destruction of the specimen.

5.2.2 Machining

NOTE See References [\[3\]](#) and [\[4\]](#).

5.2.2.1 This method requires a sample that is fairly regular in shape. It usually involves the destruction of the specimen. Measure the thickness of the specimen between two areas that have not been affected by general corrosion. Select a portion of the surface on one side of the specimen that is relatively unaffected, then machine the opposite surface where the pits are located on a precision lathe, grinder or mill until all signs of corrosion have disappeared. Some difficulty from galling and smearing can be encountered with soft metals and pits can be obliterated. Conversely, inclusions can be removed from the metal thus confusing the examination. Measure the thickness of the specimen between the unaffected surface and subtract from the original thickness to give the maximum depth of pitting. Repeat this procedure on the unmachined surface unless the thickness has been reduced by 50 % or more during the machining of the first side.

5.2.2.2 This method is equally suitable for determining the distribution of pit depths in a sample. Count the visible pits then machine away the surface of the metal in measured stages (the amount of material removed in each step will determine the uncertainty in pit depth). Continue this process, noting for each pit the depth of material removed at which it is no longer visible. The depth of the pit will lie between the depth of last observation and the depth of material at which it is no longer visible.

5.2.3 Micrometer or depth gauge

5.2.3.1 This method is based on the use of a pointed needle attached to a micrometer or calibrated depth gauge to penetrate the pit cavity. Remove surrounding corrosion products or debris thoroughly, then zero the instrument on an unaffected area at the lip of the pit.

Insert the needle in the pit until it reaches the base. The distance travelled by the needle is the depth of the pit. It is best to use constant-tension instruments to minimize metal penetration at the base of the pit. It may be advantageous to use a stereomicroscope in conjunction with this technique so that the pit can be magnified to ensure that the needle point is at the bottom of the pit. The method is limited to pits that have a sufficiently large opening to accommodate the needle without obstruction. This eliminates those pits that have undercutting or strong directional orientation.

5.2.3.2 In a variation of this method, attach the probe to a spherometer and connect it through a microammeter and battery to the specimen (see References [4] and [5]). When the probe touches the bottom of the pit, it completes the electrical circuit and the probe movement is a measurement of pit depth. This method is limited to very regularly shaped pits because contact with the side of the pit or conductive debris would give a false reading.

5.2.4 Microscopy

5.2.4.1 This method is particularly valuable when pits are too narrow or difficult to penetrate with a probe type of instrument. The method is amenable to use as long as light can be focused on the bottom of the pit. This would not be possible in the case of example e) in [Figure 1](#).

5.2.4.2 Use a metallurgical microscope with a magnification range from $\times 50$ to $\times 500$ and a calibrated fine-focus knob (e.g. 1 division $\cong 0,001$ mm). If the latter is not available, a dial micrometer can be attached to the microscope in such a way that it will show movement of the stage relative to the microscope body.

5.2.4.3 Locate a single pit on the metal surface and centre it under the objective lens of the microscope at low magnification (e.g. $\times 50$). Increase the objective lens magnification until the pit area covers most of the field under view. Focus the specimen surface at the lip of the pit, using first the coarse and then the fine focusing knobs of the microscope. Record initial readings from the fine-focusing knob, refocus on the bottom of the pit with the fine-focusing knob, and record the reading. The difference between the initial and the final readings on the fine-focusing knob is the pit depth.

5.2.4.4 Repeat the steps in [5.2.4.2](#) for each pit to determine the distribution of pit depths. Alternatively, many contemporary instruments are equipped with software for automating the measurement of pit depths from optical microscopy images.

5.2.4.5 A variation of this technique employs the use of an interference microscope. A beam of light is split, and one portion is projected on to the specimen and the other on to the surface of a reference mirror. The reflected light from these two surfaces is recombined, and interference fringes are formed that provide a topographical map of the specimen surface. These fringes can be used to measure vertical deviations on the metal surface. However, the method is limited to the shallower pits, i.e. less than $25\text{ }\mu\text{m}$ in depth, because the number of fringes increases to the point where they are difficult to count.

6 Evaluation of pitting

6.1 General

There are several ways in which pitting can be described, given a quantitative expression to indicate its significance or used to predict the life of a material. Some of the more commonly used methods are described in this clause, although it is often found that no single method is sufficient by itself.

6.2 Standard charts

NOTE See Reference [4].

6.2.1 Rate the pits in terms of density, size and depth on the basis of standard charts, such as those shown in [Figure 2](#). Columns A and B relate to the extent of pitting at the surface of the metal (i.e. column A is a means for rating the number of sites per unit area and column B is a means for showing the average size of these sites). Column C rates the intensity or average depth of attack. A typical rating might be A-3, B-2, C-3, representing a density of 5×10^4 pits/m², an average pit opening of 2 mm² and an average pit depth of 1,6 mm.

6.2.2 This method offers an effective means of communication between those who are familiar with the charts and it is a simple means of storing data for comparison with other test results. However, it is tedious and time-consuming to measure all the pits and the time is usually not justified because maximum values (e.g. pit depths) usually have more significance than average values.

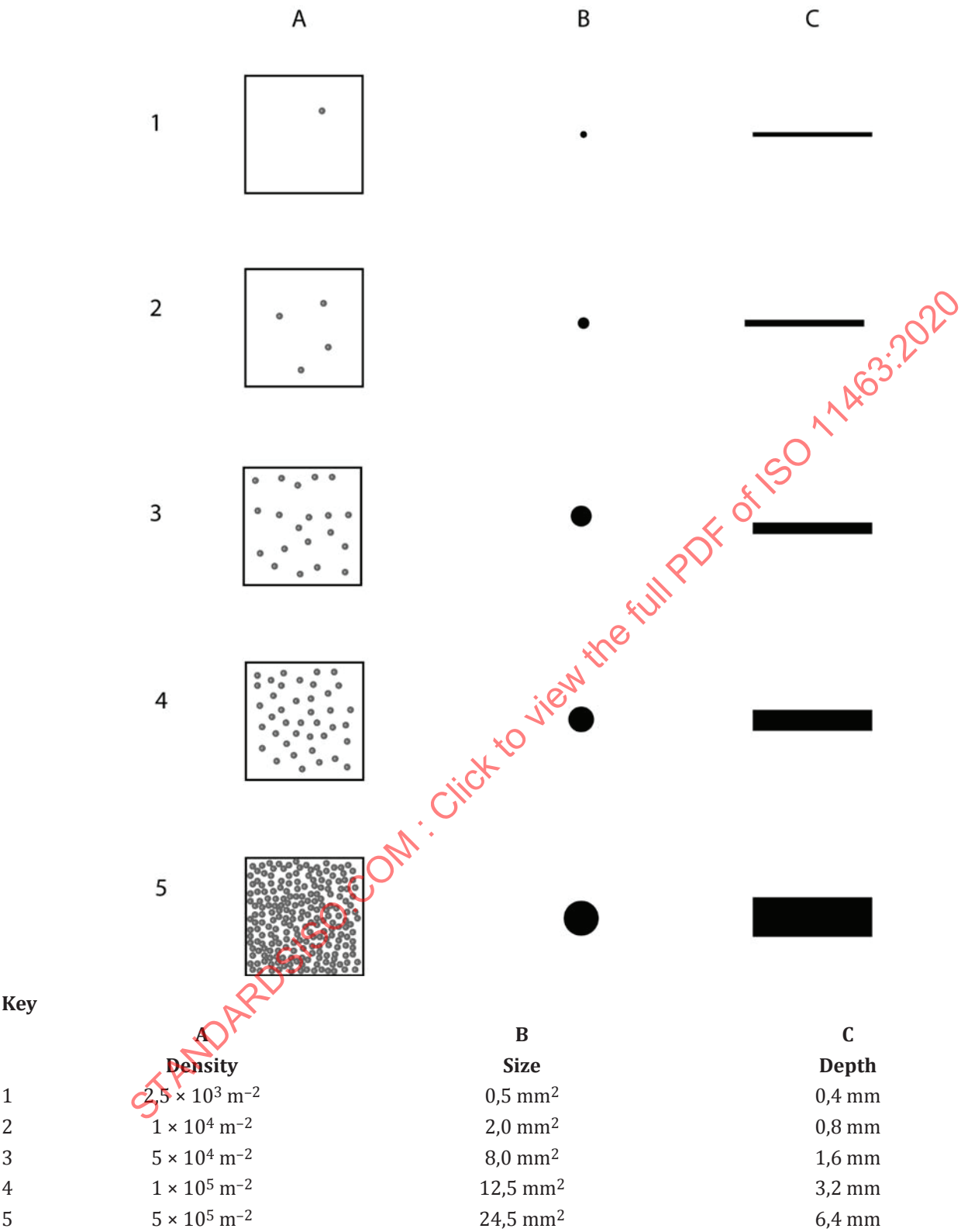


Figure 2 — Standard rating charts for pits

6.3 Metal penetration

6.3.1 Measure the deepest pit and express metal penetration in terms of the maximum pit depth or the average of the 10 deepest pits or preferably both. This type of measurement is particularly significant when the metal is associated with an enclosure for a gas or liquid, and a hole could lead to a loss of fluid.

6.3.2 Metal penetration may also be expressed in terms of a pitting factor, F . This is the ratio of the deepest metal penetration, $D_{\max}$, to the average metal penetration, D_{av} , determined from mass loss, as shown in [Formula \(1\)](#):

$$F = \frac{D_{\max}}{D_{\text{av}}} \quad (1)$$

A pitting factor of 1 represents uniform corrosion. The larger the number, the greater the depth of penetration. The factor does not apply in those cases where pitting or general corrosion is very small because values of zero or infinity can readily be obtained when dealing with a ratio where one number approaches zero.

6.4 Statistical

6.4.1 The application of statistics to the analysis of corrosion data is discussed briefly in this document to show that statistics have a bearing on the evaluation of pitting data. More detailed information can be obtained from other publications (see References [6] to [9]).

6.4.2 The probability that pits will initiate on a metal surface is dependent on a number of factors, such as the pitting tendency of the metal, the corrosivity of the solution, the specimen area and the time of exposure. A pitting probability test can be conducted to determine the susceptibility of metals to pitting, but it will not provide information about the rate of propagation (see Reference [10]) and the results are only applicable to the conditions of exposure. The pitting probability, P , in %, after the exposure of a number of specimens to a particular set of conditions can be expressed as shown in [Formula \(2\)](#):

$$P = \frac{N_p}{N} \times 100 \quad (2)$$

where

N_p is the number of specimens that pit;

N is the total number of specimens.

See References [11] and [12].

6.4.3 The relationship between pit depth and area or time of exposure can vary with the environment, the metal exposed and other variables. The relationships cited in [6.4.4](#) and [6.4.5](#) are examples that have been found to apply under certain exposure conditions.

6.4.4 The relationship in [Formula \(3\)](#) was found between the maximum pit depth, D , and the area, A , of a pipeline exposed to soil:

$$D = bA^a \quad (3)$$

where a and b are constants derived from the slope and the y-intercept of a straight line obtained when the logarithms of the mean pit depth for successively increasing areas on the pipe are plotted against the logarithms of the corresponding areas.

See References [13] to [15].

The dependence on area is attributed to the increased chance for the deepest pit to be found when the size of the sample of pits is increased through an increased area of corroded surface.

6.4.5 The maximum pit depth, D , of aluminium exposed to various waters was found to vary as the cube root of time, t , as shown in [Formula \(4\)](#):

$$D = Kt^{\frac{1}{3}} \quad (4)$$

where K is a constant that is a function of the composition of the water and alloy.

See References [\[11\]](#) and [\[16\]](#).

This relationship has been found to apply to several aluminium alloys exposed to different waters.

In the case of stainless steels under atmosphere exposure, the relationship shown in [Formula \(5\)](#) was found between the maximum pit depth, D , and the exposure time, t :

$$D = ct^m \quad (5)$$

where m and c were constants.

The constant m was dependent on the corrosivity of the atmosphere and it increased with the concentration of airborne chloride. The relationship between the constant c and the concentration of the alloy elements was obtained through multi-regression analysis, which made it possible to predict the maximum pit depth of various grades of stainless steels.

See Reference [\[6\]](#).

The pit growth rate can be determined by differentiation of [Formula \(4\)](#) or [\(5\)](#).

6.4.6 Extreme value probability statistics (see References [\[7\]](#) and [\[17\]](#)) have been successfully applied to maximum pit depth data to estimate the maximum pit depth in a large area of material based on examination of a small portion of that area (see References [\[4\]](#), [\[11\]](#) and [\[16\]](#)). The procedure is to measure specimens that have pitted, and then arrange the pit depth values in order of increasing rank. A plotting position for each order of ranking is obtained by substituting in the relation, $M/(N+1)$, where M is the order of ranking and N is the total number of specimens or values. For example, the plotting position for the second value out of 10 would be $2/(10+1) = 0,181\ 8$. These values are plotted on the ordinate of extreme value probability paper versus their respective maximum pit depth. If a straight line is obtained, it shows that extreme value statistics apply. Extrapolation of the straight line can be used to determine the probability that a specific depth will occur or the number of observations that must be made to find a particular pit depth.

7 Test report

The test report should include as much detailed information as possible and a minimum of the following information:

- a reference to this document, i.e. ISO 11463;
- material composition and product form, supplier and production details, metallurgical treatment of the metal, surface preparation and final surface finish before exposure to test or to service;
- environmental conditions and duration of exposure;
- appearance of the corroded surface before and after cleaning;
- identification of corrosion products and distribution;