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The kinetics of pitting corrosion of carbon steel

Progress report to June 1987

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Materials Development Division
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February 1988

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Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20), 1986 (TR 86-31) and 1987 (TR87-33) is available through SKB.

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ABSTRACT

The report describes progress between April 1986 and May 1987 in a programme studying the kinetics of pitting corrosion in carbon steel containers for the disposal of high level nuclear waste in a granitic repository.

Much of the effort during this period has been devoted to the development of an improved statistical method for analysing pit growth data to take account of the difference in area of laboratory specimens and full sized waste containers. Statistical analysis of data from pit growth experiments lasting 1218-1314h and 3240h with large area (460 cm^2) plates of BS 4360 steel have indicated that the depth distributions correlate most closely with a limited distribution function. This contrasts with previous data with small specimens (8 cm^2) of carbon 20 steel which gave a better correlation with an unlimited exponential distribution function. This difference may arise because the larger specimens give a more accurate sample of the pit depth distribution, particularly the "tail-off" at high pit depths which is crucial in determining the overall shape of the distribution. This correlation of the pit depth data with a limited distribution implies that previous statistical analyses to estimate the maximum pit depths in full size containers, which were made using unlimited distribution functions, will be pessimistic.

An evaluation of the maximum feasible pitting period based on estimating the period during which the oxygen diffusion flux is sufficient to stabilise a passive film on carbon steel containers has indicated that this is of the order of 125 years rather than the full 1000 year container life. The estimate is sensitive to the value of the leakage current assumed to flow through the passive film, and therefore work is planned to measure this accurately in relevant granitic environments.

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1. INTRODUCTION

Between 1980 and 1985 Harwell undertook a programme, jointly sponsored by the UK-DoE and the CEC (DoE/CEC), to investigate the corrosion behaviour of carbon steel containers for the disposal of High Level Nuclear Waste (HLW) under granitic repository conditions[1]. This work showed that, with certain groundwater compositions, carbon steels could be subject to comparatively fast localised corrosion. Kinetic studies, using an extreme value statistical approach to make allowance for the difference between practical specimen areas and the larger surface areas of containers, showed that for tests at 90°C the maximum pit depth increased with time in years according to the expression

$$P = 8.35\ T^{0.46} \quad \text{(mm)} \qquad (1)$$

This inferred that a metal thickness of 200 mm would be needed to prevent containers being penetrated by pitting attack over a 1000 year period. Clearly such a large corrosion allowance, although feasible, will complicate container design, manufacture and subsequent handling in the repository. It is therefore important to be confident of the accuracy of equation (1).

In the final report of the DoE/CEC project it was concluded that equation (1) was likely to prove conservative for the following reasons:

(a) The equation was based on experiments lasting up to 10,000h in which the maximum pit depth was $\sim$ 3.5 mm. The extrapolation of such short term shallow pit data to long term deep pitting assumes that the same pits will continue to propagate. In practice it is more likely that restrictions on mass transport and ion migration will cause the periodic stifling of deep pits and subsequent initiation of new pits at the outer metal surface.

(b) The particular form of extreme value statistics used to analyse the maximum pit depth data assumed that the overall pit depth distribution fitted an unlimited distribution function. In practice the mass transport and migration restrictions mentioned above are likely to set an upper limit to the depth distribution producing a limited distribution.

(c) It may be unrealistic to assume pitting will occur during the full 1000 year life required from the containers. Localised corrosion is only possible in environments which are sufficiently oxidising to stabilise a protective oxide film on the bulk of the metal surface. This condition may not prevail in a repository for 1000 years.

In 1986 SKB contracted Harwell to advance the assessment of localised corrosion of carbon steel containers in granitic environments through a research programme which addresses the three issues described above. This report describes progress in this programme during the first 14 months to May 1987. It is divided into three sections which deal respectively with

(1) Kinetics of deep pit propagation.

(2) Statistical analysis of pit growth.

(3) Estimation of the aeration period at the container/ backfill interface.

2. KINETICS OF DEEP PIT PROPAGATION

The approach proposed to investigate the propagation of deep pits involves:

(a) The formulation of a mathematical model for pit propagation.

(b) An experimental study of the electrochemical conditions and rate of dissolution within deep artificial pits.

2.1 Mathematical Modelling

The development of a mechanistically based mathematical model for predicting the rate of propagation of pitting attack as a function of time and pit depth was initiated during the 1980-85 DoE/CEC programme[1], and is continuing with renewed sponsorship from DoE, UK Nirex and the CEC. The purpose in mentioning it here is to give a complete picture of the work addressing localised corrosion. Results from this work will be published, and the model may be used by SKB if such a requirement arises.

The original formulation of the model[1] gave a steady state solution to the mass conservation equations describing the chemical and electrochemical conditions within parallel sided pits. This gave good qualitative agreements with empirical data, but the quantitative comparison was less encouraging[2,3]. In particular the predicted corrosion currents were as much as several orders of magnitude higher than the measured ones. More recently a new finite element method for modelling pit propagation has been developed which enables time dependent solutions to be obtained. It also has the advantage of permitting two-dimensional modelling which enables the lateral dissolution of pits to be investigated.

The new model has shown that the presence of solid corrosion products within pits exert an important control over propagation rates. This arises partly because of the blocking effect of the solid phases, and also because precipitation limits the conductivity of the pit electrolyte. Preliminary results show that the inclusion of these effects reduces the models predictions of the propagation rate to values comparable to those observed experimentally.

With regard to the SKBF programme the intention is to use the model, when it has been sufficiently well developed, to investigate the rate of dissolution and electrochemical conditions within deep pits. More specifically attention will focus on the electrode potential at the base of the pit to determine if deep pits tend to repassivate. Also the ratio of the perpendicular to lateral dissolution rates will be evaluated to detect any tendency for the pits to blunt and stiffle.

2.2 Experimental Study with Deep Artificial Pits

The mathematical model discussed above can only be used with confidence once it has been validated against experimental data. Because of limited funding the only validation work planned in the DoE, UK-Nirex, CEC project is to compare the predicted pit growth rates with those measured experimentally over times scales up to 30,000h. If the model is to be used to investigate deep pits further validation is required, particularly with regard to its predictions of the electrode potential and lateral and perpendicular corrosion currents within pits of various geometries. Work to make this validation forms part of the SKB project, to be undertaken in 1987/88.

3. STATISTICAL ANALYSIS OF PIT GROWTH

The depths of pits formed in carbon steel after a fixed exposure period are not all the same, but have a statistical distribution. This occurs because of three factors:

(a) Pits initiate at different times.

(b) Some pits cease to propagation before the end of the exposure period.

(c) Pit propagation rates may also be variable.

Because pit depths are statistically distributed the probability of finding a pit of depth greater than x increases with surface area of metal exposed. This factor must be taken into account when predicting the maximum depth of pitting in HLW containers from tests with comparatively small surface area specimens.

In the DoE/CEC sponsored programme pit depth data were adjusted to take account of surface area using Type I Extreme Value Analysis which assumes that the overall distribution of pit depths is unlimited(4). However, as mentioned in the introduction, intuitively it would be expected that there would be a physical upper limit to the pit depth attainable after any particular exposure period, which will be fixed by the charge and mass transport kinetics within the pit. It was therefore recognised that this analysis may well have given a pessimistic assessment.

Given this background the SKB programme has the following objectives:

(a) To investigate whether the overall distributions of pit depths in carbon steel fit limited or unlimited distribution functions.

(b) To evaluate the accuracy of the Type I Extreme Value Analysis with tests on large area specimens.

(c) To widen the experimental study to investigate how pit growth is influenced by temperature and solution concentration.

A major part of the programmes resources have been directed at these tasks over the last 12 months.

3.1 Development of Statistical Analysis

The distribution of any continuous statistical variable x can generally be described by a cumulative distribution function F(x). This gives the probability that a single sample from the population will have a value less than or equal to x. The most commonly used distribution function is the Gaussian or Normal Distribution, but other useful distributions include Log-Normal, Poisson, Weibull, Binomial and Cauchy.

In the present study two distribution functions are being investigated, the first being the exponential distribution, ie:

$$F(x) = 1 - \exp\left[-b(x-x_o)\right] \tag{2}$$

This is a particular form of the Weibull Distribution with a shape parameter C = 1; b is the scale parameter characterising the spread of the distribution and x_o a location parameter. This distribution was selected because the Type I Extreme Value Analysis, to be discussed later, assumes that the tail of the overall distribution does not decay any faster than this form.

The second distribution to be investigated is the generalised limited distribution, ie:

$$F(x) = 1 - \left[\frac{w-x}{w-u}\right]^K \tag{3}$$

where w is the upper limiting pit depth and u the lower limiting pit depth.

For both distributions the cumulative probability F(x) can be calculated from the experimental results using the expression:

$$F(x) = \left[\frac{n}{N+1}\right] \tag{4}$$

where n is the number of pits in the specimen of depth $\leq x$ and N is the total number of pits in the specimen. With regard to HLW containers the parameter of main interest is the probability of finding a pit of depth $> x$ (ie P(x)). This is calculated from the distribution functions by:

$$P(x) = 1 - F(x) \tag{5}$$

and from the experimental data as

$$P(x) = 1 - \left[\frac{n}{N+1}\right] \qquad (6)$$

In the case of the exponential distribution, where there are only two fitting parameters b and x_o; regression analysis of the experimental data is simple. However, with the limited distribution there are 3 fitting parameters, w, u and K. To overcome this problem a computer programme has been written which makes repeated regression fits for a selected range of w values. By this means it is possible to identify the w giving the best correlation. Clearly the distribution function giving the best fit to the experimental data is the one with the highest correlation coefficient.

This method of data analysis was first applied to the existing results from the DoE/EEC project, and has been described in a report; soon to be published by Harwell and SKBF[5]. The main finding was the unexpected one that in general the data correlated best with the unlimited exponential distribution function. However, it was noted that the correlation was heavily dependent on the last 4-5 high pit depth data points, which were also the ones having the greatest scatter. It was therefore concluded that a tendency for a 'tail off' in the data towards a limiting pit depth might be detected if the results were extended to lower P(x) values by using larger specimens (ie a larger sample of pit population).

Turning now to the Extreme Value Analysis, as the title suggests this is a statistical method for predicting the probability that the maximum pit depth in a specimen will be $\leq x$. For a number of specimens of equal size the deepest pits in each will have a cumulative distribution $\phi(x)$ can be derived from F(x) as follows.

The probability that the N pits in a single sample all have a depth $\leq x$ is $F(x)^N$. This is also the probability that x will be the deepest pit in a specimen containing N pits, ie

$$\phi(x) = F(x)^N \qquad (7)$$

Therefore

$$\log \phi(x) = N \log F(x) \tag{8}$$

and expanding log F(x) using the Taylor series gives

$$\phi(x) \approx \exp \left[-N(1-F(x)) \right] \tag{9}$$

The probability of finding a pit deeper than x is 1-F(x), and in a specimen containing N pits the probable number deeper than x is N(1-F(x)). The Characteristic Largest Value is defined as the depth at which the expected number of pits exceeding this depth is unity, ie

$$N(1-F(U_N)) = 1 \tag{10}$$

$$F(U_N) = 1 - \frac{1}{N} \tag{11}$$

In the case of the Exponential Distribution

$$F(x) = 1 - \exp \left[-b(x-x_o) \right] \tag{2}$$

Substituting (2) in (11)

$$1 - \exp \left[-b(U_N-x_o) \right] = 1 - \frac{1}{N} \tag{12}$$

and rearranging

$$N \exp \left[-b(U_N-x_o) \right] = 1 \tag{13}$$

Using (13) to modify (2) gives

$$F(x) = 1 - \frac{1}{N} \exp \left[-b(x-U_N) \right] \tag{14}$$

and substituting into (9)

$$\phi(x) = \exp\left[-\exp\left[-b(x-U_N)\right]\right] \tag{15}$$

If the deepest pit is measured in m specimens the cumulative distribution $\phi(x)$ can be calculated from

$$\phi(x) = \frac{\ell}{m+1} \tag{16}$$

where ℓ is the ℓth largest pit depth of the m maxima obtained form the m specimens. If the m specimens contained approximately the same total number of pits N, and their depth distribution were all of the exponential form then a plot of $-\ln(-\ln \phi(x))$ versus x should give a straight line of gradient b and intercept $- bU_N$. The b value is the same as the scale parameter of the overall distribution function, therefore this can be used as a basis to compare the overall and extreme value distributions, assuming of course that they are of the exponential type.

The advantage of the extreme value analytical approach is that it only requires the maximum pit depths to be measured. This is much less laborious than having to measure the full size distribution, and, because it avoids the error in counting pits, should be more accurate.

Finally the technique to be used with both the overall and extreme value distributions for predicting the probability of finding a pit depth $> x$ in a container needs to be developed. Considering first the overall distribution it has been described previously that the probability that a single randomly selected pit in a specimen will have a depth $> x$ is given by equation (5). If there are N pits in the sample the probability that they will all be $\leq x$ is $F(x)^N$ (equation (7)). If the surface area of the sample is 'a' then the probability that all the pits i a container of area A will also all be $\leq x$ is $F(x)^{NA/a}$. It therefore follows that the probability of finding a pit depth $> x$ in a container is

$$P(x) = 1 - F(x)^{\rho A} \qquad (17)$$

where ρ is the average pit density per unit area (ie $^N/_A$). This can be expanded to show

$$P(x) = \rho A \exp[-b(x-x_x)] \qquad (18)$$

Turning to the extreme value analysis, the cumulative probability that x will be the deepest pit in a specimen containing N pits is $\phi(x)$.

The probability that x is the deepest pit in R samples each containing N pits is therefore $\phi(x)^R$, and the probability that a pit will exceed depth x is $1 - \phi(x)^R$.

If the experimental programme is conducted with samples of area 'a' and the containers have an area A, then assuming the pits are distributed evenly over the surface, the probability of finding a pit of depth > x in a container is given

$$P(x) = 1 - \phi(x)^{A/a} \qquad (19)$$

3.2 Experimental Study of Pit Growth

3.2.1 **Experimental Procedures**

In the previous DoE/CEC project an experimental technique was developed for measuring pit depth distributions after fixed exposure periods. The apparatus consisted of a threaded cylindrical specimen of 42 mm diameter, which was screwed into the base of a tubular PTFE vessel, so that 8 cm^2 of the specimen was exposed to the electrolyte. These assemblies were heated by immersion in an oil bath, and the specimens were subject to potentiostatic control. After the required exposure period the distribution of pit depths was measured by an incremental grinding procedure involving successive removal of 0.05 mm of metal and manual counting of the number of remaining pits. Experiments were conducted in groups of 5 so that the effective total sampling area was

40 cm^2. This also enabled the deepest pit depths recorded in each specimen to be used for an extreme-value statistical analysis.

The experimental programme on behalf of SKB is using the same procedure with the Carbon 20 steel (0.173% C, 0.05% Si, 0.75% Mn, 0.02% S, 0.02% P) used in the DoE/CEC work, and also with BS 4360 43A steel (0.2% C, 0.08% Si, 0.67% Mn, 0.038% S, 0.01% P). In addition larger (460 cm^2) specimens of BS 4360 steel are being tested. In the latter case the specimens are placed in an upward facing orientation in polymer lined tanks with their edges and lower faces screened from the test electrolyte by lacquer. Once again specimens can be subject to potentiostatic control and the pit depths are measured by an incremental grinding procedure.

3.2.2 Results of Small Scale Tests with BS 4360 Steel

These experiments are being conducted in the 0.1M $NaHCO_3$ + 1000 ppm Cl^- electrolyte established in the DoE/CEC programme(1), at a test temperature of 90°C. The first series of tests had the objective of establishing if the -200 mV potential used in previous work with Carbon 20 steel was also appropriate to BS 4360 steel. [N.B. All potentials quoted in this report are referred to the Saturated Calomel Reference Electrode (SCE)]. Single tests lasting 500-650h at potentials from 0 to -700 mV were conducted, and the maximum pit depths measured are listed in Table I. On the basis of these results it was decided to standardise on -200 mV, since at higher potentials overall breakdown of the passive film was induced, while at lower potentials the pit growth rate was much reduced.

Subsequent to these screening tests a programme was decided based on undertaking groups of 5 tests for exposure periods of roughly 1000, 3000, 5000 and 8000h. The first two of these groups have been completed and the results of the second, in the form of histograms showing the pit depth distribution in each specimen, are illustrated in figure 1. The main point to note about both these sets of results, as illustrated in figure 1, is the wide differences in the pit depths. These variations are too large to attribute to experimental error, and are unexpected, because in the earlier DoE/CEC programme very comparable results had been obtained from the groups of 5 carbon steel specimens. This specimen to specimen variability is further illustrated in Table 2 in which the maximum pit depths are compared to the time averaged current densities recorded during the tests. The current densities, with the exception of one specimen in both the 1272 and 3096h tests, are high compared to those obtained with Carbon 20 steel under the same conditions, which were of the order of 10^{-2} mA cm^{-2}. Also included in the table are aspect ratios of the maximum pit depth to the depth of general attack calculated from the time averaged anodic current using Faradays Law. A high aspect ratio indicates that most of the anodic current was used to propagate a limited number of pits whereas low ratios, as with specimens 3 to 5 in the 1272h tests, and 2-5 in the 3096h tests implies that these were subject to a more generalised form of corrosion. An aspect ratio for Carbon 20 steel is not available for the 1000h test period, but after 3000h it was 11.6. No attempt has been made to make a regression fit of the data from these tests to either the exponential or limited distribution functions. However, regression analyses were made on the values of the deepest pits in each of the specimens using the Type I Extreme Value equation (15). The 1272h data fitted the equation with a reasonable correlation coefficient of 0.97, and yielded a b value of 4.3 ± 1.99 (ie ± indicates 95% confidence limits of (b) and U_N of 0.6 mm. The corresponding results with the 3096h data were b 1.74 ± 1.1, U_N 1.32 mm with a correlation coefficient of 0.95.

3.2.3 **Results of Tests with Large Plates of BS 4360 Steel**

These tests are also being undertaken in 0.1M $NaHCO_3$ + 1000 ppm Cl^- solution at 90°C and -200 mV to facilitate comparison with the small scale tests described previously. The results for ∿ 1200 and 3200h, listed in Table 3, show that once again the anodic current densities are high and the aspect ratios low compared to those observed previously with Carbon 20.

The overall pit depth distributions were measured by making separate counts of the number of pits in eight equally sized grid areas covering the full specimen area. It was found through this procedure that the depth distributions in these areas varied considerably within any single specimen, and at least to the same extent as the specimen to specimen variations with the small BS 4360 specimens reported in the previous section. This was not unexpected given the visual appearance of the specimens which had large broad areas of corrosion separated by equally large areas of passive material. Clearly some of the grid areas would contain a larger proportion of the corroded zones than others, hence the difference in the pit depth distributions.

Regression analyses were made with the pit depth distributions from each of the four specimens using both the exponential (eqn (2)) and limited (eqn (3)) distribution functions and the results are listed in Tables 4 and 5. Considering first the ∿1200h results reasonable correlations were obtained in all cases with both distribution functions, although in three of four cases somewhat better correlations were obtained with the limited distribution. In the fourth case equally good correlations were obtained with the exponential distribution and with the limited distribution using a w value of 1.72 mm. With the 3240h data Table 5) better correlations were obtained with the limited distribution function in all cases, although even with these data good correlations were also obtained with the exponential distribution function.

An Extreme Value analysis has been made of the maximum pit depths measured in each of the eight counting areas on each specimen. The results in Table 6 show that the maximum pit data correlated less well with the extreme value distribution function than the full depth distributions did with either the limited or unlimited distribution functions. Significantly the b values estimated from this analysis are generally less than those obtained from the full distributions; the differences in many cases being greater than the 95% confidence limits.

3.2.4 **Small Scale Tests with Carbon 20 Steel**

These experiments were conducted with the small (8 cm^2) specimens of Carbon 20 steel used in the previous DoE/CEC programme. Their objective was to investigate the effect of temperature and solution concentration on pit propagation by comparing results obtained at 50°C and others obtained in a dilution solution (ie 0.01M $NaHCO_3$ + 100 ppm Cl^-) with the previous results for 90°C in 0.1M $NaHCO_3$ + 1000 ppm Cl^-.

Considering first the experiments at 50°C; subsequent to some short term exploratory tests it was decided to conduct these at 0 mV (versus SCE). The first set of five tests was run for 1007h, and as shown in Table 7 high anodic currents were recorded. This was surprising bearing in mind that this steel had shown comparatively low anodic currents of $\sim 10^{-2}$ mA cm^{-2} in the same solution at 90°C. The maximum pit depths measured in these tests was exceptionally high, but the aspect ratio (ie maximum pit depth to average corrosion depth) was only in the region of 6. A second set of 5 tests has recently been completed for an exposure period of 3024h. In this case the anodic currents form the specimens were so great that the control potential had to be reduced from 0 to -300 mV after about 500h. Even so the currents remained high compared to those measured with the same steel at 90°C, and Table 7 shows once more that the pitting aspect ratio was low. The full depth distributions obtained with the specimens are not shown, but once more the spread was too great for the distributions from each specimen to fit a single distribution. Consequently The statistical analysis of the results from these two sets of tests has so far been limited to the Type I Extreme Value approach. For the 1007h results this gave a b value of 1.87 ± 0.90 and a U_N of 2.75 mm with a correlation coefficient of 0.97. The 3024h test results gave a b of 2.99 ± 1.16, a U_N of 1.91 mm and a correlation coefficient of 0.98.

Turning to the tests in the tenth dilution solution ie 0.1M $NaHCO_3$ + 100 ppm Cl^-) at 90°C; exploratory tests showed that a suitable test potential would be -200 mV. Only one set of experiments has been completed so far under these conditions for a period of 1200h,and the resultant maximum pit depths and aspect ratios are listed in Table 8. Here again the aspect ratios indicate variable behaviour, with specimen 2 in particular pitting to a greater depth than the others. Type I extreme value analysis gave b = 1.23 ± 1.18, U_N = 0.42 mm and a poor correlation coefficient of only 0.89. However, the anodic currents were lower than with the 50°C tests, and were only about a factor of 5 greater than those recorded in previous tests with Carbon 20.

3.2.5 **Discussion**

The first feature of the results requiring discussion is the high anodic currents recorded in many of the tests. These contrasted with the low currents of the order of 10^{-2} mA cm^{-2}, obtained in the previous DoE/CEC programme with Carbon 20 steel. It was first thought that these high currents indicated that the BS 4360 steel, used in many of the tests, formed a less protective passive film, but subsequently similar behaviour was obtained with Carbon 20 steel at 50°C. It is now believed that the high currents arose because of the initiation of an enhanced population of pits caused by the spread of acidity over the specimen surface from the first pits to initiate. In some cases the effect of this was so severe that it produced attack which resembled an uneven form of general corrosion, with an aspect ratio (ie ratio of maximum to average corrosion depth) as low as 1-2. This was particularly true with the small specimen tests with BS 4360 steel (Table 2).

Why this process should not have been so pronounced in the earlier DoE/CEC work is unclear. However, it is significant that the present results show the process to be extremely variable. For example with the small BS 4360 specimens (Table 2), one in both the 1272h and 3096h tests passed low anodic currents and hence yielded high aspect ratios, although the other four specimens in both sets gave low aspect ratios. The same also applied to one of the carbon steel specimens tested in 0.01M $NaHCO_3$ + 100 ppm Cl^- (Table 8). The above observation leads to an important point concerning the relevance of the results to repository conditions, since it could be rightly argued that the high corrosion currents recorded in many of the tests could not be supported under the limited oxygen transport prevailing in a repository. The significant result is that in some cases pitting occurs with a low overall anodic current, which may be sustainable at least for a limited period under repository conditions, and then the aspect ratio is high (ie 20-30).

Turning to the statistical analysis of the results, it is difficult at this stage to draw any meaningful conclusions from the results of the small specimen tests on either BS 4360 or Carbon 20 steel. This is partly because, as illustrated in figure 1, there is no obvious correlation between the pit depth distributions obtained from individual specimens, and also because the low aspect ratios make it uncertain whether true pitting attack was produced in these tests. The analysis of the full pit depth distributions for the large area specimens is given in Tables 4 and 5. Here again the distributions from the individual specimens were different. This is clearly demonstrated by the fact that the b values of the exponential distribution function, which define the spread of the distribution, do not lie within each others 95% confidence limits. The same also is true of the K values for the limited distribution. Statistically, the implication of this is that even these 460 cm^2 specimens are not large enough to yield a pit size distribution characteristic of that which will develop on larger area containers. This point will be returned to at the end of this discussion.

Another important observation from the large specimen data is that these, with one exception, correlate more closely with a limited distribution function rather than the unlimited exponential distribution. This lends support for the proposition, stated in the introduction, that the use of an exponential distribution or Type I extreme value analysis is likely to give a pessimistic estimate of the maximum pit depth in a container. The degree of pessimism can be gauged if the limiting pit depths are compared with the maximum pit depths having a probability of 10^{-6} of being found on a container of 3 m^2 surface area, calculated from equations (18) and (19). This comparison is made in Table 9, which confirms that the analyses based on unlimited distribution functions do in general predict significantly greater pit depths.

Returning to the problem of the high anodic currents and consequent low aspect ratios discussed previously, it is unlikely that this will be overcome with the present potentiostatically controlled tests in which the electronic control supplies whatever current the specimen demands. A closer simulation of actual repository conditions can be obtained if the pitting tests are carried out under constant current (ie equivalent to a constant oxygen flux). It is therefore proposed to discontinue the potentiostatically controlled tests and revert to constant current testing. It is also proposed to explore the possibility of producing pitting without any external electrochemical control by undertaking tests in which it is attempted to polarise the specimens to pitting potentials simply by bubbling oxygen into the electrolyte.

4. AERATION PERIOD

It was explained in the introduction that another uncertainty concerning the evaluation of pitting corrosion is the period during which the process may occur. In the DoE/CEC programme this was assumed to be the full life of the containers, but this was considered to be pessimistic, because it was by no means certain that the oxygen flux required to sustain pitting could be maintained over this period.

An analysis of the maximum period for pitting in a SKB tunnel repository design has been made based on the following well established mechanistic principles[6].

(a) The deep pitting associated with acid occluded cell corrosion is only possible when the bulk metal surface adopts a potential positive to the $Fe \rightarrow Fe^{2+}$ equilibria.

(b) Such positive potentials can only be attained if the metal surface is covered by a passive film.

(c) The minimum requirement for the maintenance of stable passivity is that the small anodic current associated with passive film growth and/or dissolution must be balanced by a cathodic current produced by the reduction of oxygen or some other oxidising agent.

The latter condition defines the minimum requirement for pitting corrosion to be feasible, and can be expressed mathematically as

$$\frac{I_{pass}}{4F} \leq \frac{D\ \partial c(o,t)}{dx}$$

A preliminary evaluation of the maximum pitting period based on the above inequality has been made as part of the SKB programme and reported separately(6). This showed that the maximum pitting period was likely to be of the order of 125 years rather than the full 1000 year container life. However, the analysis showed that this estimate was sensitive to the value of the passive leakage current (I_{pass}). Consequently careful measurements are being made of I_{pass} before repeating the theoretical analysis.

5. SUMMARY

This report describes progress between April 1986 and May 1987 in a programme studying the kinetics of pitting corrosion in carbon steel containers for the disposal of high level nuclear waste in a granitic repository. Experimental studies are being undertaken with the following objectives.

(a) To improve the validation of a mathematical model for the propagation of pitting corrosion which is being developed in another programme sponsored by UK Nirex, DoE and CEC.

(b) To develop an improved statistical method for analysing experimental pit growth data to take account of the difference in area of laboratory specimens and full size waste containers.

(c) To estimate the maximum period during which pitting attack is feasible under repository conditions by calculating the time during which the diffusion of oxygen to the containers will be sufficient to maintain carbon steel in its passive state.

Work in the first 14 months of the project has concentrated on (b) and to a lesser extent (c).

Experiments with a BS 4360 carbon steel have, unlike previous tests with a compositionally similar Carbon 20 steel, encountered problems due to widespread pitting producing what was effectively low aspect ratio general dissolution. It is considered that the problem arises because of the potentiostatic control used in the tests, and future work will use constant current tests.

Analysis of data from pit growth experiments lasting 1218-1314 and 3240h with large area (460 cm^2) plates of BS 4360 steel have indicated that the depth distributions correlate most closely with a limited distribution function. This contrasts with previous data with small specimens (8 cm^2) of Carbon 20 steel which gave a better correlation with the unlimited exponential distribution function. This discrepancy may arise because the larger specimens give a more accurate sample of the pit depth distribution, particularly the 'tail off' at high pit depths which is crucial in determining the overall shape of the distribution.

The correlation of the pit depth data with a limited distribution function implies that previous statistical analyses to estimate the maximum pit depths in full sized containers, which were made using unlimited distribution functions will be pessimistic. This has been confirmed by comparing the limiting pit depths with the maximum pit depths estimated firstly by fitting an exponential distribution function to the pit depth data and secondly by making a Type I Extreme Value analysis of the maximum pit depth results.

An evaluation of the maximum feasible pitting period based on estimating the period during which the oxygen diffusion flux to containers is sufficient to stabilise a passive film has indicated that this is of the order of 125 years rather than the full 1000 year container life. The estimate is sensitive to the value assumed for the leakage current from the passive film, and therefore work is planned to improve confidence in the estimate by measuring this accurately in relevant granitic environments.

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Table 1

Maximum Pit Depths Measured in Screening Tests with BS 4360 43A Carbon Steel in 0.1M $NaHCO_3$ + 1000 ppm Cl^- at 90°C

Potential mV (vs SCE)	Test Time (h)	Maximum Pit Depth (mm)	Observations
-700	650	0.15	
-600	"	0.10	
-500	"	0.14	
-400	"	0.13	
-300	"	0.19	
-200	480	0.55	
0	650	-	Overall film breakdown

Table 2

Results of Pit Growth Experiments with BS 4360 43A Steel in 0.1M $NaHCO_3$ + 1000 ppm Cl^- and -200 mV at 90°C

Specimen No	Test Period (h)	Maximum Pit Depth (mm)	Time Average Anodic Current Density (mA cm^{-2})	Aspect Ratio
1	1272	0.50	0.008	36.7
2	1272	0.78	0.073	6.27
3	1272	1.05	0.38	1.62
4	1272	0.71	0.49	1.27
5	1272	0.81	0.19	2.50
1	3096	0.864	0.009	23.2
2	3096	1.359	0.179	1.83
3	3096	1.753	0.21	2.01
4	3096	1.830	0.216	2.04
5	3096	2.11	0.248	2.05

Table 3

Results of Pit Growth Experiments with Large Area (460 cm^2) BS 4360 Carbon Steel Specimens in 0.1M $NaHCO_3$ + 1000 ppm Cl^- at 90°C and -200 mV (SCE)

Specimen No	Test Period (h)	Maximum Pit Depth (mm)	Time Average Anodic Current Density (mA cm^{-2})	Maximum Aspect Ratio
1	1218	0.93	0.091	6.27
2	1218	1.03	0.170	3.71
3	1314	1.25	0.144	4.93
4	1294	1.16	0.122	5.49
1	3240	1.604	0.044	8.38
2	3240	1.529	0.094	3.73
3	3240	1.88	0.088	4.92
4	3240	1.47	0.073	4.64

Table 4

Results of Regression Analyses of Data From Large Area Specimen Tests in 0.1M $NaHCO_3$ + 1000 ppm Cl^- at 90°C and -200 mV (Test Period 1218-1314h)

(a) Correlation with unlimited distribution function

$$F(x) = 1 - \exp\left[-b(x-x_o)\right]$$

Specimen No	b	x_o (mm)	Correlation Coefficient
1	12.61 ± 0.59	0.40	0.994
2	11.36 ± 1.01	0.46	0.978
3	7.94 ± 0.64	0.50	0.977
4	8.32 ± 0.45	0.39	0.989

(b) Correlation with limited distriubtion function

$$F(x) = 1 - \left[\frac{w-x}{w-u}\right]^K$$

Specimen No	w (mm)	u (mm)	K	Correlation Coefficient
1	1.72	0.41	12.96	0.994
2	1.20	0.42	4.61	0.998
3	1.42	0.37	3.72	0.994
4	1.72	0.36	7.63	0.996

(± Indicates 95% Confidence Limits)

Table 5

Results of Regression Analyses of Data From Large Area Specimen Tests in 0.1M $NaHCO_3$ + 1000 ppm Cl^- at 90°C and -200 mV (Test Period 3240h)

(a) Correlation with unlimited distribution function

$$F(x) = 1 - \exp\left[-b(x-x_o)\right]$$

Specimen No	b	x_o (mm)	Correlation Coefficient
1	5.76 ± 0.31	0.56	0.986
2	7.97 ± 0.35	0.74	0.993
3	6.09 ± 0.28	0.79	0.989
4	7.77 ± 0.37	0.70	0.992

(b) Correlation with limited distriubtion function

$$F(x) = 1 - \left[\frac{w-x}{w-u}\right]^K$$

Specimen No	w (mm)	u (mm)	K	Correlation Coefficient
1	2.0	0.43	4.76	0.993
2	2.0	0.68	6.34	0.997
3	2.5	0.73	6.76	0.997
4	2.1	0.68	7.52	0.997

(± Indicates 95% Confidence Limits)

Table 6

Results of Extreme Value Analysis of Maximum Pit Depths Measured in the Large BS 4360 Steel Specimens after testing for 1218-1314h and 3240h in 0.1M $NaHCO_3$ + 1000 ppm Cl^- at 90°C and -200 mV

Test Period 1218-1314h

Specimen No	b	U_N (mm)	Correlation Coefficient
1	7.75 ± 1.63	0.71	0.979
2	11.32 ± 4.40	0.90	0.93
3	8.53 ± 4.076	1.11	0.90
4	7.24 ± 1.67	0.92	0.975

Test Period 3240h

Specimen No	b	U_N (mm)	Correlation Coefficient
1	2.89 ± 1.31	1.10	0.911
2	5.92 ± 1.77	1.24	0.958
3	4.63 ± 0.71	1.42	0.988
4	5.43 ± 0.87	1.107	0.987

(± Indicates 95% Confidence Limits)

Table 7

Results of Pit Growth Experiments with Carbon 20 Steel in 0.1M $NaHCO_3$ + 1000 ppm Cl^- Solution at 50°C and 0 mV Potential

Specimen No	Test Period (h)	Maximum Pit Depth (mm)	Time Average Anodic Current Density (mA cm^{-2})	Aspect Ratio
1	1007	2.46	0.41	4.48
2	1007	3.073	0.40	5.74
3	1007	2.845	0.39	5.44
4	1007	2.858	0.39	5.47
5	1007	3.708	0.41	6.75
(*) 1	3024	1.91	0.129	3.66
(*) 2	3024	1.75	0.143	3.02
(*) 3	3024	1.93	0.123	3.87
(*) 4	3024	2.46	0.168	3.62
(*) 5	3024	2.26	0.201	2.78

(* Potential had to be reduced for 0 to -300 mV after 500h to prevent anodic current increasing excessively)

Table 8

Results of Pit Growth Experiments with Carbon 20 Steel in 0.01M $NaHCO_3$ + 100 ppm Cl^- Solution at 90°C and -200 mV Potential

Test Period 1200h

Specimen No	Maximum Pit Depth (mm)	Time Average Anodic Current Density (mA cm^{-2})	Aspect Ratio
1	0.724	0.049	9.2
2	1.905	0.058	20.44
3	0.483	0.05	6.01
4	0.368	0.059	3.88
5	0.457	0.053	5.37

Table 9

Comparison of Predictions of the Probable Maximum Pit Depth in a Container or 3 m^2 Surface Area Base on Limited, Exponential and Type I Extreme Value Distribution Functions

Specimen No	Test Period (h)	Limiting Pit Depth (mm)	Max Pit Depth Having 10^{-6} Prob from Exponential Dist (mm)	Max Pit Depth Having 10^{-6} Prob from Extreme Value Analysis (mm)
1	1218	1.72	1.26	1.51
2	1218	1.20	1.48	1.45
3	1314	1.42	1.95	1.84
4	1314	1.72	1.70	1.78
1	3240	2.0	2.52	3.25
2	3240	2.0	2.14	2.30
3	3240	2.5	2.68	2.77
4	3240	2.1	2.07	2.26

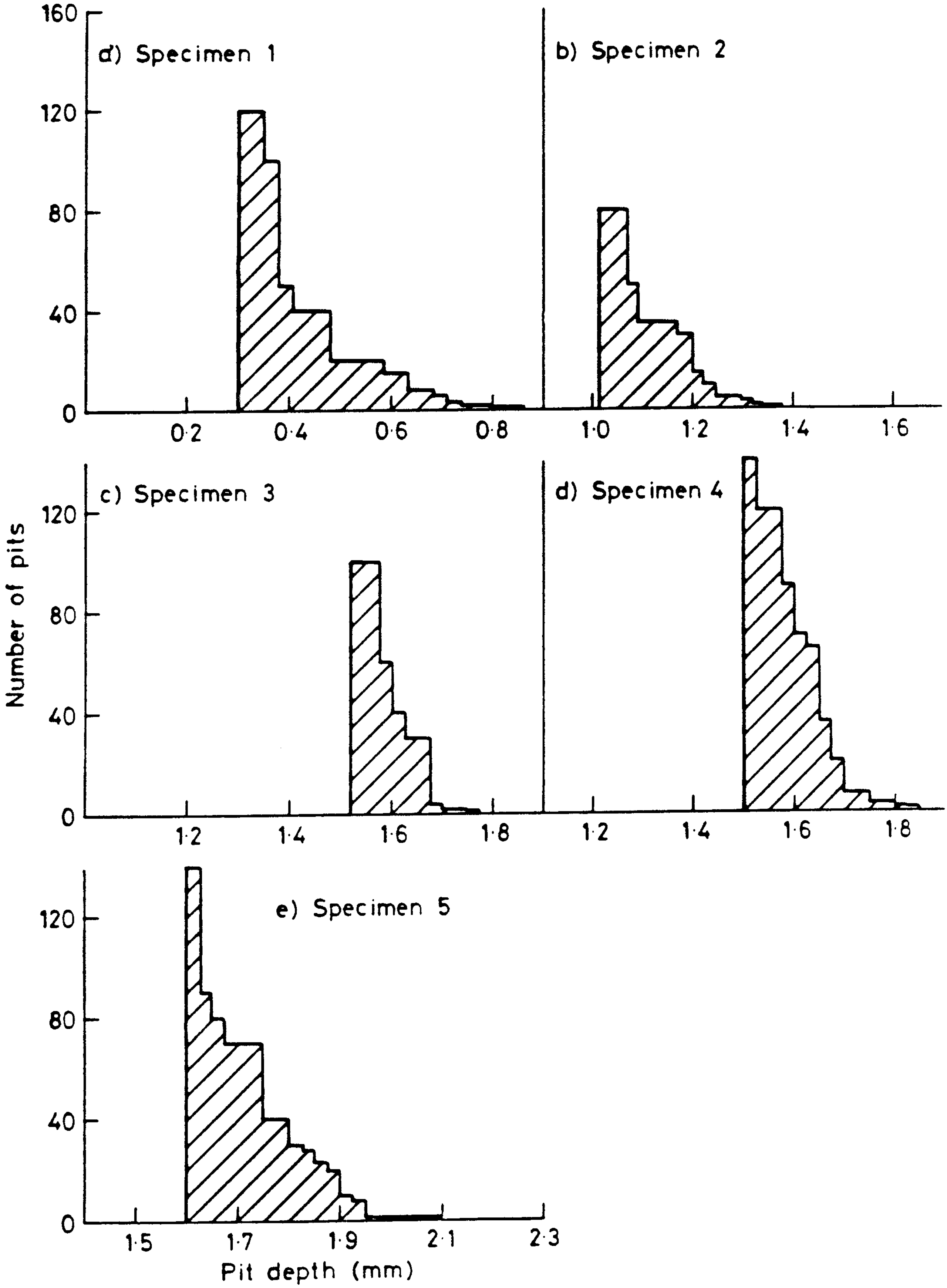

FIG. 1. HISTOGRAMS SHOWING THE PIT DEPTH DISTRIBUTIONS MEASURED IN SMALL SPECIMENS OF BS 4360 STEEL AFTER 3096h IN 1M Na_2CO_3 + 1000ppm Cl^- AT −200mV AND 90°C.

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