

# New Insights into Chemical-Physical Processes from Analysis of Observational Data using Extreme-Value Probability Distributions

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**ABSTRACT:** Conventional extreme value (EV) theory has the Gumbel EV distribution as the theoretically correct distribution to represent the maximum depth of corrosion pits. It has long been used for prediction of the probability of leaks or major content losses in oil and gas and other pipelines subject to internal or external corrosion or both. This history is based largely on limited numbers of data, often laboratory data. Recent availability of very extensive field data, gathered in real-life long-term applications such as 'intelligent' pigging of pipelines shows much more complex statistics, not easily reconciled with classical theory. The paper shows that, properly interpreted, these data can be interpreted as consistent with the development of pit depth as a function changing of exposure period. Together with improved understanding of the interaction between physical-chemical processes and pit depth statistics the data also show that that pitting corrosion develops in a renewal process. This is not generally recognized in the corrosion literature and may account for the sometimes very large statistical uncertainty. Examples drawn from actual pipeline pigging data and from other sources are used to illustrate these points and to indicate the importance of understanding the physical phenomena for the practical prediction of the probability of exceedance. Some recent new developments for interpreting pit depth experimental data also are presented, indicating that the use of probability theory can have wider implications.

## 1. INTRODUCTION

This paper has its origins in the prediction of the probability of corrosion causing failure of pressure pipelines. This is an important issue for the safety and continued operation of offshore oil, gas and water injection pipelines and also for containment systems such as tanks and for shipping. The main problem is known to be pitting corrosion, responsible for leaks from a pipeline or other system. Pitting also may be the instigator of pipe bursts. Both aspects are considered further below.

The next section reviews, briefly, some aspects about the pipelines used in the offshore oil and gas industry and the manner in which corrosion can cause failure. Typically failure is associated with the deepest pits. This implies a degree of uncertainty. The conventional way in which the depth of the deepest pit(s) is considered in the framework of structural

reliability theory is then reviewed briefly. The approach can be simplified considerably for extreme events such as the deepest of deep pits using Extreme Value theory (EVT). This has been the classical choice for the pipeline industry and remains the technique of choice for the oil and gas industry for risk assessment. There is a long history for its use. However, most of that history is based on relatively small data sets. The modern availability of large data sets for pit depths reveals some unexpected characteristics when that data are analysed using EVT. These characteristics are explored using an example data set derived from observations for an actual pipeline. The data show that there are multiple trends, not just one as predicted by classical EVT and this then leads to how such data should be interpreted. This has both practical and theoretical implications. These are considered. Apart from the multiple trends, close examination of the data shows that the trends are composed of

repetitive smaller probability distributions. These have been interpreted recently to represent a repetition in the pitting process. This indicates that the pitting process is more complex than a simple monotonic development of maximum pit depth. In turn, this indicates that the development of maximum pit depth tend to develop in steps with on-going exposure with time. Other recent observations support this interpretation. These observations and interpretations represent a major departure from the conventional wisdom about pit depth development.

The final part of the paper considers electrochemical experimental observations of the pitting process. A recent review of such experiments shows that when interpreted on EV plots these also show non-monotonic behaviour. From this it is possible to conclude that even very early pitting occurs in steps - a possibility not previously evident in the corrosion literature. It is currently being explored in a new experimental test program. Importantly, this development would not have occurred without the connection between probability distributions for maximum pit depths and the complexity of the trends on probability (e.g. EV) plots. In other words, the application of probability theory to an otherwise pedestrian problem has thrown new light on the physico-chemical behaviour of corrosion pits.

## 2. BACKGROUND - OFFSHORE PIPELINES

The exterior surfaces of offshore oil, gas and water-injection pipelines typically have protective coatings and often also external cathodic protection. However, the interior surfaces of such pipelines typically are left bare since protective coatings seldom are feasible or economic. This is because the fluids conveyed by these types of pipelines often contain particulate matter (sand, rust products), may be aggressive chemically and invariably operate under high water pressures (e.g. 200 bar) and at relatively high velocities (e.g. 1-5 m/s).

The main materials for offshore pipelines are mild and high strength low alloy (HSLA) steels even though they have a limited life.

Common practice is to abandon older dis-functional pipelines and leave them on the sea floor. For example, some 30,000 km of abandoned pipelines, plus many abandoned wellheads, are estimated in the Gulf of Mexico alone (Giltz, 2022). There is increased concern about environmental impacts (USGAO, 2021; Seo 2022) and it follows that accurate estimates of pipeline reliability and remaining service life are of increasing importance.

Corrosion resistant steels are seldom used since both fundamental corrosion science and practical experience show that they do not offer significantly extra durability in seawater conditions and therefore tend not to be economic.

Since pipelines essentially are containment systems, failure through pipe-wall perforation by corrosion pitting is of most practical interest. Pitting is, as noted, very localized loss of steel by corrosion, often progressing at a rather rapid rate (perhaps approaching 0.5 mm/year in warmer seawaters). Pitting on the interior wall of pipelines often originates under interior deposits (Comanescu *et al.* 2016). For the exterior, pitting may originate at spots of localized lack or failure of protective coatings (Figure 1).



Figure 1: Local failures of protective coating.

Collections of pits over small areas may cause enough metal loss to set up high localized stresses under the high internal pressures usual in most pipelines. The result can be pipe-wall rupture (Mokhtari & Melchers, 2020) (Figure 2).

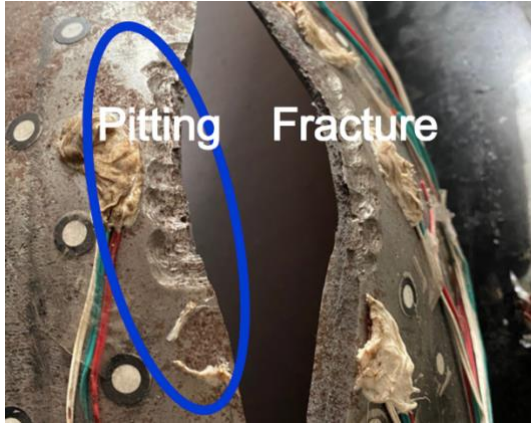


Figure 2: Rupture of high pressure pipeline initiated by localized exterior corrosion pitting.

In both cases the depth of the deepest pits are of interest. For many years already it has been conventional to treat the depth of pitting as a random variable, and specifically as one best described by an Extreme Value distribution. This may be used in a structural reliability formulation or be used independently. The background for the choice, based on practical aspects, is considered below.

### 3. STRUCTURAL RELIABILITY

Application of structural reliability theory requires knowledge of probability distributions for loadings and for structural strengths. For cases involving corrosion it also information about longer-term deterioration processes such as pitting corrosion. Very little such information is available. Most research is based on short-term, mainly laboratory testing, often electrochemical in nature and difficult to translate to field expectations and focussed mainly on corrosion resistant alloys such as stainless steels. An important exception is the 16 year field testing program carried out in the Panama Canal zone following WW2 concerns after concerns by the US military about the apparently high rate of corrosion of materiel in the south Pacific (Schumacher 1979). The data so obtained, and various other field data from a variety of sources has provided the basis for improved mean-value models of the progression of corrosion (average penetration, pit depths). There also is now some

field data for statistical uncertainty but only for a few years of exposure and based on relatively modest sample sizes (Melchers 2004, 2018).

The traditional approach to modelling pit depth uncertainty is through the use of the Gumbel Extreme Value (EV) distribution. This is also the approach used in the offshore pipeline industry for directly predicting the likelihood of future pipeline failures, using, entirely empirically, the extensive pitting data now available from the modern use of so-called 'intelligent' pigging'. This involves running a set of sensors through the pipeline in an operation known as 'pigging', with the sensors picking up variations in pipe-wall thickness. These so-called 'features' can then be translated into estimates of pit depth, both for internal and for internal pits. The uncertainty in pit depth estimates associated these processes are relatively small compared to the depths of pits after several years of operations (Comansecu et al. 2016).

### 4. EXTREME VALUE THEORY - REVIEW

For the probability of failure by corrosion pitting from the inside of the pipe-wall outwards, and for similar cases of plate perforation the conventional structural reliability problem can be much simplified. The event of most interest is that at time  $t$  the depth of the deepest pit ( $d_{max}(t)$ ) that occurs in the area of interest exceeds the local wall thickness  $D$ , or in limit state terminology:

$$G(X, t) = R(t) - Q(t) < 0 = [D - d_{max}(t)] < 0 \quad (1)$$

where  $G()$  represents the limit state function with parameters  $X$ , at time  $t$  and  $R$  and  $Q$  are the generic resistance and loading random variables. In the case of corrosion pitting the uncertainty in pit depth  $d_{max}$  far exceeds that of the variability of the pipe wall thickness  $D$  and thus  $D$  may be treated as a constant. This means that the probability of limit state violation becomes simply the probability of the maximum pit depth anywhere along the pipeline is greater than the thickness of the pipe-wall. Since the maximum depth of the deepest pits anywhere along the

pipeline (or on a plate) is required, the formulation becomes essentially an exceedence problem (Melchers 1998), one that can be handled by classical extreme value theory (Galambos 1987) and for which the calculation procedures are well-established.

The theoretically correct EV distribution for the maxima of maximum values (i.e. the extreme of the largest) is the so-called Gumbel EV distribution (Galambos 1987). It was derived directly from asymptotic arguments. Its application to corrosion pit depth values has been termed the 'arch-typical' application (Galambos 1987). While other probability distributions, such as the other EV distributions like Frechet, Weibull and Generalized Extreme Value distributions and also asymptotic distributions such as Lognormal have been applied to maximum pit depth data (Coles 2001), none has the authority of the Gumbel distribution. Their application, usually justified as providing a 'better fit' to the available data, only can be empirical, and thus without theoretical foundation. As will be shown below, there are important reasons why in some applications much better understanding of the underlying characteristics of the variable being considered is necessary before application of a Gumbel EV distribution. In simple terms, for any distribution, Gumbel included, to be valid, the population from which the data are drawn must be 'homogeneous' and data obtained for independent observations, even if only asymptotically independent (Leadbetter et al. 1983). To judge these requirements, sound understanding of the characteristics of the problem is required - empiricism is not enough.

In theory, if a set of data is Gumbel distributed, the data points will form a straight, sloping, line on a so-called Gumbel plot. Such a plot is like a Normal probability plot except with the vertical axis that shows cumulative probability distorted to the Gumbel cumulative probability (Figure 3). For each value  $y_i$  of pit depth in the data set the cumulative probability can be obtained in a number of different ways

(Galambos 1987). The simplest is the 'rank-order' procedure in which the values  $y_i$  in the random variable vector  $Y$  of pit depths are sorted in ascending order. They are then assigned an unbiased estimator of cumulative probability  $P_i(Y < y_i)$  that starts from  $1/(n + 1)$  and increases by this amount with each increasing value of  $y$  such that:

$$F_Y(y_i) = P_i(Y < y_i) = \frac{i}{(n+1)} \quad i = 1, \dots, n \quad (2)$$

The  $y_i$  values for pit depth are plotted along the horizontal axis against the corresponding cumulative probability  $P_i$  on the vertical axis. Usually the corresponding standard Gumbel variable  $w$  is used on the alternative vertical axis, with  $w$  defined as follows:

$$w_i = (y_i - u)\alpha \quad (3)$$

where  $u$  is the defined as the mode and  $\alpha$  as the slope, related to the mean and the standard deviation of the Gumbel distribution as (Galambos 1987):

$$\mu_Y = u + 1.1396/\alpha \quad (4)$$

$$\sigma_Y = 0.40825 \pi/\alpha \quad (5)$$

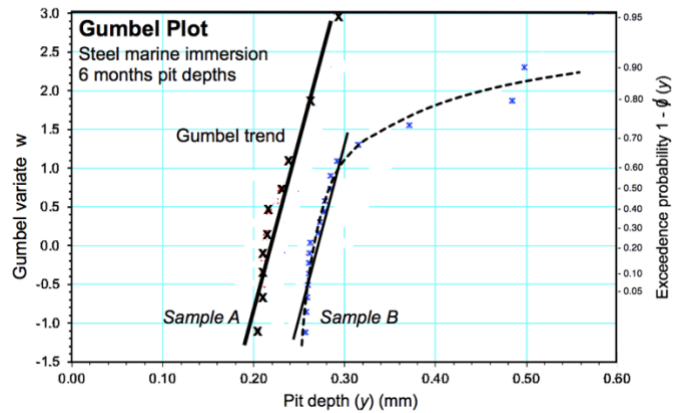


Figure 3: Pit depth data for steel plates immersed in near-quiescent seawater (Melchers et al. 2010) showing near perfect Gumbel trend for Sample A and departure from Gumbel trend for Sample B, both exposed at the same time for 6 months at the same location.

The data set for Sample A in Figure 1 is sparse. This has been the typical case in most historical applications of the Gumbel EV distribution, as illustrated for example in the classical plots of pit depth by Aziz (1956) and also more recently in reviews and specially collected data (Melchers 2018). For these it was reasonable to infer straight-line plots (Gumbel lines) through the data. However, as shown in Figure 3 by the pit depth data for Sample B, this is not always the case. A simple linear Gumbel plot would not be appropriate for this data set.

The possibility that simple linear fitting may not always be correct can be seen already in the data plotted on Gumbel plots as reported by Provan and Rodriguez (1989). These plots were for pit depth data for different periods of exposures of stainless steel rollers used in the aggressive waters ('white water') used in for papermaking. Largely ignored until recently, the non-linear Provan and Rodriguez Gumbel plots were recently associated with the change in pitting behaviour as pit depth progresses (Melchers 2021a) - in other words, the population of pit depth values changed as pitting progressed. However, apart from very early pitting over a few hours or days (meta-stable pitting) such change in pitting behaviour has not been recognized in the conventional corrosion literature. As can be seen by Sample B in Figure 3, non-ideal Gumbel trending is not a unique situation. This departure from Ideal Gumbel behaviour forms the basis of the discussion that follows, using the extensive data sometimes available for the pitting corrosion of offshore oil, gas and water injection pipelines.

## 5. EXAMPLE

The modern pipeline industry relies increasingly for asset management and risk assessment on the data extracted from intelligent pigging operations inside pipeline (Uzelac 2015). Pigging is an expensive and somewhat disruptive operation but provides voluminous observations of 'features' that can be interpreted as pit depths (Comanescu et al. 2016). In practice these features often occur as relatively short grooves along the pipeline,

This suggests the depth associated with them is likely correlated. However, by considering only values of maximum pit depth as measured within, say, each 10 or 25 m length of pipe, the values obtained can be considered independent random samples from the underlying population, relying on the accepted notion of asymptotic independence (see above) (Leadbetter et al. 1983). Moreover, the population of pit depths can be considered homogeneous owing to the essentially same fluid affecting very similar steel all along the pipeline. The features themselves are, like corrosion pits, much dependent on initiation at microscopic alloy inclusions and material imperfections, and these tend to be more frequent along welds (longitudinal welds, hoop welds). Again, these usually are considered to occur randomly within the pipeline and randomly on the steel surfaces.

An example of a Gumbel plot obtained from pigging data for a water injection pipeline in the North Sea is shown in Figure 4 for maximum pit depth extracted for each 25 m length of the 15 km long pipeline. Water injection pipelines are used to pump water (fresh water, aquifer water, seawater or water extracted from produced oil or gas) at high pressure into wells that are nearing depletion to extract more product. They are known to be prone to extensive pitting corrosion both along the bottom of the pipeline and at welds (Comanescu et al. 2016).

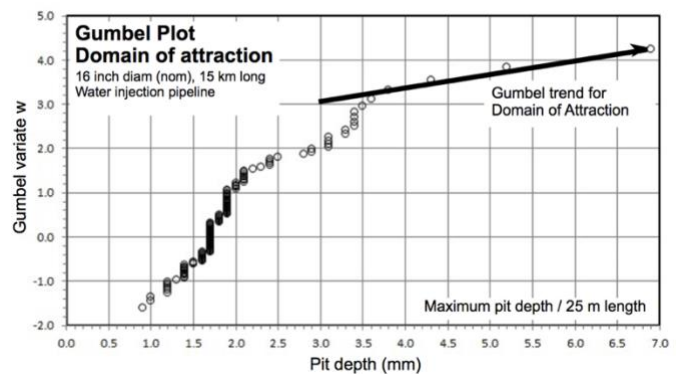


Figure 4: Pit depth data extracted from intelligent pigging operation on a water injection pipeline in the North Sea showing extreme pit depths and the most suitable Gumbel trend for that subset of data.

It is clear that the pit depth data trend in a distinctly non-linear and irregular fashion. It is obvious that it is difficult to fit a straight line closely through all the data, as would be required on the Gumbel plot to justify a Gumbel distribution. The fitting of other continuous, monotonic probability distributions including other EV distributions and skewed distributions such as the lognormal, would have a similar difficulty, noting that there are mathematical relationships between the extreme value distributions (Castillo et al. 1989). Since the extreme pit depths are of most practical interest, the approach usually taken in the offshore oil and gas industry is to focus only on the deepest pits (Larsen 2013). This means, in essence, only the trending for the very deepest pits, that is, those to the upper right in Figure 4. The others are ignored. This concept is sometimes referred to as the finding the 'domain of attraction' for the tail of the distribution, for the deepest pits. Its use immediately permits extrapolation to deeper pit depths with associated probabilities of exceedence than those in the data set. It also would permit a first estimate of the likely increase in pit depth for the extreme pits using linear extrapolation in time. As shown elsewhere (Larsen 2013), linear extrapolation in time of maximum pit depths likely sufficiently accurate for practical purposes. More accurate extrapolation also is available.

Not usually of interest to the offshore oil and gas pipeline industry is what interpretation to give to the rest of the data for less extreme. These data are those in the lower left portion of Figure 4. It is clear that the data may be divided into several cohorts, each with its own linear trend. Since the data are plotted on a Gumbel plot, these linear trends can be interpreted as piece-wise Gumbel trends (Figure 5). The uncertainty in the data reflected in the slopes of the Gumbel trends can be associated with a specific part of the bimodal model (Figure 5 inset). That model represents the overall progression of corrosion and also of pit depth

with time (Melchers 2004, Melchers and Jeffrey 2022). Earlier it was shown, through matching of pit depths between those in the bimodal pit depth development trends and those in corresponding Gumbel plots, that such association exists. It can be expected also for the data in Figure 3, given that other sets of date for pitting of water injection pipelines have shown the validity of the bimodal for pit depth development (Commenescu et al. 2016). The relationships are shown, schematically, see inset in Figure 5.

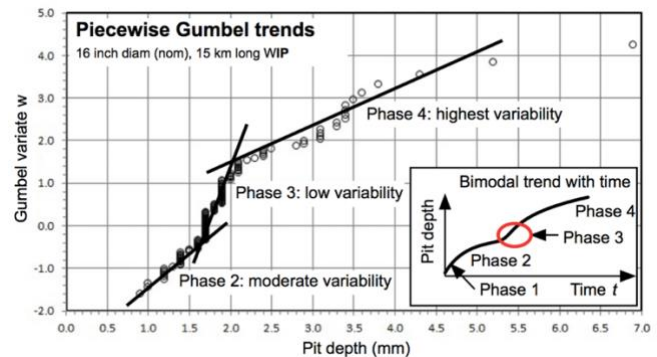


Figure 5: Pit depth data as in Figure 4 showing different Gumbel trends and relationship to Bimodal model for pit depth as a function of exposure time.

The overall trending in the data demonstrates that the pit depths selected as the extremes for each of the pipeline lengths for which the deepest pit was selected to be included in the data cohort, are themselves only extremes in a relative sense, since the data clearly shows that for some lengths of pipe, pit depths have developed much less than for other lengths of pipe. It is clear that there is a large range of pit depths, even within the one pipeline and after a defined, known, period of exposure. Figure 5 also shows, through its irregularity and thus the piecewise Gumbel trends, that there are several probability distributions 'active' at the same time for pit depths. It follows that a single probability distribution is insufficient to describe the variability in pit depth. As evident from the interpretation of the partial trends in Figure 5, there are several probability distributions involved, each with its own underlying population and its with its own variability.

The above example of a water injection pipeline and the observed multiple trend lines has parallels for production pipelines for oil and for gas (Melchers 2023). These parallel scenarios that have been identified for the external corrosion of cast iron pipes buried in soils (Asadi and Melchers 2017). Moreover, there are parallel observations, much earlier that wind velocities generated by windstorms or thunderstorms have their own probability distribution (Gomes and Vickery 1976). These data show an overall plot that, on Gumbel paper, has a 'kink' similar to the several 'kinks' in the data trends in Figure 5. In practical terms it means that while some parts of a pipeline may be close to perforation, other parts may still have significant reserve capacity.

The data in Figure 4 also can be interpreted in a different way. This is shown in Figure 6, that has the same data points as Figure 4. Close observation shows that there is an apparent waviness in each of the trends in the data and that this repeats in a similar pattern at regular intervals in pit depth. These intervals are defined in Figure 6 by short vertical lines. For each such short cohort of pit depth values there are a (small) number of very similar pit depth values (each with its own cumulative probability value, or Gumbel variate value) and one or two slightly larger pit depths followed by another group of very similar pit depth values, etc. Thus at any time a considerable number of very similar values of maximum pit depth are present, on the metal surface, at different depths of pitting, with very few pit depths between these steps. In the present data set the steps in the pit depths are about 0.38 mm for pits deeper than about 2.0 mm and about 0.25 mm for shallower pit depths. In both cases the degree of uncertainty in these estimates of pit depth step is small, about  $\pm 0.02$  mm.

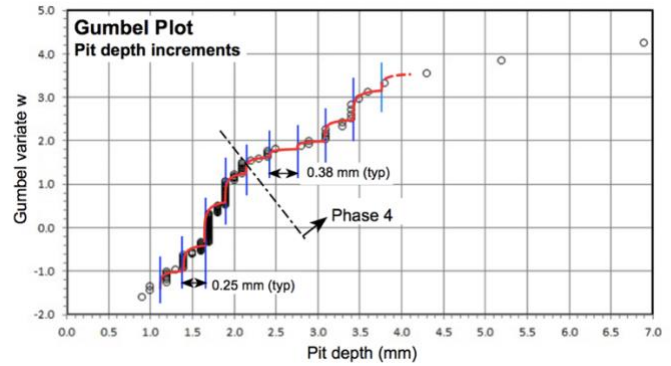


Figure 6: Pit depth data as in Figure 4 showing interpretation as steps in pit depth (at a given period of exposure).

## 6. PRACTICAL AND THEORETICAL IMPLICATIONS

Comparing the observations in Figure 6 with the phases in the bimodal model (Figure 5 inset) the change from smaller steps in pit depth to larger steps appears to occur at about the change from phase 3 to phase 4. In view of the observations for Figure 5 that the piecewise Gumbel plots indicate changes in underlying population, the change in pit depth steps indicates immediately that the associated change in pit depth population is responsible also for this change. The present example adds to similar cases observed only quite recently of similar step-wise pitting behaviour (Chaves and Melchers 2011; Asadi and Melchers 2018, Liang et al, 2018 Petersen and Melchers 2019; Petersen and Melchers 2023). In each of these cases Gumbel patterns similar to that in Figure 6 were observed, even though they were concerned essentially only with attempting to predict the expected probability of an extreme pit depth occurring and to do so using EV theory in a justifiable way. However, the interpretations presented above are more recent (Melchers 2021b).

Importantly, the Gumbel EV patterns seen in the recent analyses noted above and in Figures 4-6 were all obtained in the context of very large data sets. Sparse data sets, as traditionally available (cf. Figure 3) and at one time considered sufficient for practical extrapolation, do not have the discrimination to show the various trends revealed by modern analysis as in

Figures 4-6. From a scientific point of view the repeated occurrence of trends, as exemplified in Figures 4-6, indicates that understanding of the development of pitting corrosion, and the mechanisms involved, remains incomplete. These matters are presently under investigation, noting that the concept of renewal of pitting had been observed earlier, but not investigated, for deeper pitting (Jeffrey and Melchers 2007) and also for initiation of pitting but without considering pit depth progression (cf. Sander et al., 2020). However, the recent and the present results, revealed through the use of probabilistic notions, show that this potentially is an important matter for further investigation in corrosion science.

In terms of practical applications, the observations given above have other important implications. Since they show that the physical-chemical processes involved in pitting corrosion develop with increased exposure period it follows that longer term pitting corrosion behaviour cannot be extracted or predicted (accurately and reasonably easily) from short-term field or laboratory experiments. This lack of a clear link between short-term results and long-term behaviour has been noted earlier (cf. Melchers 2018). It is now further supported by the greater degree of detail represented in Figures 4-6 and similar recent observations.

The above comments do not address the occurrence of the 2-3 very deep pit depths at centre-right of the Gumbel plots (Figures 4-6). They are important for practical prediction as indicated by the long-term trend in Figure 4. They are of prime interest for reliability estimates. However, why these very deep pits occur is an important practical issue, at present not well understood. Also, how they might relate to the steps pit depth in Figure 6 is still unclear. Suggestions for the occurrence of such extremely deep pits include that they were initiated very early, much earlier than other pits, owing to the presence of very localized, perhaps unnoticed, surface deposits or imperfections (Pistorius and Burstein 1992, Jones 1996) or larger than typical

inclusions or alloying elements (Eklund 1974, Wranglen 1974). Evidently, they have always been involved in the physical-chemical processes. However, their extreme nature and their relationship to other pit depth values as typically observed in practice has now been brought out by the use of Extreme Value analysis, that is, by application of probabilistic methods.

## 7. FURTHER DEVELOPMENTS

Gumbel plots have been used also in a somewhat different but related context. They have been used to represent the 'transition potential'  $E$  that is used in classical electrochemical investigations to define the transition from meta- to stable pitting, where 'meta-' refers to extremely shallow pits (around 3-8 microns deep) and 'stable-' to the deeper pits conventionally observed. An example of this is shown in Figure 7 for one particular alloy (steel), but it has been shown for many others also, including stainless steels and aluminium. As shown, some of these Gumbel plots have sufficient data and detail to make the interpretation that the data in the plots show step-wise groupings of transition potential (Figure 7) (Pistorius and Burstein 1992, Gupta et al. 2012).

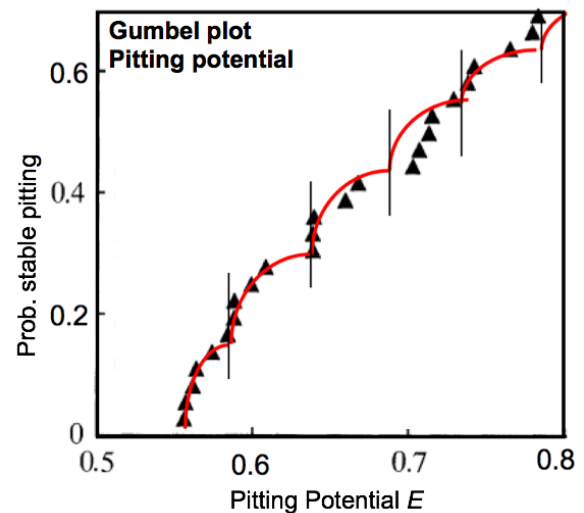


Figure 7: Gumbel plot - interpreted trending for transition potential  $E$ .



None of the various researchers who used Gumbel plots for their data noted the appearance of these steps. Neither has the subsequent literature and the reasons for the occurrence of the steps in  $E$  (Figure 7) remain unclear. The immediate research question is whether and how these steps in  $E$  relate to the step-wise behaviour of maximum pit depths for overall pitting as a function of exposure period (Figure 6). In other words, is there step-wise behaviour also for the very shallow meta-stable pitting process and how might this relate to the step-wise behaviour in longer term, deeper, stable pitting? This is a fundamental research question - again arising entirely from using probability theory to interpret trends in data.

## 8. CONCLUSION

The present paper has focussed on the use of the Gumbel extreme value distribution as the ideal theoretical model to represent the maximum of local maxima and the features such application can display about the underlying population. The development of theoretically sound probability distributions is essential for accurate system reliability analysis, such as increasingly applied for offshore oil, gas and water injection pipelines. Herein the depth of corrosion pits in those types of pipelines was considered but other examples have been provided recently elsewhere. It is demonstrated that at any period of exposure (a) data trends are not always even closely linear on Gumbel extreme value plots as commonly assumed, (b) may consist of multiple trends, each representing a different underlying statistical population and (c) tend to show what can be interpreted as clusters of similar pit depths with similar pit depth steps between the clusters. Such behaviour appears not to have been anticipated in the conventional corrosion literature. The application of extreme value analysis in this case, while following much earlier work that had available only sparse data sets, has shown that the modern availability of extensive data sets, together with probability based interpretations, can provide new impetus for exploration of the physico-chemical process involved.

## 9. ACKNOWLEDGMENTS

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