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Pitting corrosion evaluation: a review

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Pitting corrosion evaluation: a review

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Abstract:

Pitting corrosion is an insidious localized form of corrosion causing much devastating destruction to structural members such as stainless steel in chloride environment. This paper gives a review of the mechanism processes of pitting, stages, factors facilitating pitting corrosion, techniques of evaluating pitting corrosion and some research work on pitting corrosion. The rudimentary knowledge of the mechanisms of pitting corrosion from this work will be of assistance to the selection process, specification and the use of stainless steels and other structural members.

Keyword: Corrosion, pitting, repassivation, pitting potential, steel

1. Introduction

The most destructive form of corrosion among others is pitting. It is insidious and devastating than general corrosion because it occurs in small areas (pit) having much difficulties to be detected with great effect on structural integrity [1]. It is a form of localized metallic surface degradation positioned at small area in the order of cavities [2]. This localized degradation occurs on small metal surface which preferentially corrodes forming holes or cavities (pits) while bulk surface of the material not being unattacked. Pitting corrosion is considered, among others, as the main degradation mechanisms for most metals exposed to corrosion environment. This mechanism in stress corrosion cracking results into crack initiation, growth and failure [3]. Cracks, flaws, breakages, and scratches on the passive film of the metal alloy enhance the growth of the pit [4-5]. Aluminum, steel and other metals which can form passive films are more prone to pitting corrosion. Failure is caused by small percent weight-loss penetration of the whole structures. The breakdown of passivity is the main cause of pitting. It thus takes effect when surface films breakdown off metals when subjected to pitting environment [2]. Some metals and alloys have sites which are preferentially susceptible to pitting corrosion formation. These sites act as the anode while the remaining bulk mass of the alloy is the cathode. The pitting action is autocatalytic in nature, thus, penetrating the alloy insidiously. Microstructural heterogeneity effect leads to electrochemical heterogeneous behavior which enhanced corrosion susceptibility of the material [5]. The metallurgical characteristic and composition of the metal alloy, external factors like the environmental chemical composition (concentration of the electrolyte) and the pH, and other electrochemical factors affect the rate and nature of the pits. The solution pH within a pit always differs from the bulk solution with range values of 3 below as a result of metallic ions hydrolysis. This is caused by the increase in H⁺ ion act which thus decreased the acidity in-between the artificial and natural pit.

The environment mostly susceptible for pitting corrosion among others is marine environment where ions like chloride, bromide and iodide exist. At high concentrations, these ion lead to pitting of steel, aluminium, and other passive metal alloy [6]. Steel pitting can also be induced by thiosulfate ions. Pitting can be initiated by dust or dirt particles in copper pipes carrying seawater. Copper pitting occurs in the hottest part with soft water and in the coldest part with hard water of water system. Pitting is not easily detected because of its microscopic nature (at the surface pit may



be small, but appears large below the undercut surface and are covered with film or deposit). Through perforation, equipment fails by pitting actions with very little effect of weight loss. There is difficulty in measuring pit because its depth and distribution varies greatly under similar conditions. The “incubation period” of pits may be months or years. Incubation period is the total time required for a structure to go through crack nucleation to the time the crack progresses to a critical degree, which eventually ends in catastrophic failure. Induced corrosion pits can serve as concentrators of stress where cracks could be established [7]. The determinants of the rate of pit growth once it is formed are mainly the type of material, the state of the stress and local solution conditions. The use of inorganic-based inhibitors enhances the mitigation of stainless steel pitting in aggressive medium [8].

2. Economic cost of pitting corrosion

The consequence of corrosion action is a global concern. Corrosion tends to jeopardize safety and retard technological advancement. Corrosion gives negative useful service effect on lives of properties, corrosion cost incurred from manufacturers and distributors of products and services also passes cost onto the consumers. Corrosion effect can be experienced on body panel of automobile, outdoor furniture, charcoal grills, and metal tools. Some of the economic effects of corrosion are: replacement of degraded equipment and structures, overdesign of structures corrosion allowance, waste of valuable resources, shut down of equipment due to corrosion failure, product contamination, reduction and loss of efficiency and valuable products and resources, costly maintenance. The world total corrosion cost is approximately billion dollars per year. This involves the cost of material lost and cost for preventing corrosion [6]. The 1978 study of the economics of metallic corrosion effects in United States shows that the U.S. had had about \$300billion lost to corrosion annually [9].

Table 1 Corrosion costs in the U.S (Source: BCL and NIST, 1978)

| Industry | Billions of U.S. dollars | |
|-------------------------|--------------------------|-------|
| | 1975 | 1995 |
| Industries | | |
| Total | 82.0 | 296.0 |
| Avoidable | 33.0 | 104.0 |
| Motor vehicles | | |
| Total | 31.4 | 94.0 |
| Avoidable | 23.1 | 65.0 |
| Aircraft | | |
| Total | 3.0 | 13.0 |
| Avoidable | 0.6 | 3.0 |
| Other industries | | |
| Total | 47.6 | 189.0 |
| Avoidable | 9.3 | 36.0 |

The devastating action of pitting corrosion gotten from NTSB and FAA web-sites shows that out of the 91 corrosion incidents and accidents, seven were induced by pitting corrosion. Though the short coming of the report of NTSB and FAA incidents and accidents is the inability to give proper report of the real cause of the recorded failures and, he, does hence not showed up in database. Three Embraer 120 incidents which involved propeller blades, Aero Commander 680 lower spar cap, and F-18 trailing edge flap failure where also recorded to be due to pitting corrosion.

Considering this information, it was concluded that destruction due to corrosion is a great safety concern in sustaining aircraft structural integrity. This thus makes the accidents caused by corrosion like pitting, a threat to aircraft safety. The U.S corrosion cost and preventive strategies reported that corrosion eats about \$552 billion infrastructure annually (6% of GDP). A natural gas pipeline, in 1965, got explodes in Louisiana due to pitting corrosion. This led to loss of lives of about 17 people together with 9 children, and properties. Gas condensate leakage from Piper Alpha was experienced in July 1988 resulting to severe explosion. This incidence claimed about 167 lives and much of properties destroyed [10].

The report from the National Bridge Inventory Database shows that out of 586000 United States bridges, about 15% of the bridges is structurally inadequate, mainly as a result of steel and steel reinforcement corrosion. \$8.3 billion cost of highway bridges were reported for direct cost of corrosion annually, which include \$3.8 billion annual cost for structural replacement of deficient bridges, maintenance of \$2.0 billion and concrete bridge decks cost, and \$0.5 billion maintenance cost for painting the steel bridges. It is shown that the main reason for the degradation of reinforced-concrete bridge was induced by chloride corrosion which leads to the expansion of forces in the concrete creating cracks and spall of the concrete. The chloride is gotten either through exposure to marine or deicing salts for snow and ice removal. The exposure of steel bridges to atmospheric condition causes corrosion. This is being driven by exposure of marine (salt spray) and industrial activities

The main restricting factor to gas and liquid transmission service life of pipelines is determined by pitting corrosion [11]. The average cost of corrosion-related issues is evaluated to be \$7.0 billion which makes up 38% of the cost of capital, 52% of operation and maintenance cost, and 10% failures cost. The integrity of pipelines will be reduced, if corrosion is permitted to continue without being checked. Based on the size of flaw, the pipeline material properties, and the pressure either a leak may be formed or rupture occur. High-pressure natural gas pipeline rupture may lead to the release of sufficient stored energy which can get the pipeline explore out of the ground. \$471 to \$875 million per annum of direct cost of related corrosion accidents is evaluated for gas and liquid pipelines.

3. Mechanism of pitting corrosion

The main reactive pitting mechanism exists in aggressive anionic species which is mostly caused by chloride ions. The aggressiveness of pitting varies with the logarithm of the bulk chloride concentration. Chloride ion, anion of strong acid, tends to pose high level of solubility to metallic cations. This interferes with passivation of the metallic structure. This is because chloride ions have relative small anion with a high diffusivity. The pitting action on structures can be promoted by the availability of oxidizing agents in chloride environment [12]. Most of the oxidants promote the probability of the occurrence of pitting corrosion by supplying additional cathodic reactants, hence resulting to local potential increased. In general, the main oxidizing agent is dissolved oxygen [2].

Anode formation is a necessity for pitting formation. This results to local corrosion cell formation. The anode formation may be through the following:

- 1) Heterogeneity of the interface of the corrosive metal. This absence of uniformity on the surface of the metal contributes to the availability of grain boundaries, impurities, niches, rough surface, etc. Also, concentration cells can be formed due to environmental differences on the surface.

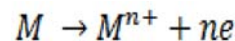
- 2) Passive film demolition: This leads to the formation of small anodes, which leads to many anode sites while the rest of surface serves as cathode. This leads to a disadvantageous area ratio.
- 3) Debris/solid deposition on the metal surface which results to the formation of anodic and Cathodic sites.
- 4) Active passive cell formation which is accompanied by high potential difference by forming small anode on the passive surface [6] .

3.1 Conditions for pitting action

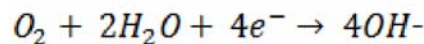
Passive metal around the anode is doesn't promote pitting because of the cathode formed. It serves as oxygen reduction sites. The corrosion products produced at the anode does not spread the cathode. This corrosion rather penetrates the metal instead of spreading thereby initiating pitting. A specific characteristic potential of the passive metal exist beyond which pitting can be initiated. This potential is called pitting potential (E_p). Pitting potential is the most determining factor to the existence of pitting. E_p is the least voltage or potential at which pits develop or grow on a metallic surface. The pitting potential is the potential below which pitting does not occur, but forms passivating film. The potential below which pitting does not propagate is termed passivation potential. Stable maintainability of the surface potential of the pitting product is essential for stable pit development [13].

4. Pitting processes

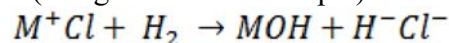
- 1) Anodic site formation is the first stage in pitting where the passive protective layer on the surface of the metal is destroyed. The destruction of the protective film may be done chemically or mechanically.



It is then balanced by reacting oxygen on the adjacent surface at the Cathode



- 2) The continuous dissolution of metal results to the accumulation of outrageous positive ions (M^+) at the anodic zone. This is a self-stimulating and self-propagating process. Neutralization of charges is sustained by the negative ions (anions), like the chloride which comes from the electrolyte (using seawater as sample).



The positive charges are also kept neutralized by the hydroxyl ions (OH^-) through hydrolysis process.

- 3) Repassivation is prevented by the presence of hydrogen ion and chloride content. This process produces free acid while the value of pH at the base of the pit is significantly decreased (1.5-1.0).
- 4) The rate of migration of chloride ion increases with dissolution rate at the anode. This makes the reaction to be time dependent and leading to the formation of more M^+Cl^- and the hydrolysis of H^+Cl^- .
- 5) These processes go on till the point of perforation of the metal. This is an autocatalytic process which advances with time leading to more metal dissolution.
- 6) The metal finally perforate thereby causes the termination of the process.

From the above processes, we have three main pitting processes which are Pitting Initiation, Pitting Propagation and Pitting Termination [6].

5. Forms of pitting Shapes

Pit with open (uncovered) or covered mouth can be formed by pitting corrosion via semipermeable membrane products [14]. Pits may also appear as cup-shaped or hemispherical shape. They are sometimes flat-walled, showing metallic crystal structure while some may be totally irregular in shape. Pit shapes are commonly classified into trough pits (upper) and sideways pits (lower) as shown in figure 1. The cavities of Pitting may be filled with corroded products forming caps over it and at times forming nodules or tubercles [15].

Trough Pits

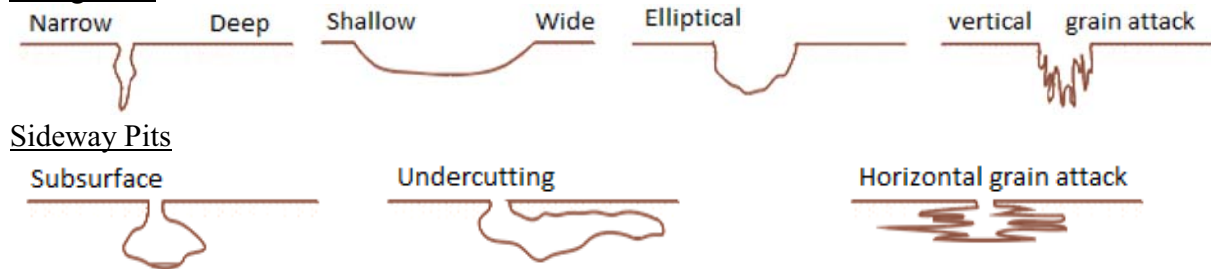


Figure 1. (Source: <https://www.nace.org/Pitting-Corrosion/>)

6. Stages of pitting corrosion propagation

The pit corrosion growth rate is measured by dissolution of metallic cations diffusion from the inner pit. This is independent on the electrode potential of the metals. The major pitting condition occurrence is an electrochemical potential shift in the direction of a more positive one than a certain critical value, considered as pitting potential [16-17]. There are three main stages in pitting corrosion: pitting nucleation or passive layer breakdown, metastable pitting, and steady-state pitting. The passive state is needed for the occurrence of pit.

(a) Passive film breakdown and Pit initiation: Mutual repulsion is formed when damaging ions are absorbed on the passive film surface thereby lowering the tension on the interfacial surface. The breaking of the passive film occurs when there is enough repulsive force [18-19]. The a phenomenon behind the passive film breakdown and its initiation details is not understood yet. Breakdown is an uncommon event that occurs on very minute scale, which caused difficulty in its detection [2], [18-20]. The site of passive film breakdown is where pit nucleation is initiated, hence susceptible to pitting corrosion. According to Caines [21], passive films exist on stainless steels surface in availability of oxygen. A genuine oxide layer at low temperatures does not form, but a thin passive film acting as barrier and thus providing corrosion resistance.

The initiation stage of pitting occurs within a very short interval. Pit initiation duration is as little as microseconds and it greatly relies on the nature of material surfaces. Surface defects as a result of manufacturing issues like installation challenges, procedure maintenance inadequacy and environment changes can influence the initiation of pits materials [21]. The parameters which contribute to pitting initiation and propagation include [15]:

- Localized chemical or mechanical damage to the protective oxide film
- Environmental parameters that can promote the breakdown of the film, such as low pH, elevated concentration of chloride, and less dissolved oxygen concentrations. These parameters have the capacity to destabilized the protective oxide film, hence initiating pits
- Inadequate protective coating application or protective damages
- Availability of irregularities the metallic structure of the component like non-metallic inclusions.

Pit initiation is classified into three mechanisms [12]:

- penetration
- adsorption and thinning
- breaking mechanisms of film.

A penetration mechanism for the initiation of pitting is concern with the aggressive movement of anions via the passive layer to the oxide interface where the promotion of aggravated dissolution occur [12]. The adsorption mechanism of pitting initiation is a function of the material's chloride and oxygen adsorption.

(b) Metastable: This is the stage of pitting corrosion that is formed and latter disappears due to passive film formed on the metallic alloy. It is only those pits which survive the metastable stage that turn into growing stable pits. Metastable pits are established on the brink of stability. The metastable pit occurs at much lower potentiostatic potentials that is highly less than the potentials of occurrence of the pitting corrosion itself. It is microscopic in nature and has short lifespan. Its low potentials described the ability of metals to resist the action of pitting. This is because lower potential of alloy repassivation corresponds to greater resistance of alloys to pitting. The passive film strength determines the ease at which a metal can resist pitting formation. Perforated cover is required for metastable growth over the pit mouth to promote extra barriers to diffusion. This keeps the aggressive pit anolyte stable. Research shows that the factors which aid the metastable pitting and its transition to stable pitting are the size and geometry of active impurities and the presence of fatigue stress [4].

(c) Stable pit: The breakdown of passive films and the initiations of pits certainly show that a stable pit will grow. Metastable pit precede the stable pitting. The termination of the passive film leads to the formation of stable growth of pit for ongoing propagation, while the pit depth serves as a diffusion barrier. Constant mean pit stability of products beyond the critical value characterized passive stability. If the film is prematurely lost prior to the attainment of critical pit stability of the product, the anolyte pit becomes diluted and repassivation occurring. The occurrence and disappearance of metastable pits is usually within some few seconds. The pit growth depends on the electrolytic composition and acidity (pH), composition of the alloy, and potential within the pit. The kinetic growth of pit is dependent on the electrolytic diffusion rate within the pit. Aggressive anion electrolytes, majorly the halogens, sulphates and sulphides often promote dissolution of anodic ions. The stability of the electrolyte at the critical concentration in the pit promotes the growth of the pit. These conditions at its lowest should be adequately aggressive to hinder repassivation. Pitting distribution current transients is dependent on electrode potential as against the rate of growth of the individual pits. Pit nucleation site, specifically its geometry, is accountable for potential distribution. More Shallow and open sites are activated only at both greater potential and current density, hence susceptible to attain stability.

7. Factor Affecting Pitting Corrosion

Environmental factors, pitting potential, metallic composition, temperature and the surface conditions, among others are the diverse parameters influencing pitting corrosion. Among these factors, environmental parameter is the most critical factor. The concentration of aggressive ion, pH, and inhibitor concentration are some of the environmental factors that affect pitting.

Alloy composition: Composition and microstructure greatly influence pitting tendency of alloys [22]. The pitting susceptibility of alloys can be mitigated by the introduction of some alloying elements. The passivation of stainless steel is enhanced by Chromium concentration. The resistance of Fe-Cr alloy to pitting can be promoted by increasing Ni concentration, which moderately stabilizes the austenitic phase. Mo in the presence of chromium inhibits the pitting

action of stainless steel. The addition of minute amount of nitrogen and tungsten can promote pitting resistance of stainless steel.

Temperature: Some materials may not pit below certain value of temperature, which could be very sharp and reproducible. Hence, temperature is considered as one of the major pitting factors. This can be influenced by altering temperature at constant range of fixed potentials, or altering the potential at constant range of temperature experiments. Greatly high breakdown potential is noticed at low temperatures which correspond to the transpassive dissolution rather than localized corrosion. Pitting corrosion is observed at a potential far below the transpassive breakdown potential just beyond the critical pitting temperature (CPT). The values of CPT are not dependent on parameters of the environment and applied potential over a wide range. This gives the estimate of the resistance to stable pit propagation. The pitting potential decreases with a corresponding increase in temperature and chloride concentration.

8. Techniques of evaluating pitting corrosion

Pitting Corrosion examination and evaluation can be ascertained with the ASTM G461 Standard Guide. The diverse means or ways of evaluating and quantifying the effects of pitting corrosion among others are point defect modeling, stochastic method, etc [23].

8.1 Point defect model (PDM)

This model supports point defect movement in association with electrical field. It interprets passive film's expanding behavior on metal surface. The PDM described passive films expansion/growth and breakdown formed on metal surface in a corrosive environment with respect to mass and charge flux through purpose defects across the semi-conductive, defective barrier layer of the passive film. The PDM states that "the dissolution of metal results from the flux cations to film/solution interface, deed metal vacancies or metal holes at the metal/film edge". This metal hole is immersed in the bulk of the metal. The holes compile at the metal surface by forming voids if the hole assembly rate is higher than their submersion rate. The passive film is found to collapse down into the void as the void grows into a reasonable size. This leads to accelerated corrosion with the formation of pit. There are three generations of PDM. The first generation is the primary generation model (PDM-I), which assumed the passive film to be a defective chemical compound or oxide layer containing vacancies of ion and chemical element vacancies created and annihilated at the interface of both metal/film and film/solution.

PDM I accounted for some observation such as the linear correspondence of the film thickness on voltage after a fixed time of polarization and the kinetics of film growth. It predicted the inverse logarithmic growth law. It also account for passivity breakdown which was activated by local cation condensation vacancies at metal/barrier layer interface, thus hindering barrier layer growth into the metal substrate [24]. The short coming of this model is its inability to account for the properties of the passive state on metals in contact with aqueous environment, that is, the formation of multi-layer (bilayer) passive films. Also the model failed to give account for the existence of steady states in both the passive current density and film thickness. The second generation model (PDM-II) addresses the short comings of model I. The PDM II consists of bilayer structure of film made of defective oxide/hydride layer. This bilayer is a binary compound barrier layer formed by precipitating materials from reaction of transmitted cations with species within the setting, made of water, carbonate, bisulfide, etc, It introduced metal interstitials into the defects, recognized barrier layer dissolution and shows the requirement of classifying reactions into lattice conservative or non-conservative. It assumed management of the passive current resided within the barrier layer alone. Model II gave a better precise account of the growth and properties of the barrier layer. It stated the parameters that must be available for passivity to occur in terms of the

formation of a defective metastable oxide or hydride film on the surface. This model couldn't give prove of the existence of multilayer films which was address by model III. The third generation model (PDM-III) was established to extend the theory to those cases, such as valve metals, where the outer layer is resistive that it controls the electric resistance (impedance) of the interface and thus the corrosion rate [25].

8.2 Stochastic method

The stochastic modeling is used for the extrapolation of accelerated test data and for the prediction of the effects of alteration in the environment on pit initiation and growth. The stochastic model uses the Markov chain processes to explain the effect of pitting. The stochastic model is utilized in describing the evolution time of pit depth and rate distribution. It shows the dependency of pitting rate on the pit depth and lifetime. The maximum pit depths can also be estimated when multiple corrosion pits is considered. Pitting corrosion can thus be modeled by combining two independent nonhomogeneous physical processes, one for pit initiation and the other for pit growth. The nonhomogeneous poisson process is used to evaluate pit initiation such that set of multiple pit nucleation events can be modeled as Weibull process. Nonhomogeneous Markov process is used for the modeling of pit growth. Considering the process intensity as a relation to corrosion rate, its functional form can be proposed from the results of the experimental tests [25]. Five model parameters are needed to stimulate all the pitting process. Two of the parameters are needed to activate pit initiation as Weibull process and two other parameters to activate pit growth non-homogeneous Markov process, and pit number is required to merge the two processes. Only three parameters are required when there is instantaneous nucleation of every pit to fit the model with the data of the experiment. This model is applicable for various corrosion systems because parameters and assumptions of the model are not dependent on the corroding material or its environment. Stochastic Cellular Automata (CA) modeling is used on mesoscopic scale corrosion study. The Physicochemical phenomena which cannot be properly explained by standard determinant and macroscopic techniques are made. 3D lattice is used to describe each cell of the materials. The estimation of pitting evolution is done using pit size morphology and electrolyte acidic level [26].

8.3 Other evaluating techniques

Several other ways in which pitting can be described, given a quantitative expression to indicate its significance, or used to predict the life of a material are stated below [23].

8.3.1. Standard charts:

Pits can otherwise be rated in terms of density, size, and depth in relation to standard charts. This method offers an effective means of communication between those who are used to charts. It is an easy method for obtaining data in relation to other test results. This method is tedious and time consuming to determine all pits. The time is not usually justified owing to the maximum values such as pit depth, which is of greater importance than the average values.

8.3.2. Metal penetration:

These measure the deepest pits expressing metal penetration with respect to highest pit depth or average of the ten deepest pits. This type of measurement is particularly significant when the metal is enclosed to a gas or liquid, and a hole which could lead to fluid loss.

Pitting factor may be used to estimate the metal penetration. Pitting factor is the ratio of the deepest metal penetration to the average metal penetration obtained from weight loss, as given in the relationship below:

$$\text{Pitting factor} = \frac{\text{deepest metal penetration}}{\text{average metal penetration}}$$

Pitting factor equivalent of 1 shows uniform corrosion. The pitting factors number increases with corresponding increase in the penetration depth. The factor does not apply in those situations of extremely small existence of pitting corrosion zero or infinity factor values when ratio is involved.

8.3.3. Statistical:

This method determines the pitting probability, the pit depth relation with time of exposure, and to measure the maximum depth of pit on by examining a portion of the exposed metal surface. The probability of pits initiation on metals surfaces is dependent on diverse parameters, which include pitting tendency of the metal, solution corrosivity, area of specimen, and exposure time. The pitting probability test may be carried out to measure metals susceptibility to pitting, but this does not give the information regarding the propagation rate. The result is only useful to the exposure conditions. The pitting probability (P) as a percentage (%), after exposing certain number of specimens to a particular set of conditions is given thus:

$$p = \frac{N_p}{N} \times 100$$

Where:

N_p is pitted specimens number, and N is total number of specimens.

The relation between depth and area of pit or exposure time can vary with environment, exposed metal, and other variables. This gives the relations between the maximum pit depth (D) and the area (A) of a pipeline exposed to environment (soil):

$$D = bA^a$$

Where a and b are greater than zero (0), and a and b are constants that were gotten from the gradient and the y-intercept of a straight line curve gotten when the logarithms of the average pit depth for successively advancing areas on the pipe were plotted against the logarithms of the corresponding areas. The area dependency is linked to higher opportunity for the deepest pit to be located when the size of the pit sample is increased through an increased area of corroded surface. The highest pit depth (D) varies as the cube root of time (t), gotten from the following relationship:

$$D = Kt^{1/3}$$

Where, K is the compositional constant of the water and alloy. This relationship applied to different aluminum alloys exposed to diverse waters.

Probability statistics of extreme values have been gainfully used for highest pit depth data in evaluating maximum depth pit of large region of material based on the examination of a little portion of that area. The technique is to determine the maximum depth of the pit across different replicated pitted specimens, afterward arranging the values of the pit depth values in increasing order. Each ranking order is gotten from plotting position by substituting into the relation,

$$\frac{M}{(n+1)}$$

Where M is the ranking order and n , the total specimens number.

If plotting values on extreme value probability against maximum pit depths, a straight line is obtained; it shows that extreme value statistics apply. Extrapolation of the straight line can be utilized to evaluate the probability that a certain depth will occur.

8.3.4. Loss in mechanical properties:

Changes in mechanical properties may be utilized to evaluate pitting level, if pitting occurs predominated and its density relatively high. Some of the considered characteristics are elongation, tensile strength, impact resistance, fatigue strength and burst pressure. The safety measures for these mechanical test procedures can be through most standard methods. It is important to use as nearly replicate specimens as possible for both the exposed and unexposed specimens. Hence, edge

effects, direction of rolling, surface conditions, etc. should be considered. The Metallic replicative specimens are subjected to similar conditions except for the corrosive environment. The subjected and unsubjected specimens' mechanical characteristics were determined after the exposure and the differences between the two results are related to corrosion. The unpredictable characteristic of pitting and the position of pits on specimens influence the outcomes. The change in mechanical properties sometimes is due to the minute nature of pitting to produce tangible results. The effects from pitting cannot easily be separated from the effects caused by other corrosion types.

9. Review of previous research on pitting corrosion

There had been much research works done to study the characteristics, effect and the occurrence of pitting corrosion. This section gives a brief review of past work carried out to establish the existence and actions of pitting corrosion.

It was discovered that surgical implants manifest different forms of localized corrosion like pitting corrosion, among others. The diverse corrosion interaction phenomena were studied by Mori [27], using cyclic loading of electropolished tensile specimens at various constant and varying potentials of surgical implant steel X2CrNiMo18-15-3 in a solution of physiological NaCl. It was concluded that pitting corrosion is not the main cause of fatigue cracking, but that crack formation favored pitting. Investigation on microbiologically influenced corrosion (MIC) of 2707 hyper-duplex stainless steel (2707 HDSS) by marine pseudomonas aeruginosabio-film in the marine environment using electrochemical analysis showed a responsive advancement in corrosion potential and a corresponding corrosion current density increase in the presence of the P. aeruginosabiofilm. This leads to concluding that 2707HDSS is not totally resistance to MIC by the P. aeruginosa biofilm[28]. Investigation was carried out by Yu, [1] to assess the consequence of pitting corrosion degradation on P-3C safe lives using the developed methodology in P-3C service life assessment Program. Through spectrum loading of corroded and uncorroded states, fatigue test was performed on high Kt specimens of 7075-T6. The equivalent crack size method and the crack initiation method were used to analyze the samples. The equivalent crack size distribution approach indicated that fatigue lives were not reduced by pitting corrosion below the safe life values. Estimation of the corrosion effect through crack initiation technique by the P-3C Service life assessment program likewise indicated that the fatigue life was not reduced below the safe life values postulated utilising the P-3C SLAP method by pitting corrosion. Pitting corrosion was discovered through FASTRAN modeling to reduce crack initiation time by 26%. 0.2% initiating crack length from corrosion was noticed. From the equivalent crack size and crack initiation methods, pitting corrosion invalidation of the safe life estimates of fatigue life with the given distribution of corrosion pit sizes was not established. Cuevas-Artega et al [3] investigated the damages of pitting on predicted useful life geothermal turbine blade made of 410 stainless steel (410 SS). Corrosion rate of 410 SS with/without crack with respect to time at different temperatures was worked upon using high content of sulfates and chlorides. Numerical models were used to evaluate the stress intensity factor and the useful life. The result showed that both 410 SS with and without cracks experienced mixed corrosion process of both uniform and pitting corrosion. Corrosion is thus a great mechanism of failure in blades of steam turbines which can effectually results into crack propagation. Maier, 2010 made a case study on pitting corrosion behavior of stainless 304 steel (SS304) in chloride medium droplets (between 3.0 and 8.4 M of $MgCl_2$ at different volumes) using Kelvin probe (KP) exposed to constant low relative humidity. Results show that Pits under droplets first grow off the defect forming disk in the lateral direction, followed by pitting action in a confined region inside the disk resulting to an ear-shaped hole. The susceptibility of pitting at a lower chloride concentration was more under a large drop than under

a small drop, as a result of larger electrolyte-covered area and hence a higher probability of covering thereby causing more defect. No relationship was found between the drop height and the critical chloride concentration, while the cathodic current decreased with time, while the pit stability criterion was much lower than the potentiostatically controlled pits in dilute bulk chloride solutions.

Characteristic morphology and kinetics estimation of pure commercial aluminium pitting was analyzed using digital image analysis [29]. The investigation was made with laboratory immersion test in natural aeration of NaCl solutions with the aid of an image processing method. Prior and after each corrosion testing metallographic examination and statistical analysis were done to different pits from any pre-existing cavities. The study of pit evolution against the immersion time and chloride concentration showed the shapes and sizes of pit to be more proportional to immersion time than chloride concentration. The pits were observed to be larger than their depth, but some nucleated in cavities of liked geometrical characteristics. The Pits were more hemispherical, undergoing geometric transitions and increased in immersion time occurring without substantial change in depth. The chloride ions catalyzed the pit nucleation process. Jiang, [13] made a study on pitting corrosion behavior of new corrosion-resistant reinforced bars of alloy steel and low-carbon steel in simulated concrete pore solution using 5mol/L concentration of chloride. The electrochemical behavior of the bars was measured by linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). CR bars were found with greater inhibition to pitting corrosion when compared to LC bars due to the difference in occurrence frequency of metastable pitting during the development of pits. The pitting depth in CR bars grows more slowly than LC bars. This thus reduces the risk of pitting in CR bars, because of the ability of the CR bars to re-passivate. Study made by Yang [30] on the hydrostatic pressure effect on metastable pitting corrosion using X70 steel pipe showed through potentiodynamic tests, that hydrostatic pressure has the capacity to retard the breakdown potential of pit leading to a decrease in transpassivity region. This was achieved through the evaluation of the metastable pitting probability, in chlorine ion solution, of the samples via electrochemical tests and immersion corrosion tests. It was discovered that the hydrostatic pressure is capable of increasing the frequency of metastable pitting formation and enhances the metastable pitting growth stability. Through the Electrochemical Impedance Spectroscopy (EIS) tests, charge transfer resistance was found to decrease by hydrostatic pressure thereby increasing the dissolution rate within the cavities. Hydrostatic pressure was discovered to enhance pitting initiation and propagation.

The corrosion polarization behaviors of API X-80 (550 Grade) and API X-100 (690 Grade) steel pipes in bicarbonate/chloride environment study were made using electrochemical techniques [31], in bicarbonate free chloride solutions. Results show that under the same condition, API X-100 steel grade in comparison with API X-80 showed lesser rate of corrosion in all the bicarbonate solutions (with and without chloride ions), offering higher level of pitting corrosion resistance in different chloride concentrations, due to the higher alloying content in API X-100 steel. The pitting morphology of SEM indicated that low bicarbonate concentrations solutions (0.01 and 0.05M) have much larger sizes of pits, whereas higher bicarbonate concentrations solution (0.1 and 0.5M) gave no pits. This explained that higher bicarbonate concentration enhances stable passive films on steel surface. Also pit morphology of the SEM of different chloride ion concentration of the bicarbonate solutions showed density and average diameter of the stable corrosion pits to increase with corresponding chloride concentration increased. The study of concentration effect of sodium chloride on the behavior of pitting corrosion of AISI-304L austenitic stainless steel was carried out by Asaduzzaman, [32]. Results show austenitic stainless steel pitting corrosion to be more

susceptible in chloride ion concentration in acidic chloride media. The pitting potential (E_{pit}) was noted to retard with a corresponding chloride ion concentration increased. Also, the induction time decreases with chloride concentration increased and anodic hold-potential in the passive region. The investigation on 304 stainless steel of its Passivity and passivity breakdown was made by El-Egamy [33] in alkaline sodium-sulphate media at a concentration of 0.5M and pH 10. The study of the effect of the presence of Cl^- ions and applied potential was also made in the electrolyte. The steel electrode was observed to passivates in open circuit conditions and potentiostatic control. Results showed a decrease in the passive regions of sulphuric acid and chloride media when compared to sulphuric acid solution resulting passive breakdown of chromium oxide. This occurred due to greater level of chloride ions diffusivity through cracks and film breakages which rate of repassivity is faster thereby resulting to pit formation by autocatalytic mechanism. The formation of pits may be delayed by the increment of sulphuric acid concentration but the corrosion rate will still be enhanced. The investigation thus indicates that the chloride ion advances the rate of propagation of pitting corrosion.

10. Conclusion

Much research works done affirm the destructive effect of pitting corrosion. The factors of pitting aggravation such as environment, subjecting temperature, nature of metallic alloy, among others should be critically put into consideration before setting up any metallic system in the industries. The severity of pitting corrosion necessitates the need for more research to further understand the mechanism of its electrochemical actions and the diverse methods to mitigate its action.

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