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Future and Benefits of Corrosion Research

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The subject of corrosion is a design science. The subject of stress analysis is a design science as is the subject of heat transfer. When the subject of corrosion is considered in the framework design a clear framework of the priorities and objectives becomes apparent. Further, corrosion becomes a more explicit and important subject in the overall design, manufacturing, and operation phases of equipment; in this framework, the funding and support of corrosion work is necessary to the designers and users of equipment. The subject of corrosion is usually less important in the early stages of operation of equipment; in these early stages, the subjects of stress analysis and heat transfer are usually more important as are similar performance-related subjects. Corrosion becomes important to the longer term reliability and safety of equipment. Corrosion is often a principal determiner of design life. Corrosion is often more important after the manufacturing warranty is expired; therefore the subject is often more important to the user than to the manufacturer.

In order that the subject of corrosion is considered and incorporated in the design as well as in user specifications, there must be a language and means of easily understood communication between the design-operation community and the corrosionn community. For example, the designers do not understand the language of "pitting potential;" rather, they understand design life and permissible stress. Thus, corrosion must be put into terms that can be understood and utilized by designers and operators. Two methodologies have been developed for communicating effectively between the corrosion and the design communities; these are the "Corrosion Based Design Approach" and the "Location for Analysis Matrix." These provide simple check off lists to designers for asking questions and assuring that credible answers have been obtained on issues that affect reliable and cconomic performance. Both of these subject are discussed in this presentation.

The future of corrosion research is its effective linkage with design and operation of equipment. The benefits include lower life cycle cost, higher reliability, and public safety.

Keywords : *Corrosion research, benefits, future, design science, CBDA*

1. Introduction

The purpose of this paper is to place the future and benefits of corrosion research into a context that is useful both to the corrosion and the design/operating communities. The title and scope of this paper respond to suggestions of the organizers of this meeting. The essential task of the field of corrosion is to assure the reliable performance of equipment through mitigating corrosion; otherwise, this field would be a part of physical or organic chemistry. In fact, these disciplines contribute importantly to understanding corrosion processes. The extent to which the field of corrosion both accomplishes this task and communicates its work to the design/operating communities is the extent to which the work of the members of the corrosion community will be supported and encouraged.

To simplify this discussion of the future and benefits of corrosion research, I identify three communities. One is the corrosion community that generates scientific and technological data and guidelines as well as provides various services such as cathodic protection, water treatment, and inhibitors. In this discussion I refer to this community simply as "corrosion." One beneficiary community is comprised of those who design, manufacture, and sell equipment. This community responds to buyers and operators. I identify this second community as "design" since this indicates the intent to develop configurations, select materials, specify manufacturing, and set the design life. The third community is comprised of those who use equipment. For example, domestic users of household goods belong to this community as do those who operate chemical- and energy-producing plants. This community purchases equipment provided by designers, and the design community is anxious to please the operators as the latter buys and uses products. This community I refer to simply as "operators" although this term may be pretentious for the householder. Designers and operators have different priorities and inherently different interests as they affect corrosion.

Since the extent of research that could be conducted in the field of corrosion is quite extensive, there needs to be some approach to focusing the research that needs to be undertaken in terms of what is important and critical in the field. Thus, one task of this discussion is to describe a framework within which research in corrosion is useful and relevant. This is approached in two parts. First, I have identified a set of ten perspectives that describe the texture of the field as it affects the purpose of the present discussion. These perspectives should be understood when organizing research . Second, specific research areas that should be considered in the future, together with the benefits, are described in the framework of the "corrosion based design approach (CBDA)."[1] This structure identifies relevance and justifies why certain areas of research should be considered. The main factor that controls the extent of research in corrosion is the willingness of designers and operators to pay the cost. This implies that corrosion research provides a benefit directly to customers who needs the information. Corrosion work is not usually undertaken and funded if it does not provide some direct value to the reliable performance of equipment. Even at the level of federal funding, corrosion research is rarely funded that does not have some clear objective relative to design or operations. This, incidentally, is unfortunate but is the prevailing reality especially in view of the large national cost of corrosion and other modes of degradation.

Researchers, today, have access to tools that are substantially more powerful than those of even a decade ago. Essentially, there are three kinds of tools that have produced this change. One, of course, is computers with their increasing speed and memory. Whereas, once, thermodynamic calculations by hand and even with calculators were laborious and error-laden, software is now available including large data bases that can provide thermodynamic calculations rapidly and in graphical formats. Second, instruments today are now capable of seeing atoms. The FEG-TEM, typical of modern powerful instruments, has revolutionized the capacity to study SCC through its capacity to image atomic arrays as well as to determine chemistry and structure at tips of cracks. The third tool is the large pool of accessible information about corrosion. Searches into this literature usually provide direct or at least very useful insights into the resolution of complex problems.

The essential problem in corrosion research is not really addressed by the capacity to perform high speed calculations or measure phenomena at increasingly small dimensions; rather, the essential problem is the matter of judgment, as it has always been. For example, engineers are prone to select materials for applications when the local environments have not even been defined. Engineers who are not steeped in corrosion are not aware of concentration problems in heat transfer crevices and then proceed to design machines that are already prone to fail. Engineers who are unaware of materials consider any material that is called "stainless" or "corrosion resistant" to be in fact immune to corrosion; and, therefore, they place little emphasis on monitoring for the purpose of controlling conditions that accelerate corrosion or for maintaining conditions that minimize corrosion. Thus, along with the research that is undertaken in the future, the importance and need for informed technical judgment has not changed. The elaborations of perspectives and the CBDA in this paper provide insights into the judgments that are required for organizing research in corrosion.

The benefits of corrosion research are directly related to funding. The extent to which the research provides clear benefits to design and operators is the extent to which financial support is available; there is a clear connection between the commercial benefits of the research and the capability to obtain funds. In general, research can only be undertaken that can be funded, and the funding is incited by the perceived benefits to products that produce revenue or great benefit to the user. Thus, "benefit" at the most pragmatic and immediate level is defined by the perception of those who benefit from the work in a commercial sense. In a larger sense, corrosion research benefits society in the sense of reducing waste of materials and energy; however, it is rare, and indeed quite unfortunate, that benefits at this level lead to funding any research in corrosion. In each of the discussions of corrosion research according to the steps of the CBDA, benefits specific to the step are described.

2. Perspectives

Generally, undertaking research in any field including corrosion depends on the researcher's view of the field as well as on the objectives of a funding group. In corrosion, there are ten perspectives that typify the texture of corrosion and that shape approaches to funding corrosion research.

First perspective: Materials are reactive chemicals

The most fundamental consideration in corrosion is that all engineering materials are reactive chemicals. The surprise is not that materials fail; the surprise is that they work. Every engineering material dissolves or reacts rapidly in some, and sometimes many, environments. For example, platinum is widely considered to be a noble element and can be expected to perform reliably in many engineering environments. However, in the presence of hot chloride solutions at modest oxidizing potentials, platinum forms a soluble $PtCl_6^{3-}$ ion and can dissolve rapidly. Such failures due to the solubilization of platinum have recently occurred where chlorine-containing chemicals have been exposed in supercritical water contained in a platinum lined vessel. Concrete dissolves in acidic solutions. Titanium sustains rapid SCC in halide gases. Moly- bdenum, widely thought to confer corrosion resistance, is totally soluble in water above about pH 3; and tungsten is totally soluble above about pH 5. Higher strength materials propagate stress corrosion cracks faster as the strength is increased. Above about 1500°C molybdenum vaporizes rapidly as a volatile MoO_3. Stainless steels and high nickel alloys sustain rapid SCC in high purity water. One ppm each of chloride and oxygen produce rapid SCC of stainless steel at 200°C. Aluminum and titanium in powder form burn sometimes explosively in air. These examples are typical of all engineering solids in common environments.

It would seem that this obvious reactivity of engineering solids would engender more respect among designers and operators. However, materials are almost always selected based on their strength, as well as cost, and rarely for their corrosion resistance in operating environments despite easily demonstrated benefits to life cycle cost. Even when possible corrosion failures are well documented and obvious, designers are not easily dissuaded from their primary interests in mechanical strength and short term cost.

Second perspective: Designers and operators

Designers and operators have fundamentally different priorities and interests with respect to corrosion. Design responds generally to specifications provided by operators or responds to perceptions of demand by consumers, who are also in the category of "operator" although on a small scale. Designers cannot know precisely the conditions of operation but can assert that the equipment meets the specifications provided by operators. Design concludes its delivery process by providing operators with a warranty that equipment will be repaired at the designer's cost for a brief period called the "warranty period" if the equipment is found to be deficient in materials, workmanship, or capacity to meet the design performance specifications. Design may also assert that equipment has been designed for a life, the "design life," over which it intended to operate reliably; however, designers usually do not accept costs over the design life beyond the warranty period although they may be liable for a design life if they assert that the promised design life is based on certain experiments.

Operators, on the other hand, deal with equipment "every day" and need to assure that it will not fail and cause down time or outages that are often expensive and, at least, inconvenient. Operators achieve their interest in maximizing operating reliability by monitoring such signals as pressure, temperature, conductivity, pH, flow rates, and electrochemical potential. Further, operators usually inspect equipment on some periodic basis and perform maintenance. Even domestic home operators, "consumers," have their cars maintained, washed, and inspected. Good practices of operating are often the differences between equipment operating reliably and failing prematurely.

A good example of the differences between designers and operators is in the production of electricity. Certain companies build power plants and arrange for starting them and assuring performance during a relatively short warranty period. The electrical utilities are responsible for operating this equipment. Each of these groups has quite different priorities and interests.

Consequently, designers and operators approach corrosion differently. Design, generally, is less interested in corrosion since the warranty period is short relative to the time required for damaging corrosion to occur. Therefore, designers are more interested in function and in stress analysis to assure that the equipment will not fail under initial stresses. Codes, for example, are generally organized around problems in design and not of operating, e.g. the pressure vessel code of ASME.

Operators are deeply interested in corrosion because damage produced thereby begins to occur over the lifetime and becomes significant often only after the warranty period is passed. Operators manage corrosion by attending to environmental chemistry of fluids, inspection, monitoring indications that relate to corrosion, and replacing components that are excessively corroded. Figure 1 illustrates the chronological domains of interest to designers and operators. Designers are mainly interested in satisfactory performance until the end of the warranty period despite other assertions about the design life. Nominally, designers, in order to support the assertion of a design life, have conducted accelerated testing that shows that the equipment can meet the design life. In reality, such assertions are not always well founded.

Third perspective: Objectives of equipment

Equipment is designed generally with three objectives:

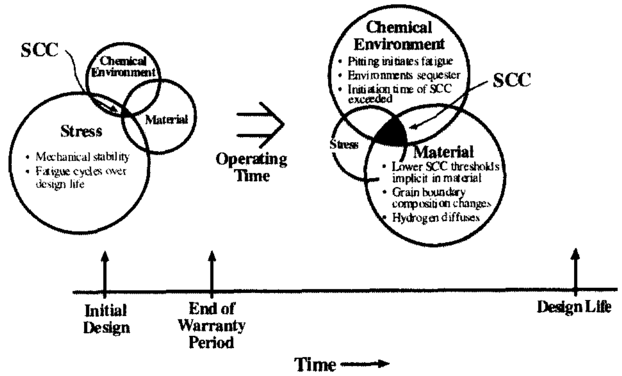

Fig. 1. Schematic view of relative importance of factors contributing to SCC over time from initial design, end of the warranty period, and at the design life. From Staehle.[2)]

- Perform functions.
- Perform reliably for some duration, e.g. warranty period or design life.
- Minimum cost.

These objectives are self-evident. A hard disc is designed to store information. A heat exchanger is designed to transfer heat. Both are required to perform reliably and for some design life. However, the capacity to perform these functions and to perform reliably for the design life generally are in the provinces of disciplines that are different from design.

Costs are viewed differently by designers and operators. Low initial capital cost often means that the materials and design used are barely adequate from a corrosion point of view. Further, while the life cycle cost is of interest to the operators, they are often unwilling to pay the cost for initially better materials and better design. The operators often assume that if the design works, then they save money. If failures occur, it is better that they occur later and are part of the maintenance budget; failures may also be covered by insurance. Further, the operating conditions may be sufficiently undefined that choosing expensive materials in the initial design may place resources into the wrong place. Resources for repairs may be required in unexpected places; then, when failures do occur, resources can be placed where they are actually needed.

Designing equipment is usually in the province of mechanical and electrical engineers, sometimes chemical, civil and aeronautical engineers. Assuring the reliable performance for the design life is more likely in the province of materials science and engineering, especially as it includes the subject of corrosion. Assuring reliable performance is often associated with the fatigue behavior which is sometimes in the province of materials and sometimes in the province of mechanics. Usually, the groups interested in the objectives and design of equipment are unaware of the subtle but powerful effects of corrosion.

Fourth perspective: Reality

It is a frequent complaint of corrosion, when premature failures occur, that design should consider corrosion as part of the initial design. On this subject there is a great deal of "wringing of hands;" there is no shortage of such views nor of quantitative justifications. In this same vein, several excellent studies[3),4),5),6)] of the cost of corrosion have been conducted and show that major contributions to reducing cost of products and of waste in society are readily accessible by paying more attention to the subject of corrosion.

Despite the obvious and well founded incentives to consider corrosion in initial design; in fact, little progress here has occurred, and progress in the future is unlikely unless operators are willing to pay the cost of incorporating such ideas in the purchase cost of equipment.

It is often suggested that design engineers should take more courses in materials science and, in particular, in corrosion. However, in a practical sense, adding more courses to university curricula will not happen. Designers are usually familiar with concepts of fatigue since this is related to the stress question of early performance. However, effects of environments on fatigue are less appreciated. It is remarkable, in fact, that the fracture mechanics community has derived and continues to derive still even better mathematical descriptions to the evaluation of the stress intensity, K. In fact, the effects of environments so overwhelm any refinements in the value of KIC that these refinements in the critical stress intensity are generally useless.

For some reason, design is enamored of high strength and high alloy compositions, with no concept of their usually inherent proneness to premature failure. These are subjects in which corrosion could help, but such help is not often solicited.

Fifth perspective: Practical initiatives by corrosion

Recognizing that design is not likely to change its inherent lack of appreciation of corrosion, corrosion needs to recognize this reality and organize a different approach. Such an approach has two avenues:

- For design the simplest approach is to provide a "check off" approach that can be used by designers who have little or no background in corrosion. The designers can be guided then by assuring that specified stages have been considered properly by an appropriate discipline. Such check off lists are described in detail by Staehle.[1)]
- For operators who have a greater inherent interest in

corrosion, although they usually have little background, a similar approach using a check off list should be developed. However, operators are more likely to appreciate the importance of corrosion, and educational ventures by corrosion are more likely to be effective. Further, the operations community is more interested in methods of monitoring and mitigating corrosion. The check off lists described by Staehle are also useful for operators.[1)]

Sixth perspective: Communication is in one direction

Designers generally are not familiar with corrosion terms like electrochemical potentials, pitting potential, passivity, and similar terms. The communications concerning what work is required or what should be incorporated in design needs to be initiated by corrosion and needs to be in terms that are readily understood by designers. Most understandable to designers would be to cast corrosion in terms of effects on warranty period, design life, material strength, time-to-fail, first penetration, rate of failure, or similar indicators.

Essentially, communication to and with designers and operators has to be organized and tailored by corrosion. Corrosion has to take the initiatives.

Seventh perspective: Cost of corrosion is irrelevant

Since the 1950s numerous studies of the cost of corrosion, wear and fracture have been undertaken. Each of these studies has shown that degradation by these modes costs the economy enormously.[3),4),5),6)] Further, these studies reckon that a significant fraction of this cost is avoidable by maintaining well supported research program aimed mitigating corrosion in the topics which are the most costly. Over the years these studies of the costs of corrosion, wear, and fracture have produced little effect on the funding of any research into methods of mitigating degradation including corrosion.

In view of the lack of effect of these studies on degradation, one must conclude that the design and operating communities are interested primarily in work that provides relatively immediate effects. This is true also for federally sponsored work.

Eighth perspective: Psychological realities

While this paper may seem to be a strange place for discussing "psychological realities," designers and operators as well as many even in materials science seem to reject some ideas about corrosion more on psychological rather than on technical grounds. For example, the occurrence of SCC at stresses far below the yield strength or initiating at smooth surfaces is often not credible- although true. The idea that such high technology materials like titanium, niobium, aluminum, tantalum, and zirconium should corrode catastrophically in some cases is not credible although the fundamental bases are quite clear. The fact that highly alloyed materials such as Alloy 600 or Alloy 690 should sustain rapid SCC is not credible.

Thus, although there are abundant and credible bases for accelerated corrosion of many materials, the occurrence of such corrosion is often not credible to designers and operators. It seems that the lack of appreciation of such corrosion is more of a psychological response than a strictly technical one. There seems to be something about shiny materials and high strength materials that prevents engineers from realizing the first perspective: materials are inherently reactive chemicals.

Ninth perspective: Corrosion is inherently probabilistic

Corrosion is an inherently probabilistic process. Such inherently probabilistic patterns arise from the multiple paths that all corrosion processes take as they initiate and propagate, the variability of structure-sensitive materials, the variability of environmental chemistry on surfaces, ranges of temperatures to which materials are exposed, and the ranges of local stresses in the materials. Data for corrosion failures are most effectively correlated according to some standard statistical distribution such as the Weibull distribution. An example of such a correlation is shown in Figure 2 that is taken from the array of corrosion failures that occur steam generators of pressurized water reactors. This particular set of data was taken from the steam generators of a single plant, Ringhals 4.[7)]

All corrosion data exhibit patterns similar to that of Figure 2, and the extent of such behavior has been discussed by Staehle.[8)] A contrary view is sometimes expressed that corrosion data are deterministic and, if the experiments are performed correctly, there would be no variability. There is no physical basis for such a view, and assertions that such determinism exist is a disservice to designers.

Tenth perspective: Corrosion as a design science

The subject, corrosion, is an apt one since it applies to the degradation of equipment. Literally, the word, "corrosion," is derived from the same root as "rodent" which comes from the Latin meaning "to gnaw." The subject of corrosion is not physics, physical chemistry, geology, or mathematics. Corrosion utilizes these disciplines and their methods; but the field is concern mainly with assuring the reliable performance of equipment. Therefore, corrosion is a design science similar to the field

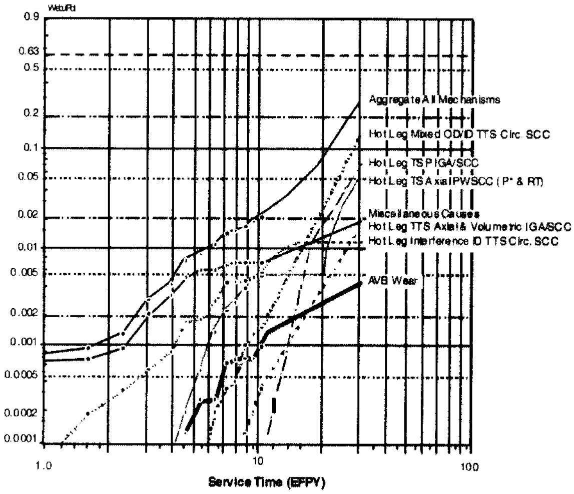

Fig. 2. Cumulative fraction of tubes failed versus service time in Equivalent Full Power Years (EFPY) for seven mode-location cases based on data taken from the steam generators of the Ringhals 4 pressurized water nuclear plant. From Bjornquist and Gorman.[7]

of mechanics which is concerned with stress.

In a general sense mechanics and the analysis of stress relate mainly to design and less to operations. On the other hand, corrosion relates more to operations as suggested in Figures 1 and 2.

The subject of corrosion is not related only to metals in aqueous solutions as is often assumed, although the reliable performance of metals in aqueous solutions commands significant attention. Corrosion is concerned with assuring the reliable performance of all materials of construction in all environments. As such, corrosion is a design science.

3. Future and benefits of corrosion research in the frameworks for prediction and assurance

The subject of the future and benefits of corrosion research should be viewed in the context of design and operations. Here, the most relevant context includes the Corrosion Based Design Approach (CBDA) and the Locations for Analysis Matrix (LAM).[1] In these frameworks, the future and benefits of corrosion research become obvious. Here, only the ten steps in the CBDA are discussed as a framework for identifying future corrosion research. In each section, the role of the respective step in the CBDA is reviewed; after each discussion, the future and benefits of corrosion research are discussed as they apply to the respective step in the CBDA. The future research that should be considered, as described in each element of the CBDA, is necessarily exemplary. Such desirable future research will be more particular as readers consider the needs of each of the steps in the CBDA are applied to specific industries and specific components.

3.1 CBDA Step 1: Environmental definition

Defining environments in intimate contact with surfaces is the most important single step in predicting and assuring performance. These environments should be defined before materials are selected. The scope of environments to be defined includes chemistry (e.g. species, pH, potential in aqueous solutions), temperature, stress, radiation such as UV and gamma, microbes and fungi, and flow. In general, environments in the bulk are not the same as on the surface. Therefore, defining an environment means to define the environment on a surface where the corrosion occurs.

A good example of the difference between an environment in the bulk and a connected one on a surface is the heat transfer crevice in steam generators of pressurized water nuclear reactors (PWR). The locations of such crevices are shown in Figure 3. An example of the details of chemicals and gradients associated with a heat transfer crevice is shown in Figure 4. Owing to the superheat present in the crevice, impurities in the pure water, regardless of their low concentrations, are efficiently concentrated. The resulting local solution is sometimes concentrated to saturation with respect to a variety of species. Many of the species found in such locations are surprising including a variety of organic species such as acetic and formic acids. Thus, although the bulk solution on the secondary side of a steam

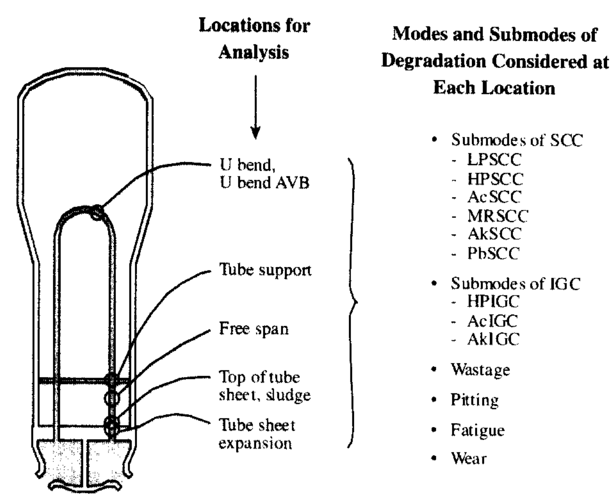

Fig. 3. Schematic view of steam generator from a pressurized water nuclear reactor with different locations for analysis and the possible modes and submodes for a single tube. From Staehle.[1]

generator may contain less than several tens of parts per billion of solids, environments in the connected heat transfer crevices may be saturated or in that range. Some examples of modes of corrosion that occur in these heat transfer crevices are shown in Figure 2.

Considerations of corrosion behavior must respond to the local environments shown in Figure 4 rather than to the pure water in the bulk environment. There is a large literature on such corrosion behavior.[9),10)]

In some components multiple environments may be producing corrosion damage. Figure 3 indicates the multiple locations where corrosion damage can occur. Figure 5 illustrates multiple locations where corrosion occurs as well as multiple modes of corrosion at these locations. This figure identifies 14 separate mode-location cases where corrosion failure has been observed in PWR steam generators. This result indicates that there are multiple and different locations where there are different environments; each of these needs to be characterized. In fact, it is typical of complex components that more than one environment needs to be characterized.

Future corrosion research on environmental definition at surfaces should consider the following, for example:

a. Mechanisms of concentration of species at heat transfer surfaces including free surfaces.
b. Migration and diffusion in porous media that lead to concentration of species.
c. Mechanisms by which separated local cells produce acidity and alkalinity.
d. Processes by which the metabolisms of microbes and fungi produce chemical species.
e. Processes by which chemical species accelerate corrosion in the steam phase.

Emphasis on defining environments provides benefits since it permits more precise predictions and provides more credible bases for choosing materials of construction. Defining local environments in intimate contact with surfaces is the most important single action that can be taken for prediction.

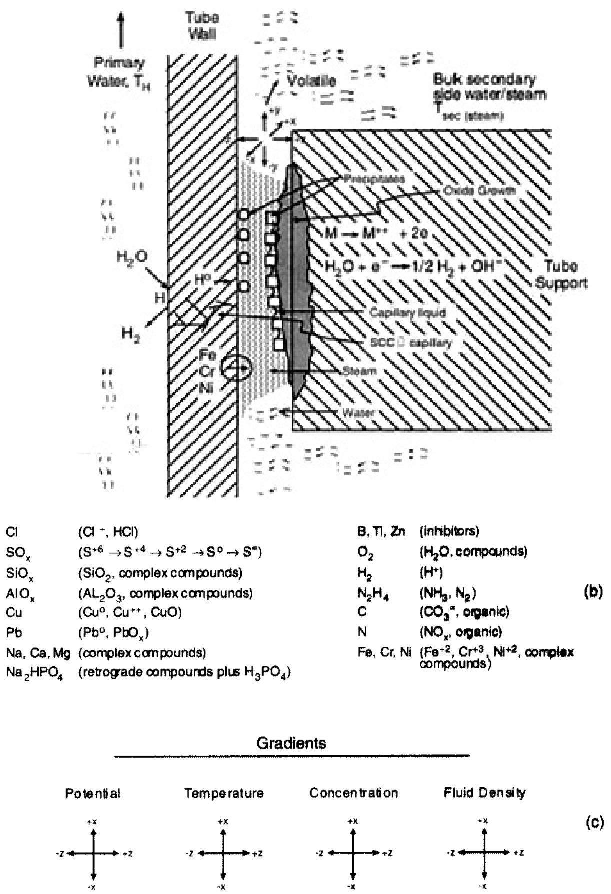

Fig. 4. Schematic view of chemical processes which can occur in heat transfer crevices at the tube to tube support location. (a) Processes and geometry. (b) Chemical species. (c) Gradients. From Staehle.[1)]

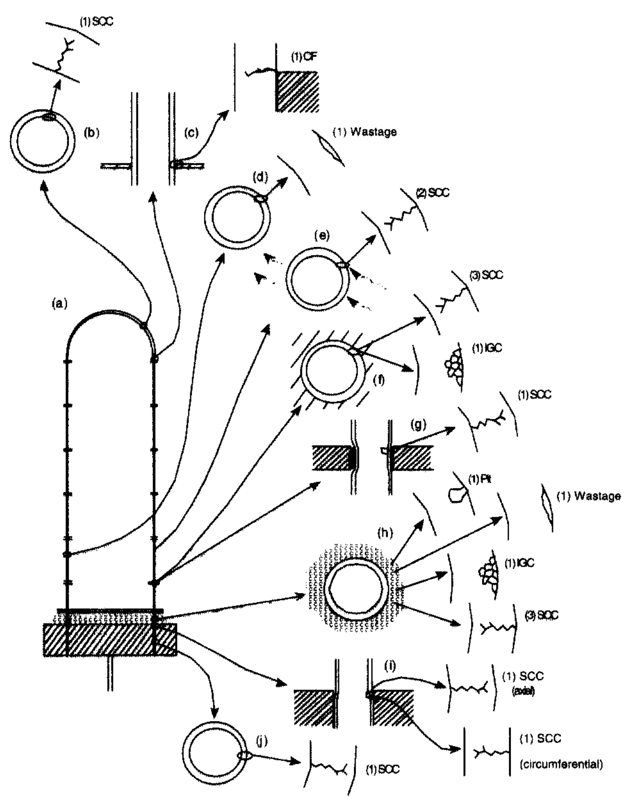

Fig. 5. Schematic view of mode-location cases of corrosion which have occurred in steam generators of pressurized water nuclear reactors. From Staehle.[11)]

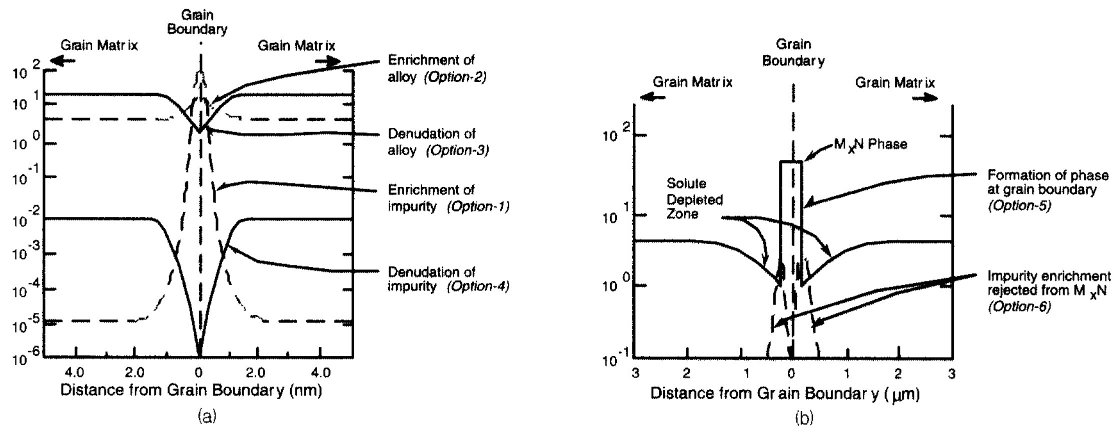

Fig. 6. Concentration vs. distance from the grain boundary for several cases. (a) Atoms adsorbed or rejected. (b) Compound formed requiring sources from surroundings. From Staehle.[12]

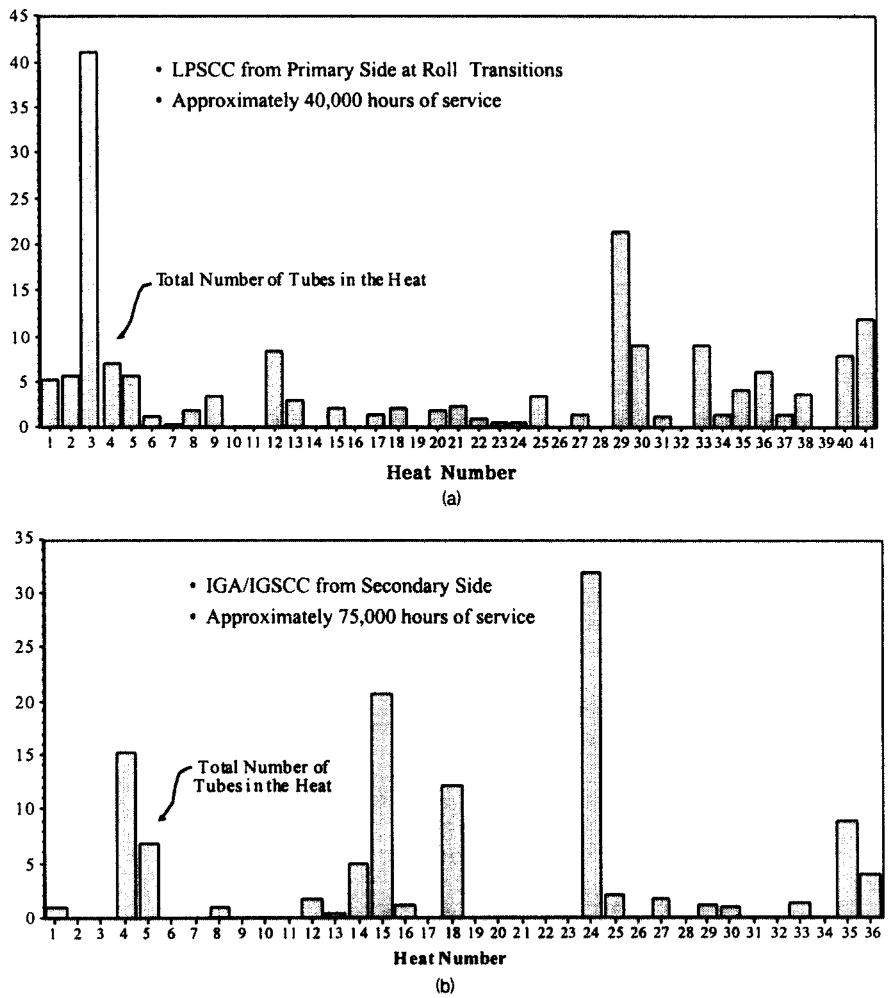

Fig. 7. Percent of tubes affected by corrosion versus heat number for steam generators at a single plant. Primary and secondary sides are not from the same sets of steam generators. Numbers at the top of each bar indicate number of tubes from each heat. (a) LPSCC on primary side at roll transitions. (b) IGA/IGSCC from secondary side. From Scott.[13]

3.2 Material definition

Defining materials of construction does not consist of referring to purchase specifications or specifications issued by standards groups. Today, well-known alloys continue to exhibit unexpected effects of alloy structures and local compositions on corrosion. Defining materials means to define those features of materials that affect corrosion and failure processes. Such features include the composition and structure of grain boundaries, composition and structure of multiple phases, distribution of second and third phases, anisotropy, effects of cold work, residual effects of surface treatments, slip processes as they occur at the surfaces boundaries, and presence of low concentrations of impurities. Figure 6 shows a schematic view of grain boundary compositions associated both with equilibrium concentrations at grain boundaries and with the formation of compounds; each of these operates over different dimensions with the latter involving microns and the former involving nanometers. The results of reactions for both cases in Figure 6 exert large effects on corrosion and mechanical properties.

A good example of the variability due to metallurgical influences is shown in Figure 7 from the work of Scott.[13] In this work, he has plotted the fraction of tubes failed from a given heat versus the heat number as it was prepared in a chronological sense. Numbers above each bar show the number of tubes from each heat in the steam generator. Data are shown both from SCC on primary and secondary sides. What is clear from these data is the large variation in the fractions of each heat that sustained SCC.

Future work to define materials should include the following:

a. Improved understanding of the segregation and rejection of species at grain boundaries and phase interfaces.
b. Improved understanding of slip at free surfaces and boundaries as affected by structure and composition of materials.
c. Effects of surface treatments on the reactivity of surfaces.

Work on metallurgical definition provides benefits by improving the understanding of heat-to-heat variations and improving the definition of initiation stages of localized corrosion.

3.3 Mode definition

Defining modes of corrosion is concerned with determining the dependencies of modes and submodes of corrosion on the seven primary variables of electrochemical potential, pH, environmental species, alloy composition, alloy structure, temperature, and stress. The modes of corrosion are illustrated in Figure 8; here, the intrinsic modes of general corrosion, pitting, intergranular corrosion, stress corrosion cracking, and corrosion fatigue are shown. The modes in Figure 8 are the intrinsic modes. Sometimes subjects of crevice corrosion and galvanic corrosion are included in the "forms" of corrosion;[14] however, these subjects are concerned only with environments and not with intrinsic modes of corrosion; e.g. SCC can occur inside crevices and in galvanic cells. A "submode," for example of SCC, refers to the occurrence of SCC but with different dependencies on the principal variables. Describing only SCC of an alloy is not an adequate description when SCC of same alloy at the same temperature depends differently upon pH, potential, metallurgy, stress, and temperature.

Mode diagrams are used to compare conditions for the occurrence of various modes of corrosion with the ambient chemistry. This comparison permits determining whether corrosion is expected.

Approaches to defining modes of corrosion are discussed in several references.[1,15,16,17] Figure 9 shows a simple identification of modes of corrosion related to a polarization curve. Here, the occurrence of modes of SCC is based on the occurrences of transitions from stable passivity to instabilities.[12] A more general mode diagram is shown in Figure 10 for Alloy 600 for the temperature range of 300-350℃. Here, four submodes are shown at

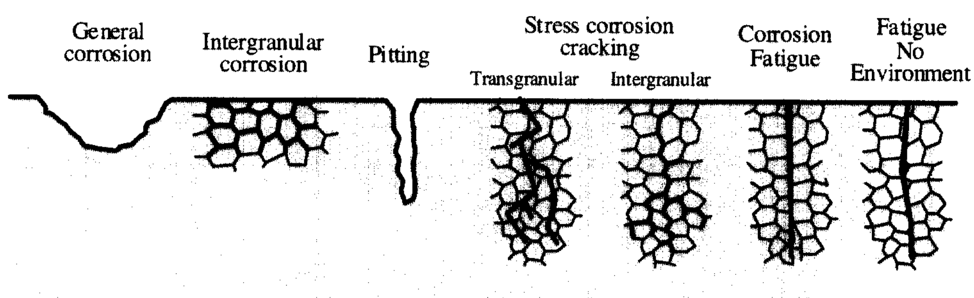

Fig. 8. Views of the intrinsic modes of corrosion.

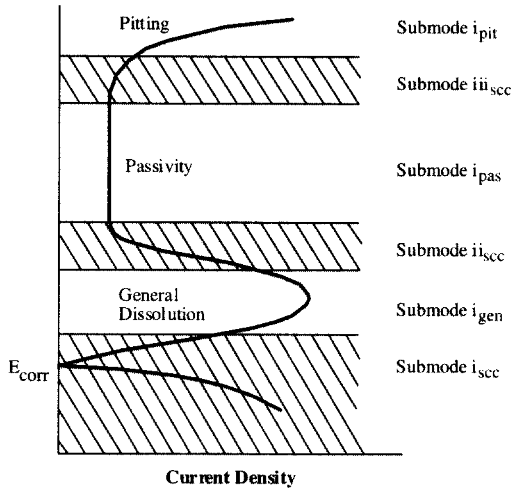

Fig. 9. Schematic view of regions of SCC, general dissolution, pitting and passivity related to a polarization curve. From Staehle.[18)]

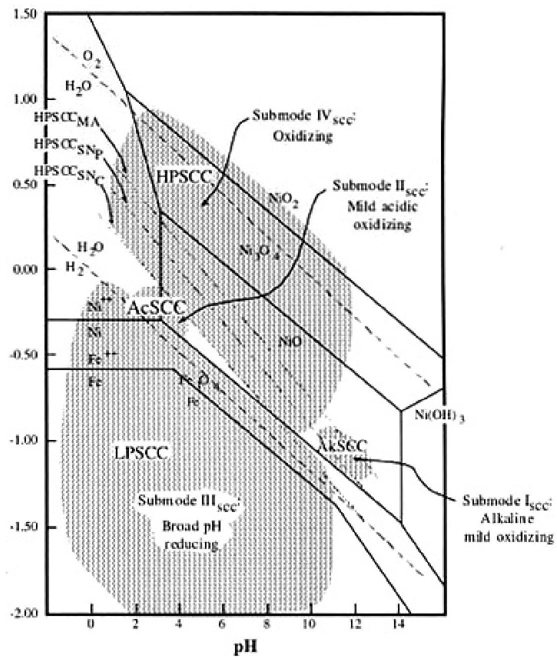

Fig. 10. Mode diagram for the SCC of Alloy 600MA in high temperature water in the range of 300 to 350℃. Boundaries are defined by the potential-pH diagrams for nickel and iron at 300℃. Shaded regions show where the submodes have been observed by direct experiments and where these results may be reasonably extended.

alkaline, acidic, low potential and high potential conditions. Each of these submodes depends differently upon potential, pH, chemical species, stress, temperature, alloying elements, and alloy structure.

The mode diagram in Figure 10 applies mainly to the initiation stage of SCC. This stage applies to about the first 200 to 500 μm of depth. Beyond this point the chemistry that controls the propagation of SCC is more related to that at the tip of the advancing SCC. Similar diagrams can be developed for pitting, IGC, and general corrosion.[19)]

Future work on mode definition should consider the following:

a. Developing mechanistic models for the occurrence of a set of submodes for a given material such as the submodes shown in Figure 10.
b. Determining the domains over which initiation and propagation can be distinguished and the respective dependencies upon principal variable.
c. Increasing the attention given to FEG-TEM analysis of localized corrosion.
d. Developing mode diagrams such as that in Figure 10 for other engineering materials.
e. Improving the modeling of passive films, especially in the short term transient period; also, modeling passive films in environments such as those containing sulfur, lead, fluorine, and other important species should be continued and undertaken.

Defining the dependencies of modes and submodes on

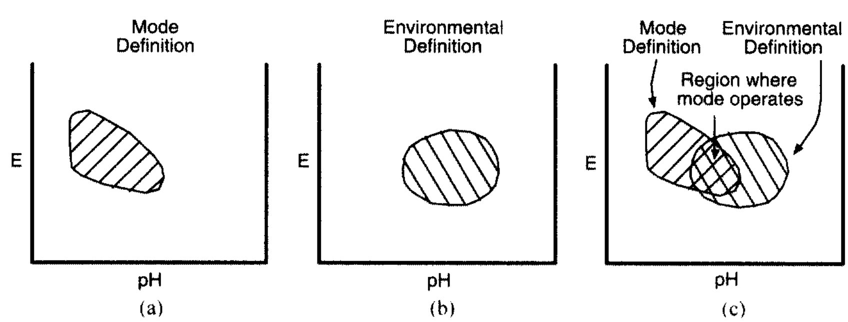

Fig. 11. Schematic view of the superposition process. (a) Mode definition. (b) Environmental definition. (c) Comparison of mode and environmental definitions. From Staehle.[16]

principal variables provides benefits for predicting the occurrence of failures as environmental conditions impinge on the domains of the modes and submodes.

3.4 Superposition

The step of superposition involves comparing the environmental definition with the mode definition for a specified metallurgical definition. Where the environment impinges on the occurrence of some modes or submodes, corrosion by the appropriate mode is likely. Figure 11 illustrates the step of superposition. If overlap occurs, then some change is required in either the material or environment.

The research that should be undertaken for superposition is that of steps #1, 2, and 3 in the CBDA.

This step benefits those engaged in predicting performance and helps avoid foreseeable failures.

3.5 Failure definition

Defining what constitutes failure determines the target for prediction and assurance. Failure depends on the equipment and the application. Failure in food packaging may be simply the occurrence of rust on the inside of a lid in a food jar. Here, there is no perforation but only an objectionable appearance. For the storage of radioactive waste, failure is a release of radioactivity greater than a rate that would harm nearby humans after many thousands of years. For a heat exchanger, some number of tubes can be plugged until it becomes inefficient; a 10% plugging is typical of the upper level that is acceptable. In aircraft, while the occurrence of cracks in structural members is sometimes acceptable, these become non-acceptable when they are predicted to become too deep before the next inspection.

Defining failure is part of defining "design life." Design life, in general, would be defined as preceding failure by some factor that should be statistically defined.

Future research in defining failure depends greatly upon the application. For example:

a. In a tube in a pressurized heat exchanger, it is often necessary to determine the depth of corrosion required for a subsequent mechanical rupture. This critical depth depends on the geometry of the corrosion and its extent.
b. The first stage of failure by cracking is some stage of initiation. These may involve pitting, multiple small cracks, or penetration at grain boundaries. How these lead to the next step of catastrophic failure should be investigated.

Defining conditions for the occurrence of failure provides benefits as bases for improving designs to achieve still longer design lives. Further, developing such a target provides a framework for integrating results from steps #1, #2 and #3.

3.6 Statistical definition

Defining a statistical framework provides a basis for correlating the intensely statistical nature of corrosion. Such a framework is used ultimately for predicting the field performance of materials and components. In order to provide such bases for the field performance, it is necessary to use the same statistical framework for correlating and organizing experimental data. The connection between field and experimental work has been described by Staehle.[8]

The most widely used statistical correlation for correlating failure data as well as corrosion data is the Weibull distribution.[20)21)] The probability density function and the cumulative density functions are given in Eqns. (1) and (2). The hazard function is given in Eqn. (3)

$$f(t)=\left(\frac{\beta}{\theta^{\beta}}\right)t^{\beta-1}\exp\left[-\left(\frac{t-t_o}{\theta-t_o}\right)^{\beta}\right] \tag{1}$$

$$F(t)=1-\exp\left[-\left(\frac{t-t_o}{\theta-t_o}\right)^{\beta}\right] \tag{2}$$

$$h(t)=\left(\frac{\beta}{\theta-t_o}\right)\left(\frac{t-t_o}{\theta-t_o}\right)^{\beta-1}=\frac{\beta}{(\theta-t_o)^{\beta}}(t-t_o)^{\beta-1} \tag{3}$$

where:

t = time
t_o = location parameter or initiation time
θ = scale parameter or the Weibull characteristic which is evaluated where the cumulative fraction is 0.632.
β = shape parameter or often called the "Weibull slope" as is evident when the linearized version of the cdf is shown in Figures 12c and 12d.
$f(t)$ = probability density function, the probability that the event will occur in the range of dt.
$F(t)$ = cumulative distribution function, probability that the event will occur by the time, t.
$h(t)$ = hazard function, the probability that the event will occur in the next interval dt given that the event has not yet occurred.

The scale parameter also called the Weibull characteristic, θ, is essentially the average value that is determined when experimental or field data are obtained with the central value being the average. Actually, in the

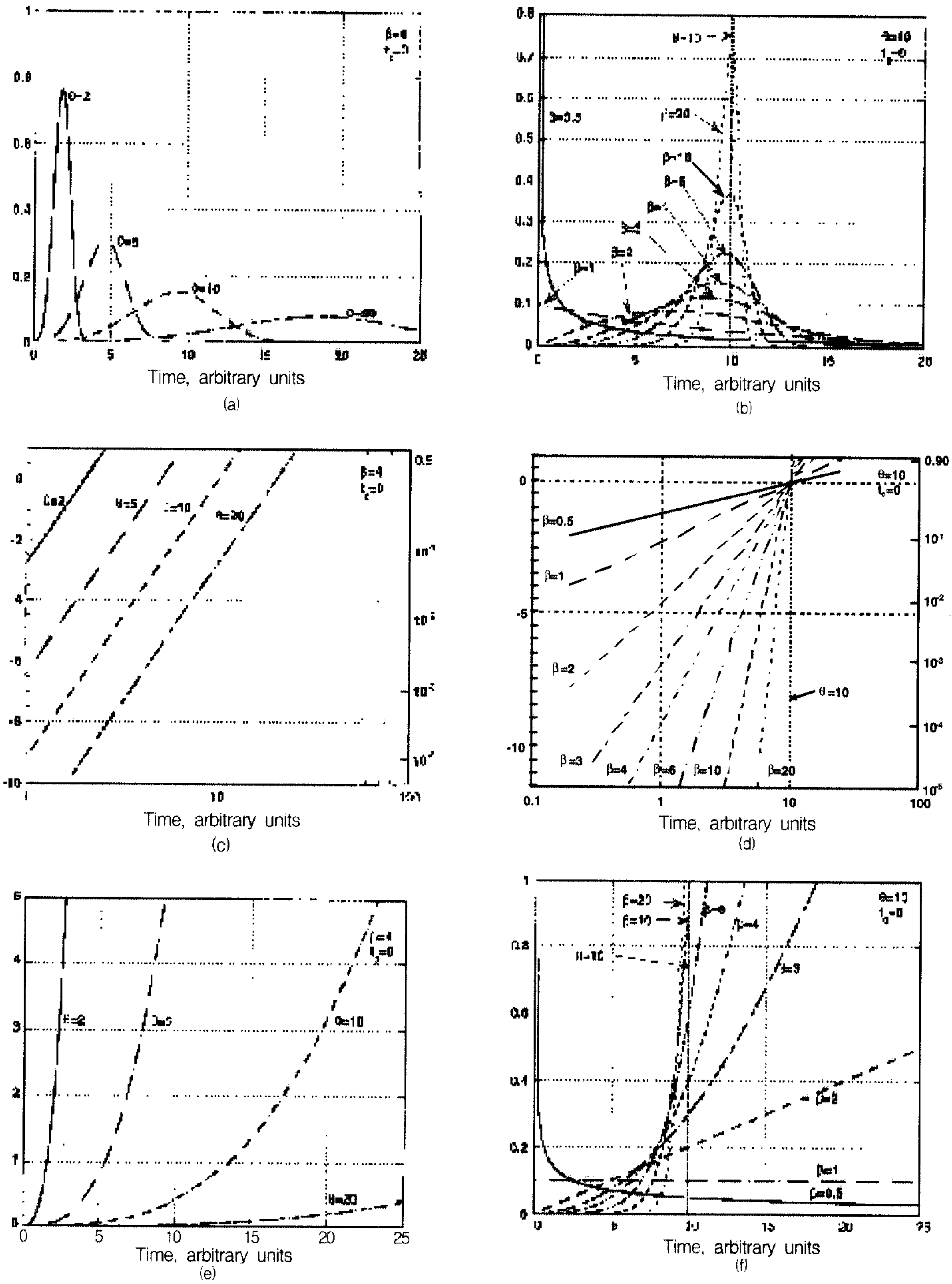

Fig. 12. (a) *f(t)* vs. time for the constant β. (b) *f(t)* vs. time for constant θ. (c) *F(t)* vs. time for constant β. (d) *F(t)* vs. time for constant θ. (e) *h(t)* vs. time for constant β. (f) *h(t)* vs. time for constant θ.

Weibull distribution the scale parameter corresponds to a probability of 0.632, which is slightly greater than the average of 0.5. Figure 12 shows Eqns. (1), (2), and (3) for constant β and constant θ. In Figure 12d it is evident that decreasing values of β increase the dispersion and consequently are associated with earlier times to failure for a constant probability. In Figure 12f when β=1 the probability of failure is independent of time. At higher

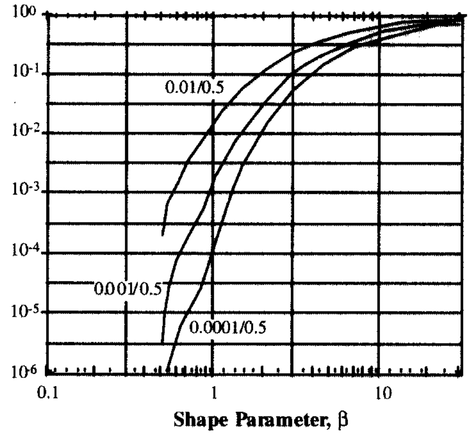

Fig. 13. Early failure ratio, t/t_μ, vs. β for 0.0001, 0.001, and 0.01 probabilities relative to mean at 0.5 probability. From Staehle.[8)]

values the probability of failure increases with time.

The location parameter, t_o, is often taken as an initiation time. However, the location parameter is primarily a fitting constant having the same dimensions as the scale parameter. Nonetheless, the location parameter can be taken as an approximation to initiation although initiation itself is a statistical quantity.

The shape parameter, β, often called the Weibull slope, describes the dispersion of data. Lower values of β correspond to broader dispersions of data. Figure 13 shows the effect of the shape parameter on the early failure ratio, which is t/t_μ (ratio of time to failure at a selected probability to the time to failure for the mean), for several populations of specimens. This figure shows that while a shape parameter of 4 produces a difference of about a factor of 10 between the mean (probability of 0.5) and a 10^{-4} probability, a shape parameter of unity produces a factor of about 10^{+4}; thus, as the shape parameter decreases, the dispersion of data increases.

While Eqns. (1) and (2) often provide excellent correlations, as shown in Figure 2, they provide no physical bases for relating to corrosion failures or the modes shown in the mode definition described in CBDA step #3. Staehle and Gorman[22] and Staehle[8] have suggested that the Weibull parameters could be modeled by determining their dependencies upon the principal variables as shown in Eqns. (4), (5), and (6).

$$\theta = A_\theta \left[H^+\right]^{n_\theta} [x]^{p_\theta} [M]^{r_\theta} \sigma^{m_\theta} e^{\frac{E-E_{o\theta}}{b_\theta}} e^{-\frac{Q_\theta}{RT}} \tag{4}$$

$$\beta = A_\beta \left[H^+\right]^{n_\beta} [x]^{p_\beta} [M]^{r_\beta} \sigma^{m_\beta} e^{\frac{E-E_{o\beta}}{RT}} e^{-\frac{Q_\beta}{RT}} \tag{5}$$

$$\frac{1}{t_o} = A_{t_o} \left[H^+\right]^{n_{t_o}} [x]^{p_{t_o}} [M]^{r_{t_o}} \sigma^{m_\theta} e^{\frac{E-E_{o t_o}}{b_{t_o}}} e^{-\frac{Q_{t_o}}{RT}} \tag{6}$$

where:

A = constant
H^+ = hydrogen ion activity
x = concentration of active species (possibly more than one)
M = metallurgical factor such as associated with sensitization
σ = stress
E = electrochemical potential
E_o = electrochemical constant being either the corrosion potential or the thermodynamic equilibrium potential
b = electrochemical constant
Q = apparent activation energy
R = gas constant
T = absolute temperature
t = time
n, p, m, r, q = constants

The dependence of the statistical parameters upon temperature is shown in Figure 14 for Type 304 stainless steel in $MgCl_2$ solutions and for Alloy 600 in high purity water.8,23,24 Here, θ and t_o follow a conventional *1/T* dependence. However, the trends of β are opposite. In Figure 14a, β increases with 1/T and in Figure 14b β decreases with 1/T. The dependency of β seems not to follow simple patterns, and the complexity of the dependencies of β have been discussed by Staehle.[8] For example, it might be assumed that β would increase with the increase in magnitude of the stressor, i.e. the higher the temperature or stress, the less dispersion in the data. Comparing the trends in β for Figures 14a and b shows that the proportionality to stressors does not always occur. Another possible pattern for β follows from the tendency of surface-related corrosion processes to behave in a Poisson sense with β=1; whereas, processes that follow accumulation patterns would follow higher values of β as discussed in connection with Figure 15. Still another pattern is associated with the agglomeration of data from different heats which produces lower values of β as described by Staehle.[8] Thus, while the scale and location parameters tend to follow patterns that follow well known correlations, the shape factor does not.

While the correlations such as in Figure 14 indicate different functional dependencies, this Figure also shows that the range of values is different. When β is in the general range of unity, the Weibull distribution is reduced to the exponential distribution that also describes Poisson

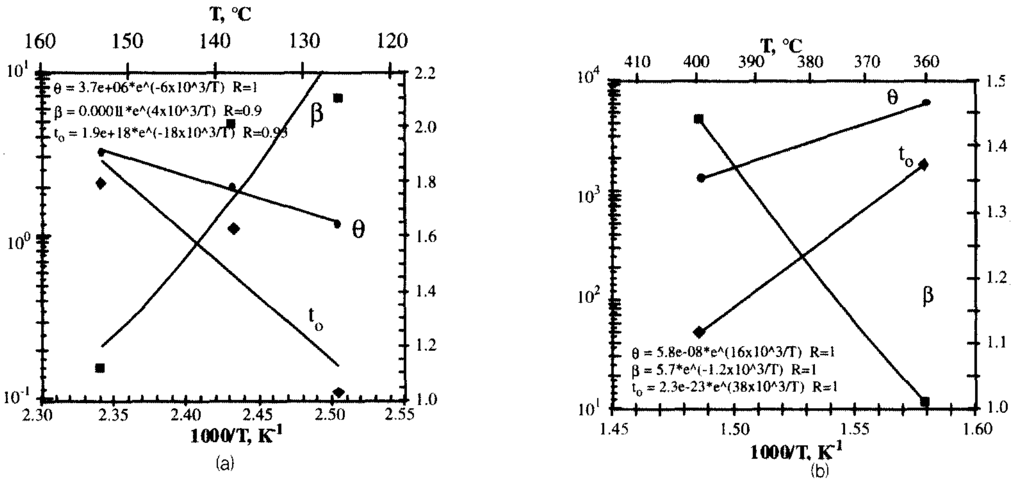

Fig. 14. (a) θ, t_o, and β versus 1/T for Type 304 stainless steel exposed to concentrated $MgCl_2$ solutions. Adapted from Shibata.[23] (b) θ, t_o, and β versus 1/T for the LPSCC of Alloy 600MA exposed to high purity deoxygenated water containing a hydrogen concentration of 10-60 cc H_2/kg H_2O. Adapted from Webb.[24)]

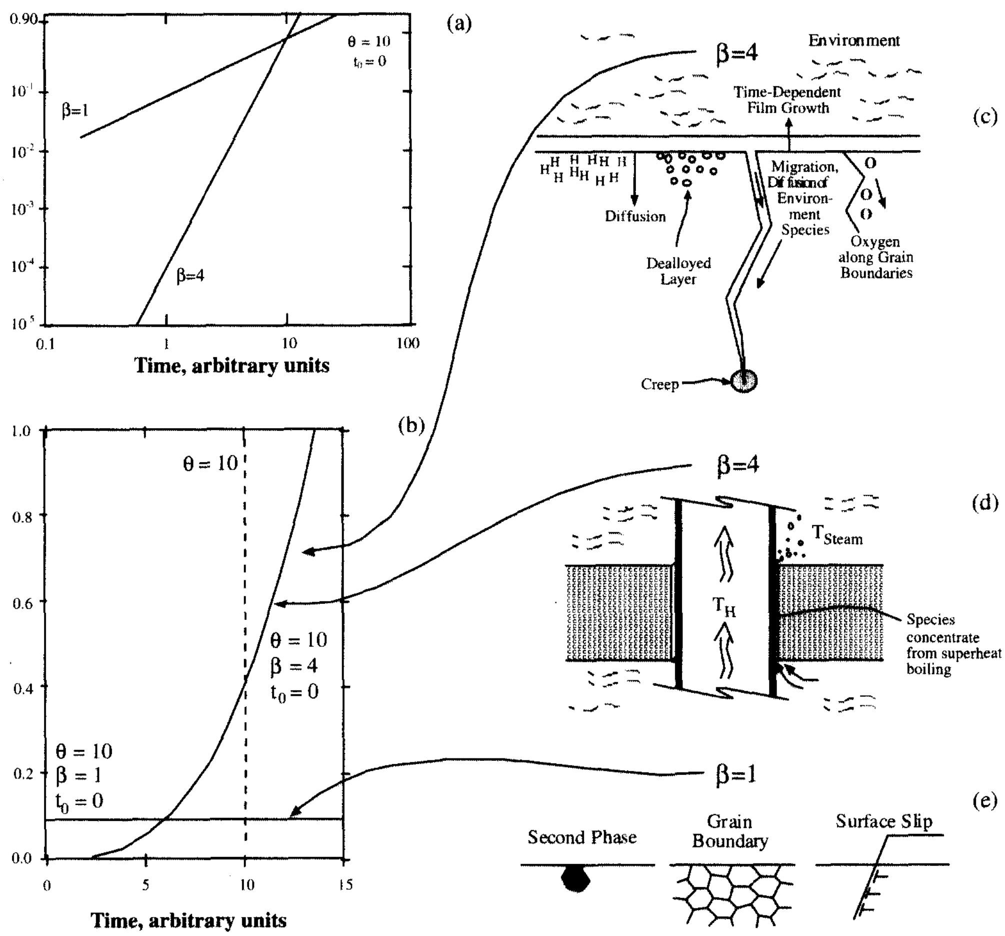

Fig. 15. (a) cdf for β=1 and β=4. (b) Hazard functions vs. time for β=1 and β=4 cases at θ=10 and t_o=0. (c) Possible contributions in the metal substrate for a growing SCC to the accumulation case for β=4. (d) Possible contributions to the accumulation case β=4 from exterior of the metal surface with a superheated tube support geometry as in Figure 3. (e) Possible contributions to the β=1 case from surface processes. From Staehle.[8)]

behavior. A β of unity relates fundamentally to processes that depend on the surface. A higher value of β involves other physical processes and tends to indicate that the physical processes that are critical are related to accumulation of some quantity. The relative effects of β of unity and of four are shown in Figure 15. Particularly relevant to the role of β is the dependence of h(t). When β=1 the h(t) is independent of time. When β=4, h(t) is low but rises rapidly above $\theta/2$. Such a pattern suggests the critical action of accumulation processes.

One of the important results of considering the CBDA step of statistical framework is to recognize that the earliest failures relative to the mean, as in Figure 13, depend on the values of β. Low values, as shown in Figures 12 and 15, indicate that a broad dispersion of data can be expected, and the earliest failure can occur in times much shorter than the mean value. In fact, by the time that the Weibull characteristic occurs, a θ = 0.632 fraction of elements have failed, which is generally much greater than can be tolerated.

Eqns. (4), (5), and (6) together with Figures 14 and 15 suggest that the Weibull parameters can be modeled with the principal variables of SCC. However, there is no formal basis for these relationships. Figure 15 suggests that the physical basis for β=1 is that of surface processes; for β=4 the physical basis is related to accumulation processes as is indicated by a low value of the hazard function below about $\theta/2$ with a sharply increasing value thereafter. Further β does not seem to follow regular patterns.

Future research that should be undertaken relative to statistical definition is the following:

a. Developing physical bases for the statistical parameters. Of particular importance, since it affects the earliest failures, is improving the understanding of β. While the basis for β = unity is generally appreciated in terms of Poisson processes at the surface, higher values of β are not so well understood. Further, the varying dependencies of β on variables such as temperature shown in Figure 14 are not understood.
b. Multiple step processes are not understood. For example, if the first step is a pit but the next step is SCC as it is initiated by pitting, this sequence is not well understood, although Wei[25] has advanced this understanding significantly.

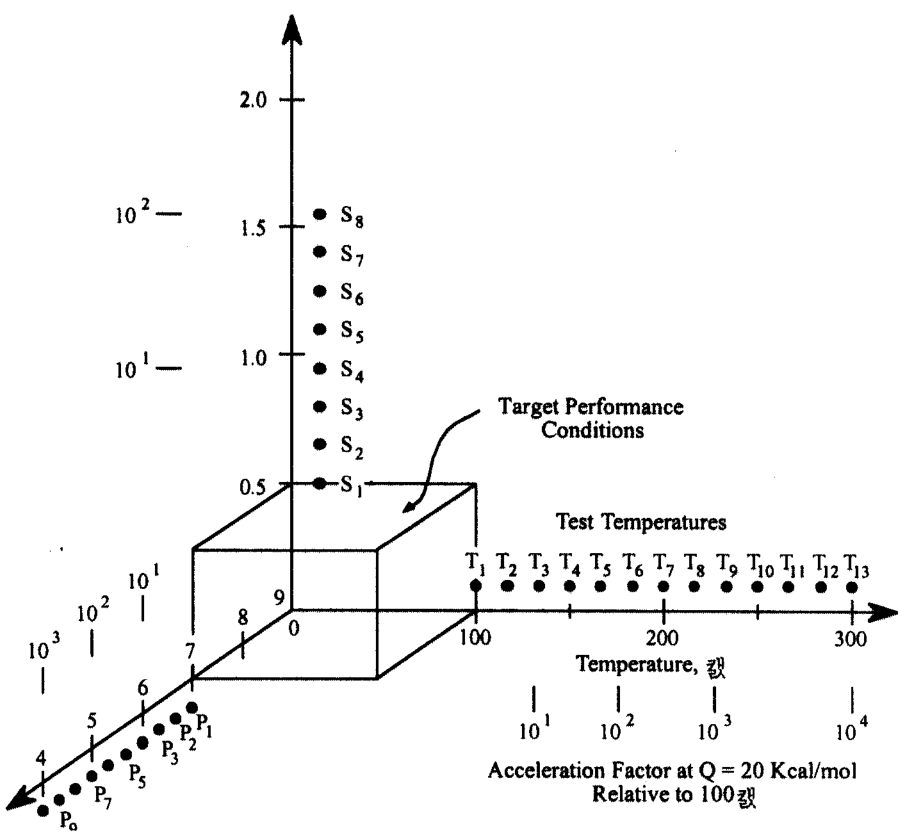

Fig. 16. Schematic view of accelerating variables of tem- perature, stress, and pH relative to a box of expected conditions. Each coordinate shows the magnitudes of acceleration.

c. Integrating the statistical properties of local environments with those inherent in the modes needs substantial attention and is necessary for predicting the combined influences of environments and materials.

This research will provide great benefits for predicting the occurrence of early failures in systems where such failures are critical.

3.7 Accelerated testing

Accelerated testing involves conducting tests in relatively short times to assess behavior at relatively long times. Such accelerations often involve conducting tests at temperatures above the nominal expected temperatures and taking advantage of the more rapidly obtained results. Other accelerations may be achieved by higher concentrations of chemistry, different electrochemical potentials, higher stresses, cold work, and others as appropriate. The most important consideration of accelerated testing is assuring that the mode of corrosion expected in the operation of equipment is the same as that in the accelerated test. In addition, it is necessary to assure that the full set of submodes which are appropriate to an application, as shown in Figure 10, is accounted for.

Accelerated testing commonly utilizes an equation like that of Eqn. (4) to obtain long term data in a relatively short time. For example if a submode such as alkaline SCC shown in the mode diagram of Figure 10 needs to be investigated for application at 300°C, then tests might be conducted at 360°C. Such an acceleration for an activation energy of 40 Kcal/mol permits conducting a test for relatively short times to assess the occurrence in 60 years. Other common accelerating variables are stress and environmental composition such as pH. The three variables commonly used for accelerated testing and their accelerating factors are illustrated in Figure 16.

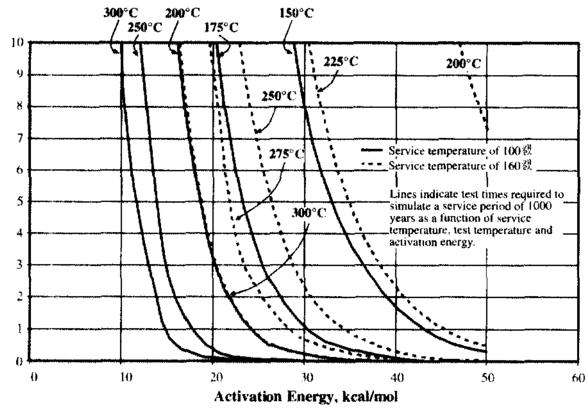

Fig. 17. Time for testing versus activation energy for different testing temperatures where the objective is determining life at 1000 years for the cases where surface temperatures are either 100 or 160°C.

The time required for accelerated testing depends on the activation energy. Figure 17 shows the effect of activation energy on the time required for testing for accelerating results of interest for 100 and 160°C nominal operating temperatures when the design life is 1000 years. What is apparent here is that processes with activation energies in the range of SCC, e.g. 30 to 50 kcal/mol can be accelerated and predict performance in relatively short test times. However, processes such as pitting and general corrosion with activation energies in the range of 5 to 15 Kcal/mol require much longer times.

Accelerated testing also depends on the values of

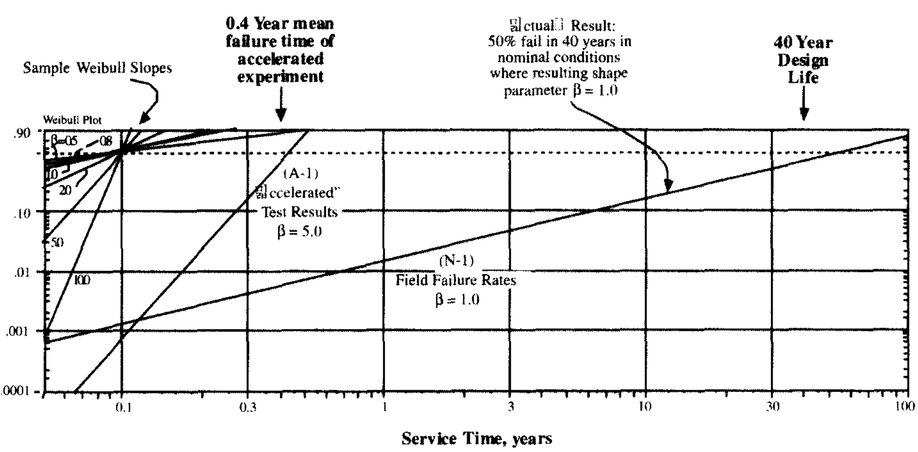

Fig. 18. Schematic comparison of hypothetical actual field results with hypothetical accelerated testing using cumulative distribution versus time. N-1 with b=1.0 is the nominal field failure rate. A-1 with b-5.0 corresponds to an accelerated test. N-2 is the desired field failure rates that does not exceed 0.001 cumulative failures in 40 years. A-2 has the same slope as A-1 for a mean life of 40 years; A-3 has the same slope but with 0.001 failures in 40 years.[8]

statistical parameters. Field failures often exhibit values of $\beta = 1$ as shown in Figure 18. Such a value of β results from the use of many heats and a wide range of environmental conditions. However, accelerated tests are usually conducted with a minimum number of heats, often one, at more intense stressors, e.g. high temperatures, and in well controlled environments. Results from such accelerated testing are shown schematically also in Figure 18.

When the Weibull characteristic of the field data and the accelerated testing are compared, the accelerated test has been successful achieving an acceleration of about 100x. However, by the time 0.632 fraction of elements has failed in the field, the equipment has already failed. In fact, failure of the component is more likely defined as occurring somewhere between 0.0001 to 0.01 probability. At these low fractions Figure 18 shows that there is little difference between the time-to-failure for the field and the laboratory results. Thus, the value of accelerated testing depends on the shape factor of the accelerated test compared with that of the field performance.

Future research that should be undertaken in support of accelerated testing is the following:

a. Determining the mechanistic basis of activation energies, exponents, and reaction orders of interest to extrapolating the important modes and submodes of corrosion.
b. Determining means for extrapolating data for long times assuming that environments and materials can be maintained constant.
c. Developing means for extrapolating where the shape parameters of the accelerated tests may be different from those expected in the field.

Improving the science of accelerated testing will provide great benefits to assuring the reliable performance of equipment.

3.8 Prediction

The step of prediction involves incorporating the inputs from the first seven steps of the CBDA into a format that permits predicting the performance of a component. While this idea is relatively simple, the implementation is quite complex. First, any component is likely to sustain failure by several different processes as shown in Figure 5. Further, the local environments may be quite complex as illustrated for the heat transfer crevices in Figure 4. Third, the nature of the shape parameter is not generally known *a priori*. Further, complex equipment is exposed to a number of evolutions that affect predictions including steady state, startup, upsets, and changes of the environment and material with time.

One approach to predicting behavior where multiple mode-location processes occur is to combine the probability of failure for each according to Eqn. (7):

$$F(t)_T = 1 - (1 - F(t)_1)(1 - F(t)_2)\cdots(1 - F(t)_n) \qquad (7)$$

where:

$F(t)_{T,\ 1,\ 2,\ n}$ = Failure probability for total, first, second and n^{th} mode-location cases

Figure 2 shows that, in fact, such a aggregation can

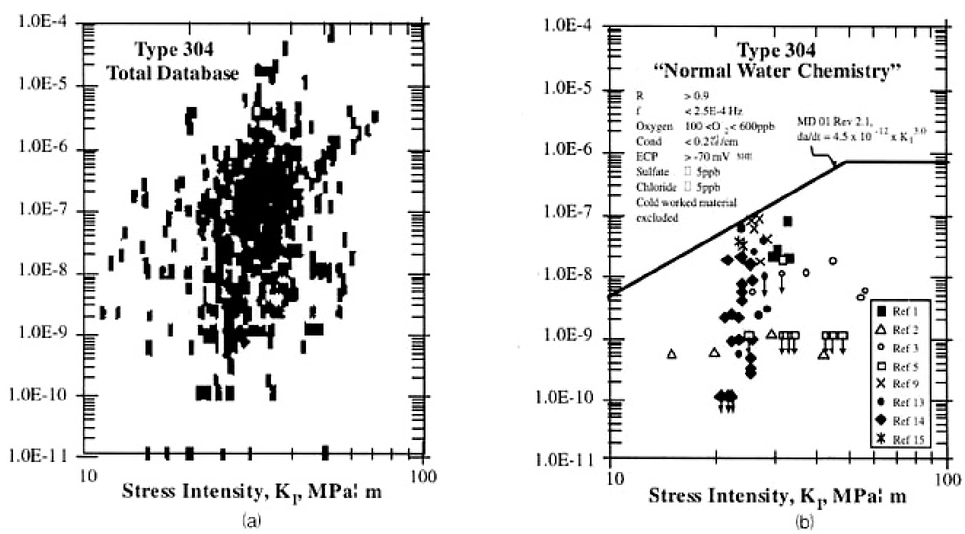

Fig. 19. (a) Available data for crack growth rates in a data base for sensitized Type 304 stainless steel exposed to boiling water nuclear reactor (BWR) environments. (b) Censored data applicable to the conditions noted on the figure. Bonding line shown. From Jansson and Morin.[26)]

be used, as in Eqn. (7),and is shown as the upper line which combines all the component mode-location cases to produce a total probability of failure. Using the approach of Eqn. (7) assumes that the failures associated with the separate mode-location cases are independent.

The reality of using data for prediction is shown in Figures 19 and 20. Figure 19 shows results from studies of crack growth rates for stainless steels exposed to oxygenated pure water at 288°C from work of Jansson and Morin.[26] When the data from Figure 19a are censored, Figure 19b results. In both cases the dispersion of data is large. These data are generally treated by developing a bounding curve and basing design thereon as shown in Figure 19b.

Figure 20 shows results from testing stainless steels in boiling $MgCl_2$ where the data are produced from studies of effects of temperature and stress as shown in Figures 20a and b.[27] The data for effects of temperature and stress were taken from multiple authors. From these data activation energies and stress exponents are determined as shown in Figures 20c and d. The data from both dependencies on temperature and stress exhibit large dispersions. Further, data for activation energies and stress exponents are quite disperse. As with Figure 19, only a bounding approach could be used to predict such data.

The purpose of showing Figures 19 and 20 is to indicate that predicting performance is often based on evaluating prior work or the work from multiple laboratories. The array of results from multiple laboratories avoids the limitations of data obtained by a single heat in one laboratory. Such an array is similar to the array of heats shown in Figure 7.

There are many other issues in prediction that are not considered here. For example, it is often considered by designers that a "leak before break" criterion can be applied in the case of corrosion failures. In fact, this is

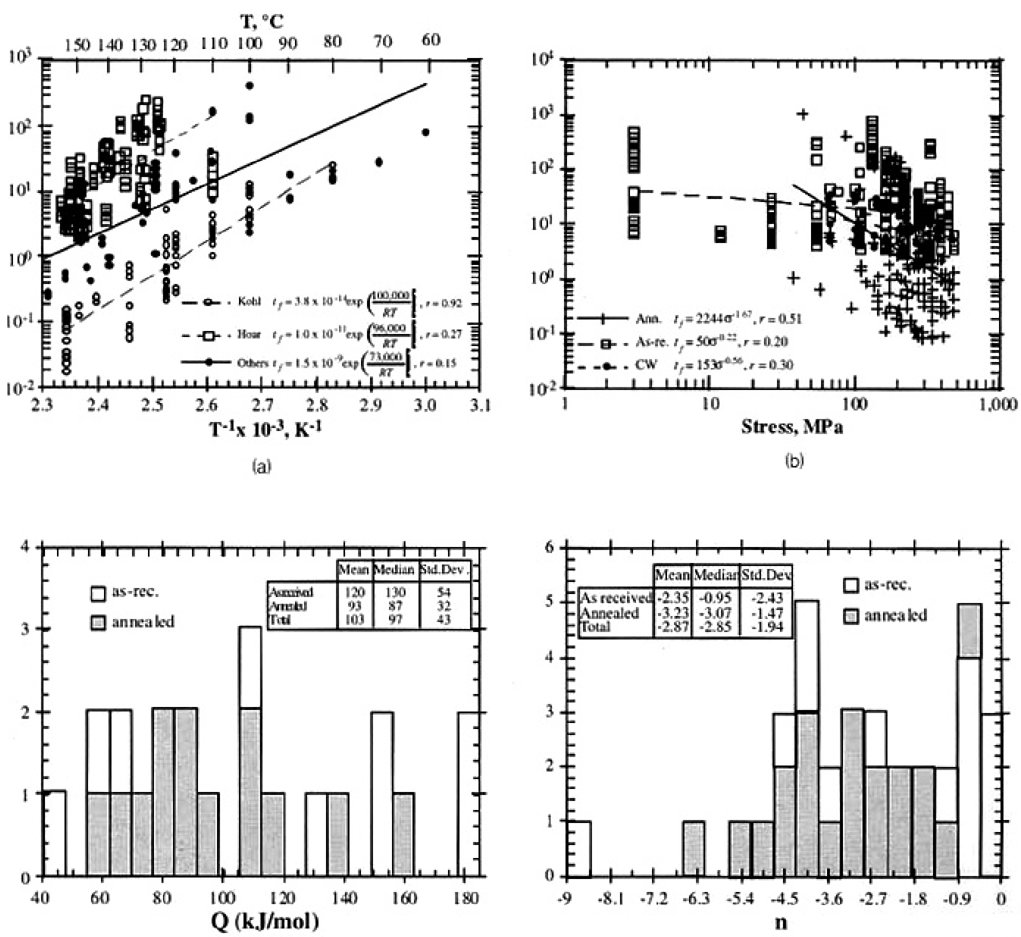

Fig. 20. Time-to-failure vs. 1/T for 23 sets of data for stainless steels in boiling 35 to 45% $MgCl_2$ solutions at open-circuit conditions. (b) Time-to-failure vs. stress for 40 sets of data measured for stainless steel in 42% $MgCl_2$ at open-circuit conditions. (c) Distribution of stress components for as-received and solution-annealed stainless steels in 42% $MgCl_2$ solutions. (d) Distribution of stress components for as-received and solution-annealed stainless steels in 42% MgCl2 solutions. From Jiang and Staehle.[27]

often a bad assumption for reasons that can be readily demonstrated. Further, the location of corrosion damage is important. For example, SCC in a long weld is more important than a random location not at a weld since the weld often has a much lower K_{IC} and lower K_{ISCC}.

Future research that should be undertaken in support of the CBDA step of prediction includes the following:

a. Development of improved activation energies and stexponents.
b. Improved modeling that includes the seven principal variables affecting corrosion.
c. Modeling that incorporates the first seven steps of the CBDA.
d. Improved analysis of "leak before break" assumptions.

Improvements in modeling prediction will provide benefits in more reliable and more economical equipment.

3.9 Feedback

Often it is not possible to predict performance exactly for many reasons including problems with specifying the local environments as well as with the initial lack of investment in adequate materials and design. This lack of capacity to predict is generally accommodated by monitoring performance and by periodic inspections. These provide feedback to the CBDA step #10 concerning modifications.

Monitoring performance includes methods for measuring:

a. Process parameters such as temperature, pressure, flow.
b. Process chemistry including concentrations, oxidizing capacity, conductivity, and special species of interest.
c. Degradation processes using linear polarization, electrochemical noise, acoustical emission, corrosion potential.

Periodic inspections include measuring:

a. Extent of corrosion such as depth of pitting, occurrence and depth of SCC and CF.
b. Buildup of deposits and their chemistries.
c. Cleaning and removing adverse deposits.
d. Conducting non-destructive measurements of crack depth, internal degradation, distribution of cracks.
e. State of monitoring equipment.
f. Removal of materials to determine extent of damage.

Future work that should be undertaken in the step of feedback includes:

a. Improvements in the robustness of monitoring equipment.
b. Improvements in the sensitivity of NDE methods especially in determining the existence of early penetrations.

Monitoring provides benefits by filling the gaps left by imperfect predictions or that result from genuine surprises. Monitoring also provides benefits that provide the bases for improved designs, materials, and methods of operating and thereby improving the reliability and lowering the cost of equipment.

3.10 Modification

As information is accumulated from the feedback step of the CBDA, the immanence of failure, or indeed the occurrence of failures, may become apparent. At this point, modifications are required in the materials of construction, fabrication of materials and components, design, environment, operation, or monitoring. Actions to mitigate damage include:

a. Replace damaged materials.
b. Change the design to eliminate undesirable features, e.g. crevices.
c. Install improved materials.
d. Add inhibitors to the environment,
e. Change the chemistry of the environment
f. Improve the cleaning process
g. Change components in the system that are causing failures.

Future work that should be undertaken in the step of modification includes:

a. Modeling and experimental research that anticipates the likelihood and rate of failures.
b. Developing alternative approaches in design and operations that account for inevitable failures.

The modification stage provides benefits of improving originally imperfect designs and methods of operation.

4. Integration of perspectives and CBDA

The ten perspectives on corrosion are essentially boundary conditions to the extent of research that can be funded and a description of who actually benefits from the research. These perspectives should also provide the corrosion community with realistic perspectives on what the design/operations community is inclined to support. Further, while federal agencies are inclined to take a broader view in the area of corrosion, they still tend to ask questions of relevance.

The CBDA describes the important steps in predicting corrosion-related performance. Using this framework should clarify the incentives for conducting research as it applies to the individual steps.

It is fashionable to argue that predictions are not possible without a complete understanding of mechanisms and that modeling needs to be derived from first principles. In fact, all of the models that presently exist for corrosion incorporate a sufficient number of adjustable constants that the theories are, in fact, neither useful nor fundamental. For reliable predictions, results from experiments need to be incorporated into predictions. Developing models from first principles requires very long times; further, small changes in environments usually produce such variations that the models from first principles are no longer applicable.

It is popular to argue that modeling from first principles provides more general predictions than experimental work which is suggested to be too narrowly defined. In fact, experimental work generally provides very useful insights into failure processes and is, by far, more credible than models derived from first principles, which are usually infested with so many adjustable constants that the models have little practical validity. Further, in the construction of first principles modeling, what is chosen for first principles is subject to the limitations of the investigator who often has little knowledge of actual behavior.

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