Managing Our Aging Physical Systems: A Corrosion Perspective

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Modern society relies heavily on complex, intertwined, physical infrastructures for their smooth functioning. Aging of the materials in the physical infrastructures is not necessarily related to service life, but to the increasing probability of failure—the hazard rate. This paper provides a holistic perspective of the hazard rates of conventional, metallic materials. Data-based approaches to estimating the hazard rate over long periods are constrained by available data and the assumption that failure modes remain unchanged. Aging structures may suffer from failure modes that change with time and some that are unanticipated—the problem of unknown unknowns. Mechanistic understanding of failure modes is essential to predicting hazard rates of aging systems. Researchers on the aging of biological systems have enumerated 12 hallmarks of biological aging. However, unlike the biological community, the engineering community has not systematically tackled the hallmarks of aging, although much is known about aging of materials. This perspective explores the opportunities for systematizing our understanding of aging physical systems and develops a framework for their interconnections. An approach is proposed to tackle the problem of the unknown unknowns.

KEY WORDS: aging, Bayesian, life prediction, microstructure, probability, stress corrosion cracking, unknown unknowns

INTRODUCTION

Modern society relies on a complex web of engineered physical systems that can be taxonomically classified as infrastructure (consisting of many systems), systems, subsystems, components, and materials. Many types of physical infrastructure include as-built or construction (roads, bridges, and buildings), energy (fuel production, transmission, distribution, and generation), transportation, communication, and manufacturing. The infrastructure may involve systems (e.g., power plant), subsystems (e.g., reactor), and components (e.g., steam generator, pumps, etc.). Ultimately, these systems depend on materials of various compositions, microstructures, and atomic/molecular configurations. The materials may undergo microstructural changes as a function of time and react to environmental/process conditions that may vary over time. The concerns about aging physical systems are not new. For example, the Aloha Airline failure in 1988 unleashed a large program on aging aircraft corrosion within the civilian and defense aircraft communities. There is an increasing concern about the aging of other infrastructure due to a combination of age-related performance reduction and climate-related external forces. The American Society of Civil Engineers issues a report card on the U.S. infrastructure every 4 y (https://infrastructurereportcard.org) that grades the state of various physical infrastructures. The latest such report, issued in 2021, graded the U.S. infrastructure as a C-minus and suggested that it has taken 20 y to get out of the D-grade. A $2.59 trillion investment (about 2.5% to 3.5% of gross domestic product [GDP]) was estimated to be necessary to raise the grade to a B. The U.S. National Academies has published reports on aging avionics[1] and critical infrastructure[2] to address defense-related infrastructure concerns. Concerns also abound about the aging fleet of nuclear power plants (many U.S. nuclear power plants will soon come to their second cycle of license renewal) and the fate of nuclear waste. The U.S. Nuclear Regulatory Commission has issued reports on the aging of reactors, called the GALL report,[3] that identify failure modes of various reactor components and spent fuel storage and transportation systems.[4] Aging life extension has also been a theme in the United Kingdom and Norwegian offshore oil and gas industry.[5] Although European infrastructure assessment does not have a grading system, it is estimated that 4.7% of GDP is necessary to meet the gaps in infrastructure. Worldwide, the estimate ranges from 3.9% to 9.7% for infrastructure investment (https://cepr.org/voxeu/columns/addressing-europes-infrastructure-gaps-fiscal-constraints-and-planning-capacity). Extending the performance of materials and systems also enhances the sustainability of society.[6-8]

Materials scientists continue to develop novel metallic materials for corrosion resistance[9-10] and novel methods to manufacture components from them.[11] It has been recognized that significant opportunities exist for improving the sustainability of metals used in our infrastructure.[12] The innovations in materials development, especially using computational tools and high throughput data collection processes, promise a great future for tailoring materials to our ever-expanding needs.[9,13-15] Although, the modern-day computational tools were not available to the early alloy developers, such alloy development was not without key metallurgical insights. For example, the development of alloy C-4 (UNS N06455[(1)]) invoked critical electron vacancy concepts to avoid precipitation of deleterious μ phase.[16] Integration of historical insights into alloy development

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with new modeling tools will usher in the age of materials developed from the atom up while still realizing commercial viability. Regardless of promising future materials, the current infrastructure is dominated by conventional alloys manufactured through essentially conventional methods. This situation will likely continue for the foreseeable future, with incremental improvements in alloy composition and manufacturing methods for major components/structures and novel materials used for niche applications with unique requirements. This is partly because of the time and resources required to scale up materials, develop appropriate data to meet the various regulatory requirements and commercialize them. For example, Ni-Cr-Mo alloys were first developed in 1931 and have seen a slow, incremental evolution to the present time.[17-18] High-strength low alloy steel tubulars continue to evolve with new thermos-mechanically processed steels coming to the fore in the last two decades.[19] More importantly, it is extremely difficult to replace major infrastructure in toto because of issues such as siting, environmental permitting, and licensing. Therefore, we can expect continued use of conventional, bulk alloys for the next few decades with the attendant aging issues. Aging of materials is a broad area of study and no single review can provide a comprehensive view of the field. This perspective's objective is to examine the various issues involved in the aging of metallic conventional materials subject to corrosion and gaps in our understanding. In metallurgy, aging connotes prolonged exposure to temperatures, typically less than $0.5T_{melting}$. Here, the word "aging" is used beyond the narrow sense of the thermal treatment effects and includes the whole set of circumstances leading to a time-dependent corrosion and cracking resistance of a material. This paper is focused on metallic materials, but the underlying philosophy is the same for other material types.

1.1 | Definition of Aging

An aging system is commonly understood to exceed its original design life. However, this is not a helpful definition as we would like to know the rate of aging before the design life is exceeded, to intervene on time. Furthermore, studies of offshore oil and gas systems in the United Kingdom and Norway have not found a correlation between service life and leak frequency.[5] This has led to a definition of aging as: "the effect whereby a component suffers some form of material deterioration and damage (usually, but not necessarily, associated with time in service) with an increasing likelihood of failure over the lifetime."[5] Thus, a more rigorous definition of aging can be derived from the hazard rate h(t), defined as

$$h(t) = \frac{f(t)}{R(t)} = \frac{f(t)}{(1 - F(t))} = \frac{f(t)}{\left(1 - \int_0^t f(t)dt\right)} \quad (1)$$

where f(t) is the probability density function of failures as a function of time, R(t) is the reliability at any given time, and F(t) is the cumulative probability of failure at any given time. From Equation (1), we can define a cumulative hazard rate:

$$H(t) = \int_0^t h(t)dt = -Ln(1 - F(t)) \quad (2)$$

Essentially, the hazard rate is the failure probability at any given time, given that the system has survived until that time. We would consider an aging system as one with an increasing hazard rate with time, i.e., the failure probability increases with time after a certain time of survival. It is apparent from Equation (1) that the hazard rate depends on the probability density function of failures. Some examples of the variation of h(t) with time shown in (Table 1).[20-21] As the common saying goes, "Age is just a number." However, it is a number related to the hazard rate, not the chronological age.

In many engineering systems, the hazard rate may initially decrease with time (infant mortality), level out (constant failure rate), and then increase with time (for frustrated consumers, this often seems to coincide with the end of the warranty period), creating the bath-tub curve of reliability. The hazard rate associated with this phenomenon can be characterized by a combination of probability distributions or the highly flexible, Weibull distribution with varying scale parameters. For leaks or fractures, we would like to know the time dependence of the maximum values of a distribution and an extreme value distribution of type I (Gumbel) may be appropriate. However it is defined, the function, f(t), is seldom available to us a priori. We can derive it from (1) accelerated testing in the laboratory or (2) observing inspection data or previous failures. If we have the hazard function from both laboratory and field data and if the h(t) vs. time slope is the same, we may be able to say that the laboratory test replicates the features of field exposure tests but we cannot be sure of this without knowledge of the mechanisms behind both. However, neither approach assures us that the probability density function will be the same in the

Table 1. *Hazard Rates for Different Probability Distribution Functions*

f(t)	$\frac{dh(t)}{dt}$
Normal distribution	> 0
Lognormal distribution	Initially > 0; then < 0
Exponential distribution	= 0; h(t) is constant with time
Weibull distribution	Depends on the scale factor, β If $\beta < 1; \frac{dh(t)}{dt} < 0$ If $\beta = 1; \frac{dh(t)}{dt} = 0$ If $\beta > 1; \frac{dh(t)}{dt} > 0$
Extreme value type I (Gumbel)	$\frac{dh(t)}{dt} > 0$ for maximum values if t is less than the location factor and $\frac{dh(t)}{dt} < 0$ after it exceeds the location factor. $\frac{dh(t)}{dt} > 0$ for minimum values

future. For example, the spatial distribution of external pitting on a pipeline has been modeled using excavation inspection data.[22-27] Still, the time distribution is difficult to derive from data as it requires matching the inspection data over several periods for the same pipeline system. Often, a corrosion growth rate involving a power law function is assumed,[24,28-33] but this is applicable mainly to active growth of corrosion under transport control. It does not apply to localized corrosion or stress corrosion cracking (SCC), where significant gestation time related to precursor events (strain rate history, dealloying, passive film growth, metastable pitting, etc.) may be involved. For systems that cannot be inspected periodically (e.g., nuclear reactors and radioactive waste disposal containers), a data-based approach to developing hazard function is untenable and must be augmented by suitable predictive models. In such cases, a theoretical model is developed from short-term data of fundamental parameters governing a failure mode.

1.2 | Aging of Biological vs. Physical Systems

Human beings have been interested in the aging problem, especially the postponement of aging, from the dawn of recorded civilization. Every culture has stories about the search for an elixir of life that promised eternal youth. However, the scientific study of biological aging started coming into its own only at the early 21st century,[34-37] with over 300,000 papers published in the last decade alone.[35] Thus, it is interesting to compare the approaches used to assess the aging of biological systems with that of physical (engineering) systems. Aging of biological systems is also not always correlated to calendar age as different organisms age vastly differently.[34,38] The standardized mortality rate (mortality rate divided by the mean value) of humans increases dramatically with calendar age, a fact used by actuarial tables. However, the standardized mortality rate of a common lizard is relatively insensitive to calendar age through most of its life, and that of white mangrove trees decreases dramatically with calendar age. The mortality rates of other organisms go through either a minimum (roe deer) or a more complex change (alpine swift) with calendar age. Explanation of such diversity in hazard rates of biological systems requires a fundamental understanding of differences in defect generation and repair at different levels of an organism and even a community of organisms (as one metallurgist put it, "materials and people are similar, it is our defects that make us interesting."). There has been an attempt to identify the fundamental hallmarks of aging of organisms (not including plants), Figure 1.[35]

These hallmarks in biological systems were assembled from studies on aging across a range of biological organisms and grouped into different scales in the architecture of an organism. They also interact in complex (and controversial) ways to produce aging symptoms at a macroscopic level. A similar question should be posed to materials scientists dealing with aging structures. What are the fundamental signs of aging in materials and how would they manifest at the structural level? Indeed, such an approach was proposed by Staehle,[39] who developed a scenario linking various microprocesses occurring under various domains (essentially size scales) of a system. This approach is discussed in the *Unknown Unknowns* section.

ASSESSING AGING SYSTEMS SUBJECT TO CORROSION

2.1 | Data-Based Approaches

As mentioned previously, the approaches to assessing aging of materials is book-ended by the data-based and model-based approaches. However, there is a spectrum of approaches involving a combination of the two. Indeed, one could argue that there is no pure data-based approach because even when we select some data to model or select a test method to obtain that data, we have a mental model of how materials behave. Data-based approaches can be powerful aids in collecting and organizing data, but extrapolation beyond the time frame of data collection is uncertain. Nevertheless, they can provide a sense of the hazard rate of a system. An example is shown in Figure 2, where the Log (cumulative failure probability) is plotted against log (equivalent full service power years [EFPY]).

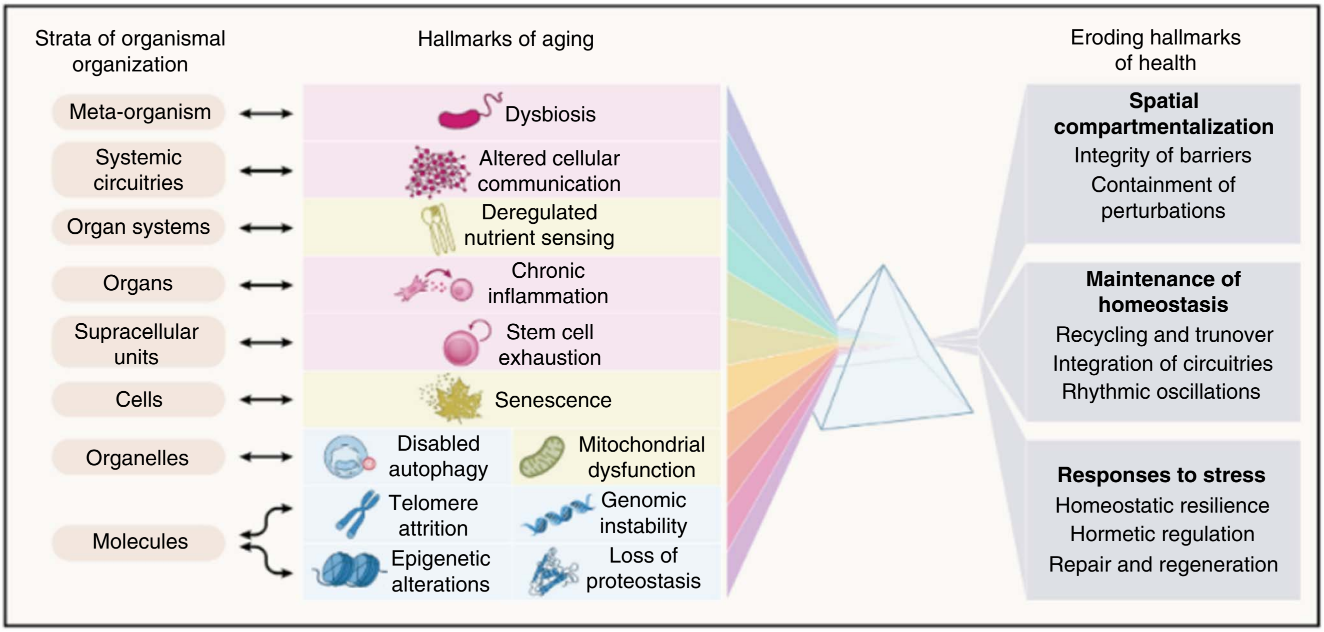

FIGURE 1. *Hallmarks of aging in biological systems.*[35]

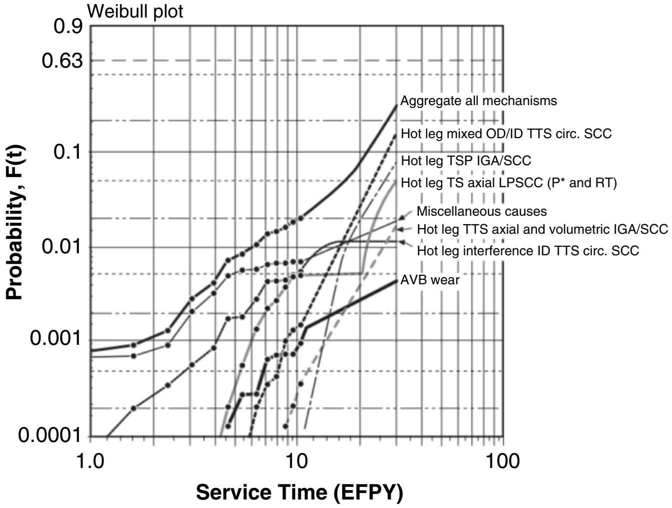

FIGURE 2. *Weibull plot of SCC in Alloy 600 mill annealed in a steam generator of pressurized water reactor.*[41]

Kowaka, et al., have suggested that if the hazard rates of an accelerated test match that in service, the accelerated test provides a way to simulate a longer time frame.[21] The Weibull slopes of different failure modes of Alloy 600 mill-annealed tubing in steam generator service (Figure 2) show various β values.[39-42] It is unclear why these Weibull slopes differ for different failure modes. Thus, a comparison of hazard rates from laboratory accelerated tests to service hazard rates may not provide us with sufficient guidance.

To improve our confidence in the predicted hazard rate, we need an understanding of why the hazard rate has a certain value—the causal mechanism. Without this knowledge, we cannot confidently extrapolate from short to long time frames. Correlation is necessary, but insufficient for extrapolation.

2.2 | Mechanistic Modeling Approaches

Mechanistic models provide causal connections, assuming that they have captured the physics of the process sufficiently for the purpose. Mechanistic models can provide greater confidence in extrapolation from short to long time frames if the parameters in the model can be considered to be insensitive or only mildly sensitive to time (depending on the time frame). In this case, the time-varying parts of the model occur either in the environmental variables (chemistry, temperature, etc.) or in other material parameters whose time variance can be established by other mechanistic models involving well-characterized transport phenomena (e.g., sensitization). For example, if repassivation potential, E_{rp}, for localized corrosion can be established as a bounding value,[43-45] then its dependence on environmental variables and alloy chemistry can be characterized.[46] In such a case, the time effect is shifted from predicting corrosion behavior over time to evaluating environmental chemistry or temperature over time. In a similar fashion, mechanistic models for other phenomena, such as passive dissolution,[47] may be established as bounding parameters that contribute to corrosion potential, E_{corr}. The superposition of E_{rp} and E_{corr} can yield time-dependent prediction of localized corrosion. Similarly, the Ford-Andresen type model[48] relies on the effect of crack-tip strain rate on passive film breakdown and repassivation events, which can be measured over short times in the laboratory, thus shifting the burden of long-term prediction to understanding the time evolution of environmental chemistry, temperature, and loading history of the system. Mechanistic models also have epistemic (knowledge-based) and aleatory (data-based) uncertainties that lead to a probabilistic output. Finally, mechanistic models are not free of causal judgments that require careful assessment. For example, we assume that condensation of point defects is a precursor to pitting, local acidification leads to pit initiation, metal-salt formation leads to pit stability, etc., but these assumptions are not in the mathematical equations representing the processes. They are exogenous information that may be derived from data or just reasonable guesses. The causality issue is discussed later in this paper.

2.3 | Accelerated Test Methods

Laboratory test methods form the backbone of modeling and assessment of aging systems. Much has been written about the role of accelerated test methods in life prediction and will not be reviewed here.[49-50] However, one major challenge in assembling data in assessing aging systems is the integration of results from diverse test methods. In the early years of corrosion research, tests were mainly of the open-circuit exposure variety and constant deflection tests were the norm for SCC. Later electrochemical, slow strain rate, and fracture mechanics tests became more prevalent.[51-53] Even among these tests, there are many variations in test methods and resulting failure metrics. In principle, this diversity in results can be handled probabilistically. This is especially valid in the Bayesian context because the probability is essentially related to our confidence in a specific outcome—localized corrosion, SCC, etc. However, rationalizing literature results in a coherent probability scale can be challenging. Furthermore, designing the appropriate acceleration vectors requires prior knowledge of the system and a starting point based on a mechanistic understanding. For example, the implicit assumption in a slow strain rate test is that imposing a slow strain rate enhances local defect movement, resulting in several different microscopic processes, such as passive film breakdown, dislocation pile-up, and local stress build-up, etc. If stress, not strain rate, were an important factor, then the slow strain rate test will not be an effective method to accelerate SCC or hydrogen embrittlement. Therefore, clearly defining acceleration vectors is an iterative process of model building, data generation, and model refinement. Furthermore, uncertainty quantification is essential in utilizing laboratory data. High throughput testing[10] can help generate large quantities of data. Presently, such methods are mainly used to generate electrochemical data for corrosion estimation. Generating other types of laboratory data, especially involving high-pressure environments and crack growth measurements, is resource intensive. Therefore, most often sufficient data is not available for uncertainty quantification. This area requires significant development of accelerated test methods and evaluation of proxies for the phenomenon of interest.

2.4 | History of the System

As mechanistic models shift the time extrapolation to environmental, mechanical, and temperature histories of the system, a critical element of predicting aging system performance is understanding the historical operation of the system, starting with the original design. This became clear, for example, in the failure of an underground radioactive waste storage tank, whose primary containment leaked.[54] In this case, the most recent waste chemistry before the leak should not have been corrosive but in the early years of the tank operation, the waste was corrosive. The fluids in the early stages most likely led to pitting corrosion that was likely plugged by corrosion products and waste solids, until the solids were removed by water sluicing. The parameters for predicting the tank localized corrosion were well understood, but the history of the tank chemistry and temperature was not appreciated before failure. The history of a system not only involves changes in operating conditions throughout its life but also is influenced by decisions to mothball the system, either temporarily or permanently, or to repurpose the system. For example, in oil and gas operations, a well may be temporarily or permanently abandoned but the chemicals left in the casing and tubing (e.g., weighted brines) may influence its performance subsequently. Former oil and gas wells have been repurposed for natural gas storage[55] and CO_2 sequestration.[56] The challenge of knowing the history of an aging system becomes more acute when one wishes to know parameters, such as strain rate. For example, a natural gas pipeline may operate under a loading mode of high minimum to maximum pressure ratio (R-ratio) at relatively high frequencies, but may also episodically see low R-ratio, for example, during hydrotest[57] or blowdown operations. In a probabilistic approach, a broad probability distribution can be assumed if the limits of some parameters can be established through physical reasoning. However, broad input probability distributions lead to long tails in the predicted failure probability distributions.[58]

2.5 | Monitoring

The performance of aging systems is critically dependent on monitoring and inspection throughout the system's life. Monitoring is a periodic or continuous operation, whereby conditions leading to corrosion or SCC can be measured or probes can be used to measure the corrosion rate in nearly real time. Monitoring probes are surrogates of the actual materials in the system. Unlike monitoring, inspection involves interrogating the actual system and, therefore is done at longer intervals. However, monitoring measurements must be translated into a judgment of the system integrity's status. For example, corrosion potential measurements have been combined with laboratory data on repassivation potentials, localized corrosion, and SCC to determine the integrity of radioactive waste tanks.[59] A suitable model is required to form the judgment from monitoring the corrosion potentials. This is especially true for SCC, where monitoring cannot be reliably done with existing tools. Inspection avoids using models to determine system integrity, but is usually limited in its ability to resolve tight cracks or pits. Additionally, inspection results are not real time or prognostic—they are post-incident measurements performed occasionally and cannot be used by themselves to estimate the next inspection time. Therefore, prognostication models are used with inspection results to estimate inspection intervals. Finally, aligning defects found by inspection is often difficult and, therefore, estimation of hazard rates from purely inspection results can be uncertain. Thus, monitoring and inspection results must be used within an overall probabilistic risk assessment framework.

2.6 | Human Factors

An aging system operates as a result of many decisions made throughout its life, therefore human factors become important including, management philosophy (safety culture), worker training, change management, etc. These are soft factors,[5,60] but there are approaches to quantify their effects through probabilistic reasoning. For example, in a Bayesian network (BN) model the probability distributions of certain factors, such as loading and defect size, will be affected by human activity and can be organically included in the overall risk assessment.[58] Other human factors are more challenging, for example, the retirement of an aging workforce. Historical construction and operation documentation of aging systems may be lost and available only through the memories of retired plant experts. The human factor has been considered in various accident scenarios using BN,[61-63] but has not been integrated into the management of aging systems subject to corrosion.

UNKNOWN UNKNOWNS

Donald Rumsfeld, the erstwhile U.S. Secretary of Defense, famously observed, "but there are also unknown unknowns—the ones we don't know we don't know." The issue of unknown unknowns, however, has been addressed long before Rumsfeld. For example, in their seminal 1981 paper on risk assessment, Kaplan and Garrick[64] stated that, "Thus, the category of scenarios not yet thought of, may be handled by the same process as any other scenario category: The relevant evidence is assembled and quantitatively assessed using Bayes' theorem." The cognitive puzzle of "unknown unknowns" is resolved if we define the unknowns and knowns. The unknowns are scenarios (the sequence of events leading to a failure). However, there are knowns—our fundamental knowledge of processes. For example, we know that corrosion of metals is an electrochemical process that must obey certain well-established relationships (e.g., Faraday's law, Nernst relationship, Nernst-Einstein equation, Poisson's equation, and Butler-Volmer kinetic rate equation), deformation of metals occurs by the movement of defects (e.g., dislocations), etc. Therefore, any new scenario not thought of can, in theory, be assembled from this knowledge in new ways using Bayes theorem. There may be data and model uncertainties, but this is routinely handled by considering the appropriate probability distributions and updated by new data collection. This type of scenario-building approach was proposed by the late Roger Staehle, who tackled the issue of predicting failures that have not been observed in nuclear reactors using a multiscale modeling approach[39] and subsequently assembled a series of quantitative micro nano workshops.[65-68] A proactive materials degradation assessment report was issued by Andresen, et al.,[69] for nuclear reactors using a phenomena identification and ranking process that involved several experts. Modeling of corrosion using multiscale domains and processes was discussed by Taylor[70] and Taylor, et al.[9,71] These efforts aimed at identifying the processes leading to known failure modes at multiscale levels.

There are two major challenges in linking processes at multiple sizes and time scales: the first is the development of appropriate interfaces between the models and the second is identifying and establishing causal linkages between events in a sequence. A completely physics-based approach to predicting a phenomenon that considers all factors through fundamental laws may imply causality,[72] but such a causality may be applicable only for a certain sequence of events, not the complete process. There are also practical issues related to model availability, as many mechanistic models are embedded in proprietary software. The BN approach provides a more flexible approach to link diverse phenomena and assess causal linkages: (1) in BN, conditional probability is the only currency used to link different events. Thus, two different phenomena can be modeled separately and may have their own dimensional characteristics but in linking them, the only requirement is to establish conditional probabilities between the two events. The issues related to varying parameter dimensions are avoided; and (2) causal connections can be established between events by techniques[73] that reveal spurious correlations and true independence between events. The principles of BN modeling and applications to corrosion systems are described elsewhere.[74-76]

3.1 | Assessing Causality

Causality is a much more difficult problem to assess in some disciplines, where control studies can be difficult to conduct or morally repugnant. In corrosion, controlled studies are only limited by research funding and imagination. However, causality can be difficult to establish even here.

A mechanistic model does not guarantee causality, if the assumptions in the model are not considered carefully. Many mechanistic models develop detailed mathematical formulation of processes but make assumptions about the resulting corrosion as a result of these processes. For example, a detailed reactive-transport model can be developed to predict the chemistry and potential distributions in a pit but an assumption is made that a specific chemical criterion leads to pitting. A well-known example is the role of local acidification[77] vs. metal-chloride salt formation[78] in stabilizing localized corrosion. This is shown in Figure 3 as a causal BN.

In the acidification model, the pit stability (as characterized by the repassivation potential, E_{rp}, but other parameters can be substituted here) is "caused" by the local acidification when it is lower than the depassivation pH. The depassivation pH is known to be dependent on alloy composition, but it may also depend on the solvent (much less is known about this linkage). The local pH is determined by the external potential and chloride activity. In the metal-salt model, the E_{rp} is determined by the competition between metal-oxide (passive) film formation and metal-chloride salt film formation. Repassivation occurs below a critical percentage of metal-salt saturation level at which point, salt film formation is no longer competitively viable. These two models are shown in two BN's for clarity. In reality, they form one BN of causal reasoning, because there are common nodes in each of them. The local acidification and metal-chloride concentrations are thermodynamically related as shown in Figure 4. As the ratio of metal-salt concentration increases (mixing fraction of bulk electrolyte becomes lower), the local acidification increases.

Thus, a common factor influences both theories—solvent, and they cannot be causally separated. Causal separation may be induced if the solvent is varied or if chloride is replaced by nitrate (nitrate does not cause localized corrosion of stainless steels, but metal nitrates hydrolyze to cause local acidification). An example of causal separation by varying the solvent is shown in Figure 5, by essentially combining the two figures in Figure 3. In this BN, only two solvents are considered: water and methanol. Recent research has demonstrated the importance of non-aqueous solvents on localized corrosion.[80-81]

As shown in Figure 5(a), when the methanol content has a 100% probability of being less than 50% by volume in water (i.e., a water-rich environment), the E_{rp} predicted by the salt-film theory has a 52% chance of being less than 0 V_{SCE}. In contrast, Figure 5(b) shows that when the solvent is methanol-rich (100% probability of being greater than 50 vol% methanol), the salt-film theory predicts that the probability of E_{rp} being less than 0 V_{SCE} is 61% (i.e., according to this theory, methanol increases the chance of pitting of this stainless steel from 52% to 61%). In the acidification theory, the probabilities are 48% and 30%, respectively, for this state, suggesting that methanol would reduce the chance of pitting. The purpose of Figure 5 is not to refute one or the other theory, but to suggest that the BN may be used to check causal implications through strategically designed experiments. Statistically designed experiments, such as factorial designs, cannot provide causal information—merely correlations.

While the above sequence of events can be causally separated through appropriate experiments without using BN, BN provides a visual means to check our implicit assumptions and identify strategies to resolve them. The BN shown in Figures 3 and 5 has three elementary types of node connections (Figure 6).

In Figure 6(a), the nodes A and C are connected through an intermediate node, I. In this case, fixing the value of I eliminates any linkage between A and C. This type of causal connection is the most familiar to investigators (e.g., an oxidant influences corrosion through influencing corrosion potential, but if potential can be fixed by a potentiostat, the oxidant has no apparent influence on corrosion). In Figure 6(b), nodes A and B converge

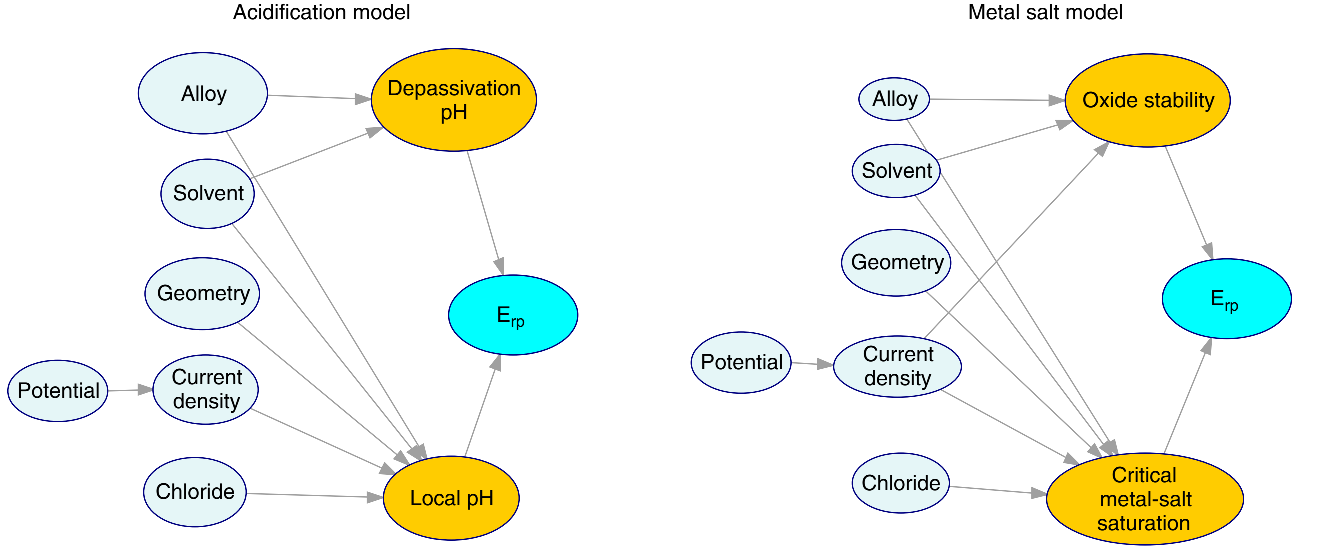

FIGURE 3. *Causal diagrams for two models of pit stabilization.*

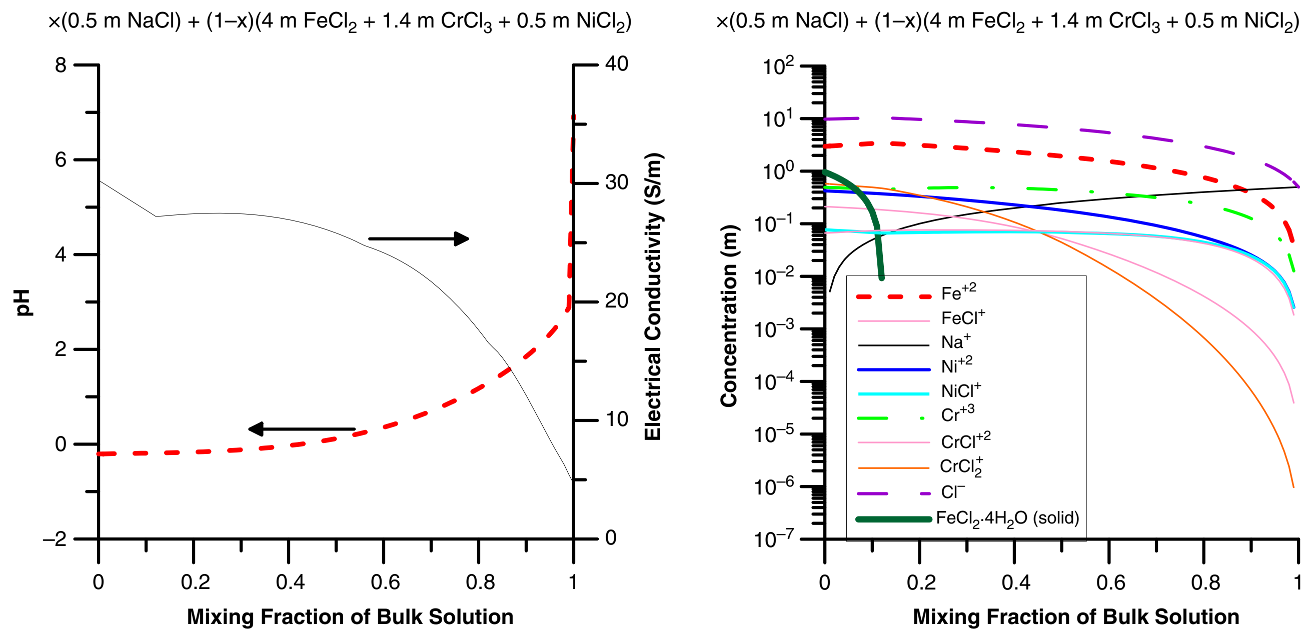

FIGURE 4. *Relationship between local pH and the metal-salt concentration.*[79]

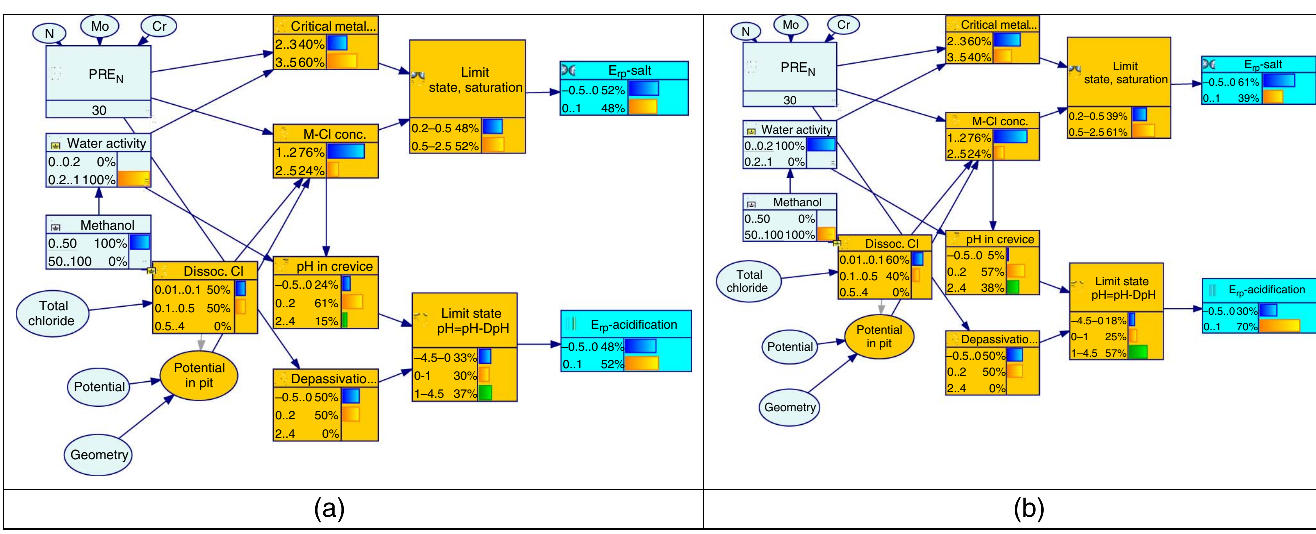

FIGURE 5. *Two different probabilities of E_{rp} by varying only the solvent from water-rich to methanol-rich.*

on node C. Although this suggests that nodes A and B are independent of each other, fixing node C will introduce a spurious correlation between nodes A and B because the Bayes theorem dictates that the posterior probabilities of both A and B are influenced by that of C. For example, if applied potential and strain rate influence SCC, fixing the probability of SCC, will indicate a spurious correlation between strain rate and applied potential. In Figure 6(c), node C is a common cause of nodes A and B. This would suggest that nodes A and B are dependent on each other. This is a serious pitfall in many results that suggest a correlation between two variables and imply causation, whereas there may be a third hidden variable that influences the two variables. However, fixing node C will eliminate the spurious dependence between A and B. The BN enables recognition of such causal pitfalls and helps us design appropriate experiments to resolve them for predictive modeling. Furthermore, a BN enables us to examine the structure of our knowledge systematically and transparently.

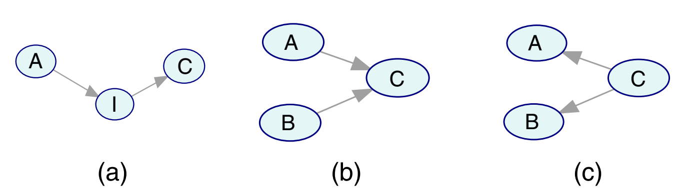

FIGURE 6. *Elementary types of node connections.*

3.2 | Hallmarks of Aging

Are there hallmarks of aging in physical systems, analogous to biological systems? As in the case of

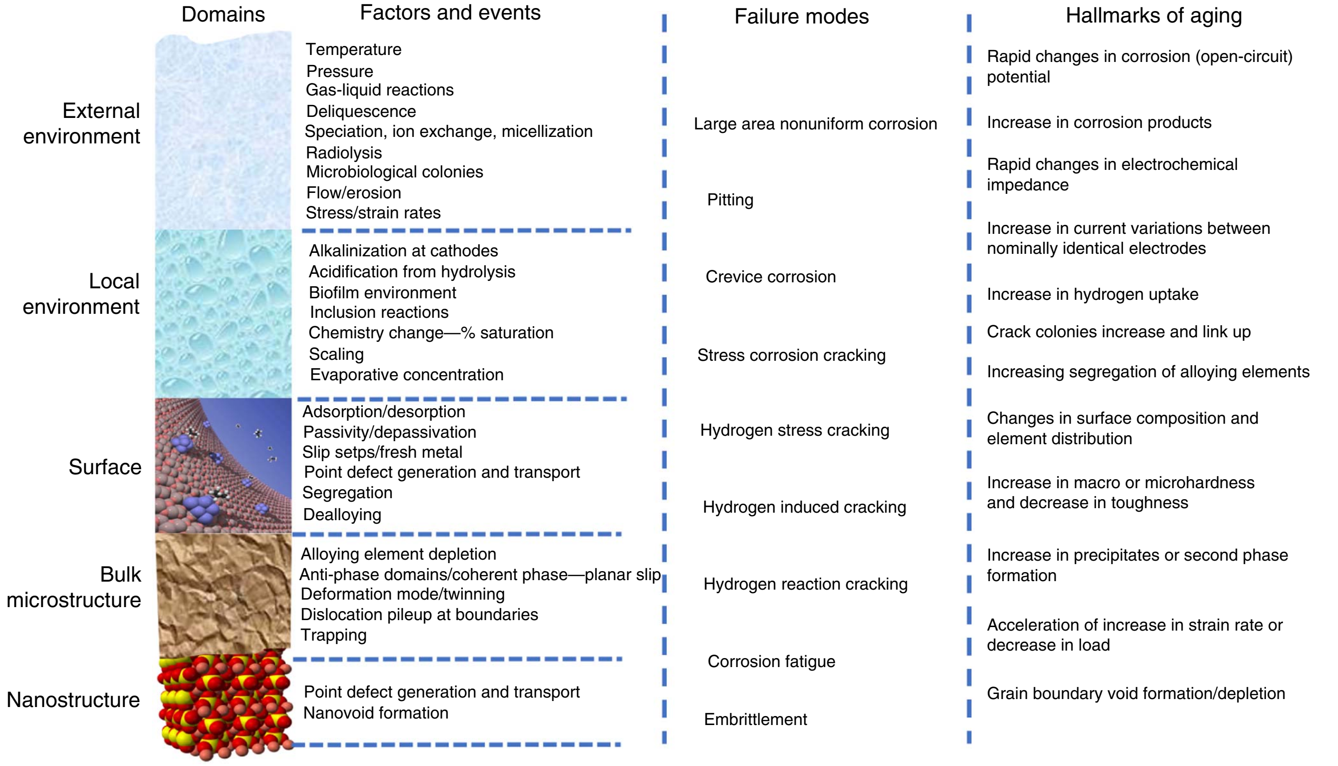

FIGURE 7. *Domains of metallic alloy corrosion with processes at different size scales and hallmarks of aging leading to observable failure modes.*

biological systems, a hierarchy of domains, processes, failure modes, and hallmarks of aging can be identified (Figure 7).

Many processes occur in the different domains and they interact in complex ways. For example, an external environment may have aerosolized salt particles that can condense into saline water droplets or film when the actual relative humidity is above the deliquescence relative humidity, which is a function of the composition of the aerosols.[82-83] Microbiological communities may be present as biofilms that influence the local environment in terms of aggressive species, such as reduced sulfur species, acidity, or increased redox potential.[84-88] The local environment on a surface may result from hydrolysis of cationic species and the diffusion of acidic gases, such as CO_2, and the local environment is influenced by the dissolution rate of the metals, setting up an autocatalytic process.[89] Local heat transfer conditions may result in the evaporative concentration of soluble species in tube/tube sheet crevices[90] of steam generators or under disbonded coatings on pipelines.[91] The condition on the metallic surface may be characterized by adsorption and desorption processes involving aggressive anionic and inhibitive species. The local dissolution at the freshly generated metal surface at slip steps may also contribute to eventual SCC or hydrogen embrittlement. The bulk of the alloy may involve processes related to microstructural and microchemical changes. These processes at the micro and macroscales are influenced by processes at the nanoscale, such as vacancy and interstitial movement and rearrangements.

However, certain measurable hallmarks of the aging effect stems from these interactions. From a metallurgical perspective, aging is often associated with thermal exposure resulting in microstructural changes. An analogous phenomenon exists for polymeric materials in terms of molecular rearrangements, cross linking, and crystallization. The hallmarks of these metallurgical changes include precipitation of second phases, including carbides and intermetallic phases, formation of coherent precipitates or Guinier-Preston zones, short and long-range ordering, segregation of alloying elements to grain boundaries and free surfaces, and nanovoid formation. These metallurgical reactions create local microchemical changes, such as alloying element depletion, increases in hardness and work hardening rate, and changes in deformation mode. At the interface of metal and environment, the hallmarks of aging may include, movement of point defects and changes in electrochemical response. For example, in many systems, a rapid decrease in the corrosion potential indicatesactive dissolution or extensive localized corrosion. On the other hand, an increase in potential may signify the formation of a protective film that reduces the anodic or cathodic reaction rates, depending on the system. Similarly, if monitoring of a system is performed using a multiarray probe, then an increase in electrochemical noise or current flow between the electrodes is a hallmark of spatial separation of anodes and cathodes and localized corrosion. Hallmarks may also include absorption of certain deleterious atoms, such as hydrogen. There are also mechanical hallmarks, such as a rapid decrease in load (under constant deflection or torque condition) or a rise in strain rate under constant load conditions. It is recognized here that this collection of processes and hallmarks is one view and other experts may modify this list according to their perspectives. However, when this is done, the goal is to identify those hallmarks, which if measured, may indicate that a metallic material is aging and susceptible to a failure mode. There are likely only a finite, manageable number of hallmarks of an aging system.

3.3 | Linking Processes and Failure Modes

The hallmarks are not the causes of failure but are diagnostic measures of eventual failures. The specific failure mode is dictated by how the processes leading to the hallmarks connect. In a previous paper,[92] an example was presented regarding using BN to identify unanticipated failure modes. This is shown in Figure 8 for a subset of conditions described in Figure 7.

It is well-known that methanolic environments containing chloride cause localized corrosion of carbon steel and stainless steels.[93] The combination of factors and processes leading to localized corrosion of stainless steels and Ni-base alloys is indicated as thick black arrows in Figure 8. The solvent properties of methanol in combination with oxygen contribute to localized corrosion of these alloys at temperatures significantly lower than those in aqueous solutions with the same total chloride concentration.[93] If oxygen is removed and potential is applied, this feature is retained. It may then be suspected that if conditions prevail for localized corrosion along with sufficient strain rate to disrupt passive film such that repassivation is impaired, then SCC may occur in these alloys. SCC of stainless steels and Ni-base alloys in methanol has not been reported (SCC is well-known for carbon steel, aluminum, and titanium alloys in methanol[94-96]). This is indicated by the dashed lines converging into SCC. This has been shown to be the case for a martensitic stainless steel in methanol-chloride solutions at high temperatures.[97]

However, the interconnections are not as simple as illustrated for the methanol case in Figure 8. It can be appreciated that the interconnections between processes at various size scales are extremely complex, as illustrated in Figure 9. Despite such daunting complexity, the situation is not completely dire. The most important message from Figure 9 is that not all factors connect to all other factors (if such is the case, we have no use for a model). There are causal connections that mean that some factors are independent of each other. Indeed, the purpose of a model is as much to show dependence as it is to show independence. A community of experts can tease out causal dependence from existing and new bodies of research.

FUTURE PROSPECT

To date, the author is not aware of any major corrosion-related failure mode that had been predicted before it happened. In the above statement, the author shares the frustration of a previous generation.[39] After a failure happens, the corrosion community has usually done thorough investigations, established mechanisms of the failure mode, and developed predictive methods. Indeed, observed failures are used as the rationale for subsequent research. A partial list of unanticipated failure modes includes:

- High pH and near-neutral pH SCC of carbon steel pipelines
- SCC of Ni-base alloy steam generator tubing
- SCC of carbon steel in nitrate-nitrite environments and in ethanolic/methanolic environments
- Boric acid corrosion of nuclear reactor control rod drive mechanism
- SCC of steel in supercritical CO_2

It is not realistic to expect all failure modes to be anticipated or even some modes to be anticipated accurately, but we now have

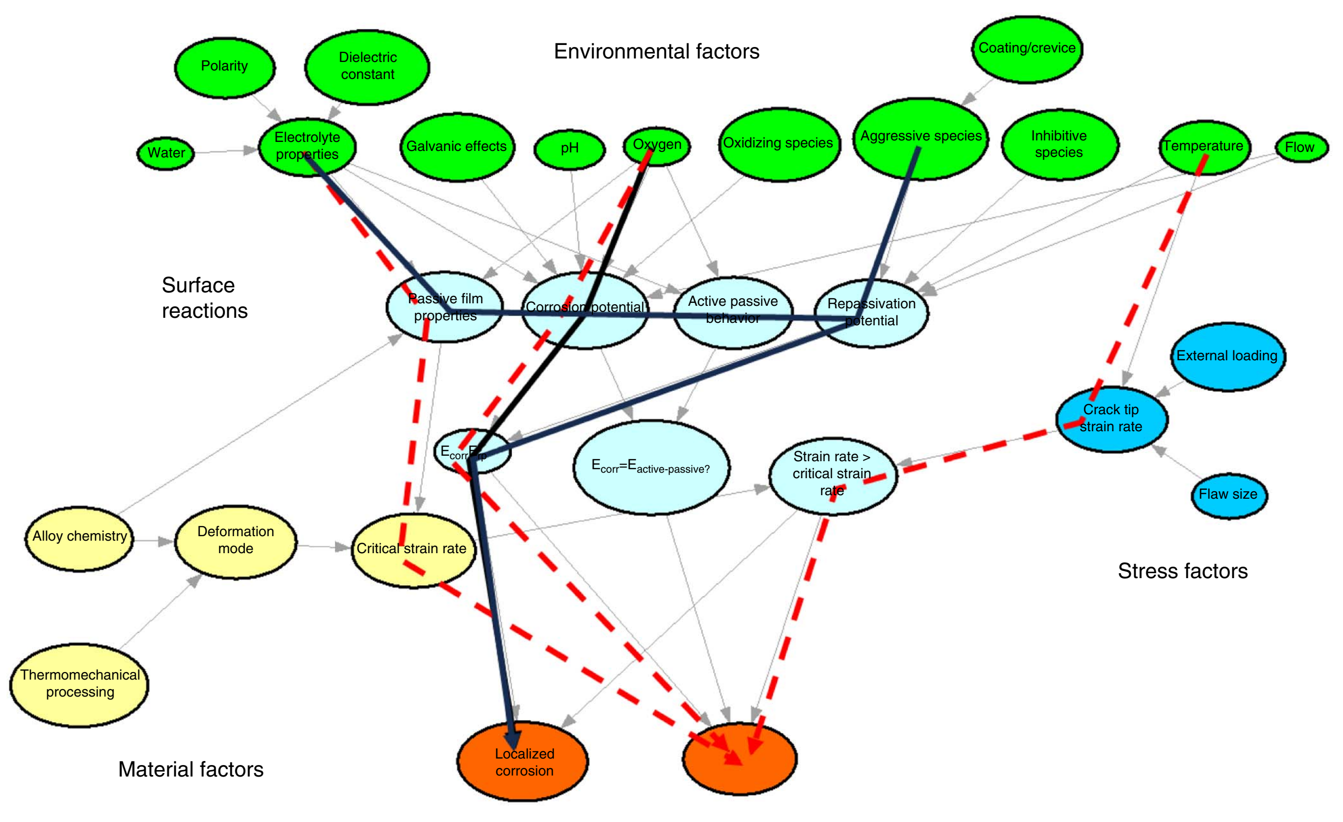

FIGURE 8. *A qualitative view of identifying unknown unknowns through using BN for a subset of conditions relevant to methanol environments.*

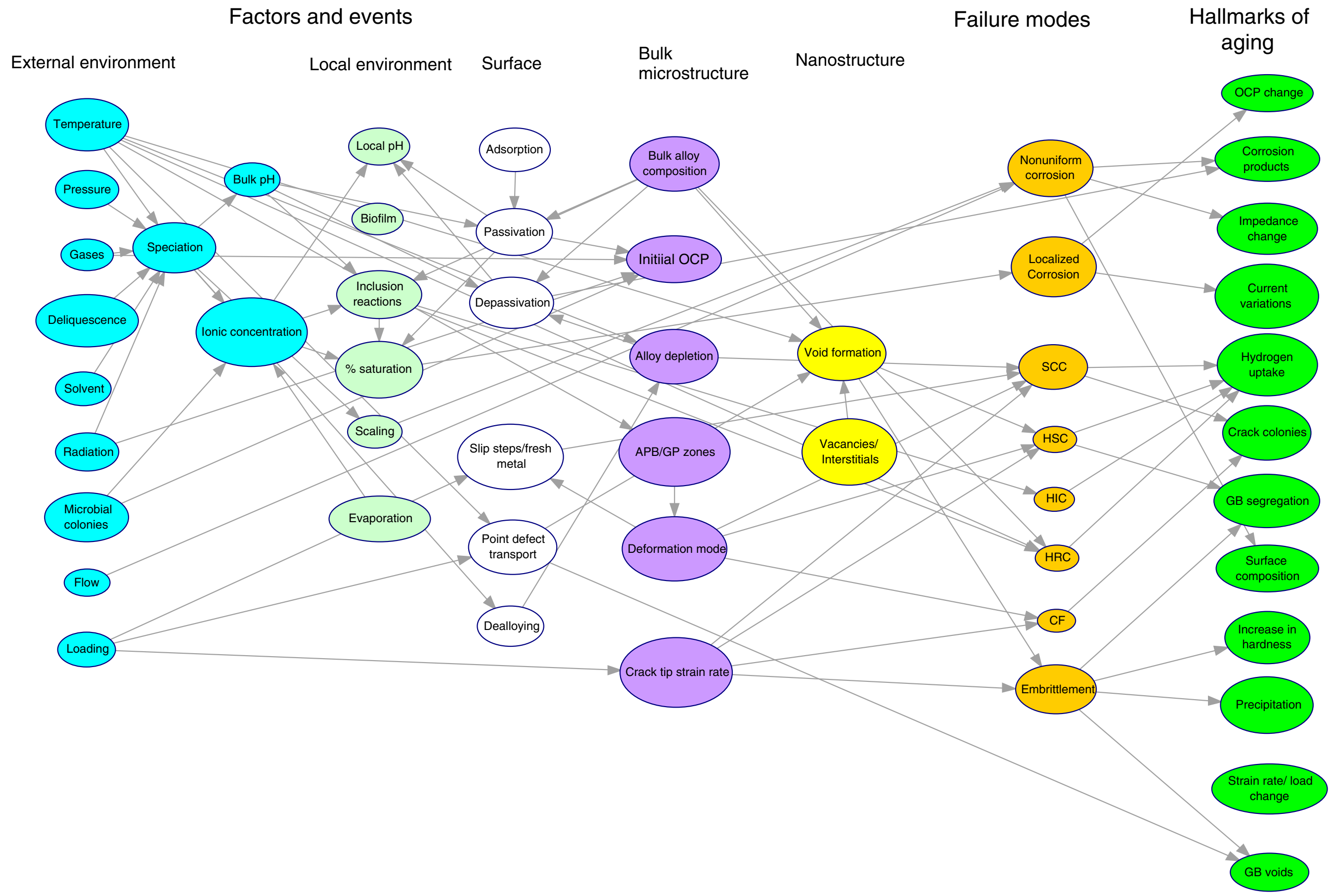

FIGURE 9. *Complex interconnections between various factors and processes at different scales leading to failures.*

a sufficient understanding of the fundamental processes of metallic corrosion and cracking that we can strive to increase the likelihood of anticipation. Such an improvement in anticipation requires diverse disciplines to come together and find a framework to integrate their knowledge. Specialization in modern science and engineering is inevitable and desirable, but there is a major barrier to assessing complex, aging systems. Those who take a panoramic view of corrosion may be eyed with some degree of suspicion by specialists as not digging deep enough into the intricacies of a specific problem. This problem seems to have existed even in ancient times. Ptah-Hotep, who lived in Egypt around the 34th century BCE, is said to have remarked,[98] "Consider how thou mayest be opposed by an expert that speaketh in council. It is foolish to speak on every kind of work, for he who disputeth thy words shall put them unto proof." However, specialists can be aided by generalists who are aware of the issues and tap into their knowledge using a quantitative framework.

An important part of aging systems is the occurrence of unanticipated failure modes. Unknown unknowns cannot be addressed by data analytics or recourse to large language models, such as ChatGPT. This is simply due to the nature of unknown unknowns—there are no failures to draw correlations from and the amount of data is sparse. Only, linking knowledge of experts in the form of mechanistic models can achieve the goal of anticipating failures that are yet to occur. Staehle and others took the first step of assembling a team of experts to identify various processes leading to SCC in nuclear power plants. This perspective proposes a more general, probabilistic framework implementing their ideas. Integrating the works of diverse disciplinary experts takes sustained commitment. The availability of AI tools for extracting quantitative information in an automated fashion and BN tools to integrate the information in a knowledge-centric manner promises a positive outcome for this arduous, enterprise. Perhaps, in the future, instead of suggesting failures as a rationale for research, we can anticipate failures as a result of fundamental research.

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