JCSE The Journal of Corrosion Science and Engineering

21st Century Corrosion Science

Volume 6 Paper C028

Corrosion Science in the 21st Century

G. S. Frankel
Fontana Corrosion Center, The Ohio State University, Columbus, OH 43210 USA,
frankel.10@osu.edu

Abstract

The discipline of corrosion science arguably has been in existence since the Wagner-Traud paper appeared 75 years ago. During the last part of the 20th century, most corrosion science projects were focused on the development and use of new techniques (e.g. electrochemical methods, surface analysis, and synchrotron radiation techniques), fundamental studies of corrosion phenomena (e.g. passivity and localized corrosion), or the properties of advanced materials (e.g. amorphous metals and "stainless" Al alloys). The understanding that resulted ultimately helped corrosion practitioners solve real problems, but problem-solving was not at the root of much of the research. In today's environment, research for the sake of fundamental knowledge is much less common because of funding constraints. This paper summarizes and contrasts the approaches taken by three large activities that are either recently concluded or ongoing in the US: corrosion and prediction of nuclear waste storage canister materials, predictive models for airplane corrosion and the effects on structural integrity, and the mechanism of chromate inhibition and chromate replacement. The future of corrosion science is in the areas of reliability and lifetime prediction, surface engineering and smart coatings, and infrastructure improvement and maintenance.

Keywords: corrosion science, nuclear waste storage, aging aircraft, chromate replacement, corrosion prediction

Introduction

Corrosion science in the 21st century has a history of 3 years and a future of 97 years. Whereas science is the practice of developing an understanding of the world around us to make it more predictable, the prediction of the future of science is a contradiction of terms if not exactly an oxymoron. Science is no doubt inherently unpredictable; we cannot know with any certainty what discoveries will be made. Interestingly, prediction of corrosion damage is in fact a hot topic of current and likely future research. Predictive models of corrosion, both probabilistic and deterministic models, must be based on a detailed understanding of past and current behavior. Similarly, any prediction of the future of corrosion science must be based on the past and current status of the field. In what follows, I will make some observations of the status of corrosion science and hazard some guesses (the best we can do!) of the future. It should be noted that the discussion will focus on the United States, which is admittedly somewhat of a myopic view to present at an international symposium. There are certainly some differences in the experiences and situation in the rest of the world, but there are more similarities.

Before launching into this exercise, I will relate a personal experience that is of some relevance. A decade ago, Norman Hackerman visited the IBM Watson Research Center in Yorktown Heights, NY, when I was a researcher there. For a long time, Dr. Hackerman has had positions (such as the presidencies of Rice University, the Univ. of Texas at Austin, and The Electrochemical Society) that have provided him with a unique perspective on research and on the field of corrosion. In a seminar during that visit, Hackerman made a statement that made me, a struggling young corrosion scientist, squirm: “Corrosion science will not solve corrosion problems.” First, it should be clear that he used corrosion science as an example of any scientific pursuit, not intending to cite it as a particularly failed branch of science. Further discussions led to an elaboration of the meaning behind this statement. In Hackerman's view, scientists pursue the underlying mechanisms of a problem. They seek the activating and inhibiting factors. In contrast, engineers solve real problems by combining the fundamental understanding provided by scientists with practical know-how and economic considerations. I do not believe that it was the intent of this statement to provide ammunition to those seeking to save money by cutting research funds, although at the time I feared it would. He meant only that there should be a clear understanding of the expectations and capabilities of scientists.

I agree with some aspects of Hackerman's view, but take issue with others. Times have changed. The distinction between scientific and engineering approaches has blurred. Scientists now play a much greater role in solving of real world problems. Engineering solutions are based less on intuition and more on scientific principles, and scientists are critical participants in large teams formulated to solve the pressing problems of the world. This is particularly true in the realm of corrosion science.

The Past

In order to understand how corrosion science has changed and how it will change further, it is necessary to look back over the past decades. It is possible to divide the focus of most corrosion science projects of the last part of the 20th century into three broad categories: the development and use of new techniques, fundamental studies of corrosion phenomena, and the properties of advanced materials. Table 1 presents some examples in each of these general areas.

It is a fair generalization that many of the research activities in the recent decades were focused on topics such as those in Table 1, with no intent of solving real problems. There are of course examples of large coordinated projects involving teams of corrosion scientists to solve important real problems. One example is the considerable effort that was put into solving a variety of corrosion and cracking problems in the nuclear power industry in the last several decades of the last century. Research at universities, government labs, and corporate labs led to many solutions, such as the reduction of impurities in the water and the development of the all volatile water treatment (AVT) to mitigate SCC of alloy 600 [1]. However, it can be argued that the involvement of large numbers of corrosion researchers in teams to solve real problems is currently much more common than in the past, when it was typically the primary intent of researchers to develop a new technique, understand a mechanism better, or explore the properties of a new material. Proof of this is the fact that many of the topics developed into “fads” or “bandwagons.” Examples of fads in corrosion science include metallic glasses and surface science in the 70's and 80's, and metastable pitting and “stainless aluminum” in the 80's and 90's. Research projects on these topics addressed no dire, real problems. Nonetheless, many different researchers from a variety of labs and countries got involved, partly to make a contribution to something new and interesting, but also to provide basic understanding and approaches that can and have been used to solve real problems.

Table 1. Past research topics in corrosion science. This table is not intended to be an exhaustive list.

New techniques	Corrosion Phenomena	Advanced Materials
Electrochemical:	Localized corrosion	Stainless steel:
Linear polarization	Passivity	duplex
EIS	Env. Assisted Cracking:	super austenitics
Electrochemical Noise	SCC	super ferritics
Surface Science:	Hydrogen embrittlement	Aluminum alloys
Ellipsometry	Corrosion fatigue	Nickel alloys
AES/SAM	MIC	Titanium alloys
XPS	Coatings	Composites
SIMS	Dealloying	Metallic glasses
STM	Rebar corrosion	Vapor deposited films
AFM	Atmospheric corrosion	Surface modifications:
Synchrotron X-ray:		Ion implantation
XANES		Laser treatment
EXAFS		

Another interesting aspect of the past and present of corrosion science is the involvement of industrial research labs. In the twentieth century, major developments in corrosion science were made by researchers at a number of corporate research centers. With time and the vagaries of financial good fortune, the active industrial labs have ebbed and flowed. A partial list of companies who have been active in corrosion research is given in Table 2.

The involvement of corporate research centers in scientific endeavors was important for bringing a connection to the real world to the scientific community. Many of the activities in these labs were truly research and were divorced from practical applications. These companies saw benefit in allowing their employees to use at least a part of their time to pursue science. Scientific activities and the connections to other scientists around the world provided the researchers with an understanding that enabled them to contribute better to solutions of real problems.

Table 2. US corporate and government research labs that were active in corrosion research in the twentieth century (not an exhaustive list).

Primary Metals	Aerospace

US Steel	Boeing
Alcoa	Lockheed
Inco	Rockwell
Chemical Process	Contract Research
DuPont	Battelle
Dow	SWRI
Union Carbide	SRI
Automotive	InterCorr
Ford	CCT
GM	Military
Nuclear	Wright Labs
GE	Naval Research Lab
Westinghouse	Government Labs
Oil and Gas	Brookhaven
Exxon	Argonne
Shell	Sandia
Electronic/computers	
IBM	
Bell Labs/Lucent	

The Present

The present status of corrosion research is quite different than it was even a decade ago, at the time of the last UMIST anniversary celebration. The NSF approach to funding research purely for the sake of research is extremely rare in the field of corrosion. Even prior to the recent economic downturn, many companies divested themselves of expensive research centers as a cost-savings measure. IBM is a good example. The IBM Corporation was extremely profitable through the mid-80's because of a cash-cow product: mainframe computers. The company could afford a world-leading research division employing thousands of scientists, many of whom never needed to provide a justification for the relevance of their work. The area of corrosion was considered to be of interest to IBM because of the dimensions of devices and the reactivity of some critical materials, in particular magnetic materials. Researchers could easily justify the pursuit of fundamental studies in atmospheric corrosion, thin film corrosion, localized corrosion, inhibition and passivity. Funding and support staff were available. However, the situation changed in the early 90's as computing switched to smaller machines, such as PCs, and the company's financial situation plummeted. By the mid 90's, most researchers at IBM had to find projects supported financially by the operating divisions. The practical applications of corrosion science at IBM were primarily performed in a fire-fighting mode, as little thought went into corrosion in the design phase of new projects. Corrosion is not a topic that leads to new products in the electronics industry. It is only a manufacturability and reliability concern. At present, no corrosion research is carried out at IBM. The situation is similar at most of the companies listed in Table 2. If one defines activity in corrosion research as necessarily involving publications in the top journals and participation at research conferences, then it can be argued that GE is the only large corporation from that list that has an active corrosion research group. (Rockwell might be included, but the Rockwell Science Center is now essentially a contract research lab.) The companies performing contract research are still active, though much of their activity is proprietary and not published. The military and government labs also still have research activities in the area of corrosion. However, in general those activities are currently at a lower level than they once were. The corrosion community suffers from the lack of involvement of industrial researchers. As mentioned, in the past industrial researchers brought to the scientific discussion table their practical experience of interacting with engineers in the pursuit of solutions to real problems in their respective companies. The absence of industrial researchers is now partially balanced by the change in the type of work now done by corrosion scientists in academia and government labs.

As mentioned, one defining characteristic of corrosion research in 2003 that distinguishes it from the past is the involvement of researchers and scientists (as opposed to engineers and practitioners) from academia and government labs in large coordinated team efforts to solve real problems. A few of these efforts will be summarized below. Again, it should be noted that this is not an exhaustive list, and is limited to activities in the US.

Nuclear Waste Storage - The Yucca Mountain Project

Long term storage of high level radioactive waste is the ultimate problem for corrosion research. For many reasons, it is clear that the canisters designed to hold the waste material must be fabricated from metal. The complete storage system, including natural and man-made barriers must maintain integrity and prevent leakage for a period of about 10,000 years to allow the radioactivity to decay to natural background levels. Therefore, nuclear waste storage presents the ultimate corrosion prediction problem. We corrosion scientists must make a prediction for a time period that is 200 times longer than the history of the field!

The US Department of Energy is responsible for designing and constructing a long-term nuclear waste repository, and the President and US Congress approved a Site Recommendation designating Yucca Mountain, Nevada as the site for a permanent waste repository. Details of the corrosion aspects of the Yucca Mountain repository can be found in an excellent review by Gerry Gordon [2] and in the final report of a Peer Review Panel headed by Joe Payer [3].

From a corrosion perspective, there are several critical issues that only can be addressed by scientists doing fundamental research. These issues include the evolution of the local environment on the surfaces of interest, the long term stability of passive films on corrosion resistant alloys (CRAs), and the conditions under which localized corrosion and stress corrosion cracking will never occur.

The repository will be in the unsaturated zone, 300 m above the level of the groundwater. The environment inside Yucca Mountain is well characterized. The rock, a volcanic tuff, contains faults and fine porosity that is filled with pore water. A fraction of the very small amount of annual precipitation seeps into the mountain, eventually permeating down to groundwater below the repository. The various waters in the mountain are very dilute, containing low amounts of chloride, nitrate, sulfate, and bicarbonate anions as well as sodium, calcium, potassium, and magnesium cations. A relatively high level of nitrate compared to most ground waters, a result of the low level of biological activity on and in the mountain, is fortuitous because of its corrosion inhibition properties. A primary issue is what exactly the environment on the waste packages will be, which is a strong function of the repository temperature profile with time and the integrity of the planned Ti grade 7 drip shields. Will water drip directly onto the waste packages or will they be exposed only to humidity? How will the composition of these waters change upon contact with a hot surface? Is it possible for trace elements such as Hg and Pb to enrich over long periods?

CRAs such as stainless steel and Alloy 22, which is the material from which the outer canister is to be made, were invented less than 100 years ago. Our experience with them is 9900 years less than the design life of the repository, so we must determine if there are processes that can occur over a period of millennia by which passivity would be spoiled and the reactive metals under the passive films would destabilize. For instance, will passive films thicken over long periods of time to the point where they spall, like high temperature oxides, and create crevices that would not repassivate? Or, is it possible that a very low S content in the alloy will with time, as the passive film slowly sweeps through the material, concentrate at the surface and spoil passivity permanently?

It is well known that CRAs, which rely on the presence of a thin passive surface film, are susceptible to localized corrosion as a result of breakdown of the film. Under the simultaneous action of a tensile stress, CRAs are also susceptible to stress corrosion cracking (SCC). The alloys of interest, Alloy 22 and Ti-Gr 7, are extraordinarily resistant to localized corrosion and SCC. Nonetheless, they are susceptible under extreme conditions. The kinetics of these processes are so fast relative to the time scale of interest that they should never occur if the package is to maintain integrity, unless the stifling processes are well understood. What then are the conditions under which one can be absolutely certain that localized corrosion and SCC will not occur? The pitting potential is certainly not a sufficiently conservative design criterion. It has been suggested that localized corrosion (both pitting and crevice corrosion) will not occur if the corrosion potential remains below the repassivation potential for a creviced sample that has undergone considerable attack [4,5]. In that case, it is important to have a good prediction of the corrosion potential as a function of time and environmental conditions. In the case of SCC, is there a true threshold stress intensity? The limitations in measurement of crack growth rate are such that a crack growing at the slowest measurable rate will penetrate the Alloy 22 canister in a fraction of the design life. In other words, even if the most sensitive measurements predict that SCC will not occur under non-accelerated conditions, it is possible that the crack growth rate is too high. Finally, the processes by which localized corrosion is stifled are not well understood.

It should be noted that other countries are taking a very different approach to long term nuclear waste storage. It is possible to use thermodynamics rather than kinetics to ensure long-term stability by using a noble metal, such as Cu, as the barrier and placing the repository in an anoxic saturated zone, i.e. in a region saturated with ground water that is non-complexing and has a very low dissolved oxygen content.

Once the oxygen introduced into the environment during emplacement is consumed, a Cu canister should be perfectly stable in such an environment. The concern in this case is long term prediction of the composition of the groundwater over the 10,000 year period. If the underground currents were to bring aerated waters to the repository, Cu canisters would be quickly breached.

The scientific questions raised above and others related to Alloy 22 and Yucca Mountain have been the focus of a considerable amount of research over the past few years that has involved an increasing number of corrosion scientists from around the world. The design and construction of the Yucca Mountain repository is a huge engineering undertaking. However, scientists have a major role in justifying the design and addressing the considerable attention and concerns raised by opponents and the public in general. Scientists also have a role in assisting those who oppose the project. Political considerations will likely dominate the decision-making process. Nonetheless, there must be a vigorous and honest debate about the underlying science.

Corrosion Prediction in Aging Aircraft

It is generally considered that the US Air Force (USAF) spends about $1B/yr fighting corrosion in its fleet of aircraft. Many planes such as KC135 tankers have been in service for about 40 years, but still have a considerable remaining life based on fatigue considerations because of the service profile [6]. Military planes fly less frequently than commercial planes, and spend more time on the ground corroding. Airplanes in the USAF fleet currently undergo regularly scheduled periodic maintenance. During maintenance, any corrosion that is found must be fixed by a repair process or the part must be replaced, regardless of whether it is critical to the structural integrity of the plane. This "find and fix" approach is partly responsible for the high maintenance cost. It would be even more expensive to purchase new planes, so it is imperative to decrease maintenance costs. Furthermore, the extensive time each plane spends in depots for maintenance affects mission readiness.

In the past, corrosion has been considered to be a small modification of the fatigue-based structural integrity programs that have successfully managed the USAF and commercial fleets with few corrosion-related disasters. However, the issues of cost and mission readiness of aging aircraft have been receiving attention at high levels in the military [7]. A new approach toward maintenance, which could be called "anticipate and manage" is being developed by a large team managed by S&K Technologies in Dayton, OH [8]. In this approach, aircraft are inspected upon entering a maintenance depot and the state of corrosion is assessed, as is the effect of that corrosion on the structural integrity. Furthermore, using assumptions about the future deployment of the plane and the Air Force bases at which it will spend time, a prediction of the change in the corrosion state of the plane with time and an assessment of the effects of those changes on the structural integrity are made. Based on that analysis, the corrosion found is either repaired, replaced, suppressed, or ignored. In essence, the analysis should be able to predict the "to be" condition from the "as is" state. This approach involves effective and thorough non-destructive inspection (NDI), knowledge of the environmental severity of the Air Force bases at which the plane will be deployed, an understanding of the growth kinetics of the existing corrosion sites and the influence of the environmental factors and suppression technologies on those kinetics, and, finally, the influence of the "as is" and "to be" states of corrosion on structural integrity. Ultimately, the prediction will be aided by a suite of on-board sensors that will report in real time or near real time on the status of the local environment and damage state.

This project is primarily an engineering task, but there are a number of scientific issues, and corrosion scientists are fully integrated into the team. The complexity of the problem necessitates the involvement of empirical considerations if any progress is to be made. However, a scientific underpinning for the framework is required if the predictive model is to be robust. For example, the growth kinetics of localized corrosion is considered to be the best understood aspect of localized corrosion, and it is possible to guess a reasonable kinetic expression based on past studies. However, a detailed understanding of the effects of a variety of factors is needed: microstructure and temper; environment including composition, time of wetness, relative humidity cycles and temperature; and stress. The concepts of stifling of growing sites and initiation of new sites must also be considered, and these are very complex issues. Initiation involves coating degradation and breakdown. The reactions inside crevices and the development of crevice chemistry and profiles over time require scientific approaches, as does the development of effective suppression technologies.

Chromate Replacement

The situation with chromate corrosion inhibitors is rather well known and is related to the last topic of aging aircraft. Chromates are widely used to protect the very corrodible high strength Al alloys used in aerospace applications, and also for other materials in a wide range of applications. However, vis-à-vis aging aircraft, part of the high cost of maintenance is from handling chromates. Furthermore, regulations are being passed to severely limit the use of chromates because of their carcinogenic nature. Chromates can be added as dissolved Cr^{VI} ions into an aqueous environment, applied to a surface as a chromate conversion coating (CCC) or added to paint as a pigment. A very important aspect of the inhibition provided by all embodiments of chromates is that they promote self-healing.

Considerable efforts have been undertaken for many years to find a replacement for chromate that is equally or more effective, but environment friendly. In the mid-90's, the USAF convened a Blue Ribbon Advisory Panel to study aircraft coatings [9]. The report of that panel indicated that developing a better understanding of the mechanisms of aluminum corrosion and chromate inhibition should be a top priority and a prerequisite for the development of a successful replacement. The Air Force Office of Scientific Research then funded a large program to study chromates. This type of block funding is another important aspect of the current landscape in corrosion science funding. Funding agencies are more willing to support multidisciplinary team efforts to address a problem, and such an approach works. In this case, the money put into this topic jump-started activities in the area of Al alloy corrosion and chromate inhibition, and these topics developed into "fad" as discussed above. Other funding agencies in the US, such as DOE and SERDP, initiated programs in this area and investigators from around the world got interested. This interest has been reflected by a large number of publications and conference presentations in the area of Al alloy corrosion and inhibition over the past several years.

The connection of the scientific work in this area to industry and real solutions has been more problematic. Coatings companies are, in general, not open with their technology, which is largely proprietary. They might be benefiting from the science described in the open literature, but a large coordinated team effort with industry and academic participation has not materialized. The funding agencies have not followed up on the initial investment in understanding of chromate inhibition to put together a similar effort specifically on the topic of chromate replacement.

A number of the important scientific issues have been addressed by the recent activities, and the results have in fact provided guidance to those who are seeking to replace chromates. Since CCCs and chromate pigments primarily act by providing soluble Cr^{VI} species to the local environment, it is critical to understand how dissolved Cr^{VI} ions affect corrosion. Are they anodic or cathodic inhibitors? Do they form a protective film on the surface? If so, what is the nature of that film and why is it so protective? Replacing CCCs requires detailed knowledge of the CCC. What is its structure and composition, and do they vary across the surface of a complex alloy containing intermetallic particle phases? What is the effect of surface pretreatments? What controls the thickness and deposition rate? How and why does it vary across the surface of an alloy? What happens during the aging process? How are Cr^{VI} ions released and at what rate? Regarding chromate pigments, it is critical to know the proper solubility, which changes with the cation. How does the pigment interact with the polymer matrix? What is the effect of loading?

The answers to some of these questions can be found in recent reports [10,11]. In summary, there are several reasons why chromate is an extremely effective corrosion inhibitor for Al alloys.

1. Chromate can be stored in conversion coatings and as a pigment in paints.

2. Chromate is released from these coatings, particularly when they are scratched to refresh the coating area. The released chromate is in equilibrium with the chromate in the coatings, and higher pH favors Cr^{VI} release.

3. Chromate is mobile in solution and migrates to exposed areas on the Al alloy surface.

4. Chromate adsorbs on the active sites of the surface and is reduced to form a monolayer of a Cr^{III} species.

5. This layer is effective at reducing the activity of both cathodic sites (Cu-rich IMC particles) and anodic sites in the matrix or at S phase particles.

6. The combined properties of storage, release, migration, and irreversible reduction provided by chromate coatings underlie their outstanding corrosion protection.

7. Inhibition of the oxygen reduction reaction at cathodic Cu-rich IMC particles is an important part of the overall corrosion inhibition mechanism.

It is reasonable to expect that replication of these characteristics of chromate using another inhibitor species is necessary to successfully replace chromate as a critical component for Al alloy corrosion inhibition.

The Future

Having glanced at the past and taken stock of the present, it is appropriate to look to the future. The model of creating large multidisciplinary teams of both engineers and scientists to solve complex problems will continue to flourish. This approach works and benefits everyone. The single investigator working in relative isolation should not be ignored, because breakthroughs can be accomplished in that mode. However, corrosion scientists can contribute significantly to large projects that are largely engineering in nature, even with important scientific contributions. And the scientists benefit from having a focus and customer for their services.

The topics discussed in the last section give a hint as to the focus of the future of corrosion science, which I believe to be: reliability and lifetime prediction, surface engineering and smart coatings, and infrastructure improvement and maintenance. These will be addressed in turn.

Reliability and Lifetime Prediction

Reliability and lifetime prediction certainly will be a major thrust of the field of corrosion. This is the focus of the projects on long term nuclear waste storage and aging aircraft described above. We cannot with accuracy predict how much the lifetime of a component will change if the chloride concentration in the environment is cut in half even though we know precisely how the pitting potential will change. If the field of corrosion is to have any impact in design science, as has been promoted by Roger Staehle in recent years [12,13], then we will need to develop lifetime prediction tools. The situations of a buried waste canister or a military airplane are relatively simple. The environments of both are quite limited; the repository is perfectly defined, and military planes will land at one of a hundred or so bases around the world (corrosion during flight is typically minimal since the temperature at high altitude is far below the freezing point.) Nonetheless, definition of the local environment for both is very tricky and extremely important. The situation is more complicated for an automobile, and even more so for other applications, such as an Army vehicle, which might see a very wide range of environments.

There is no doubt that advanced statistical concepts need be adopted in the field of corrosion to deal with these complexities. Weibull distributions allow predictions of the earliest failures from a distributed population of data [12,13]. Other approaches are suggested from medical and epidemiological studies, which have made wide use of advanced statistical theories. One can correlate "disease" to "corrosion", "patient" to "component", and "death" to "failure" and see that there is a perfect analogy between medicine and corrosion. Two approaches to deal with these types of problems are survival analysis and logistic regression analysis [14,15]. Finally, artificial neural networks (ANNs) comprise another tool that recently has been applied to predicting corrosion [16].

Survival analysis is appropriate for situations when time to an event, such as death or failure, is monitored. In general, observations are made until death or failure. However, observation often ends before failure occurs because the study ends or the subject is lost to continued observation. Making full use of available information from these "censored" observations underlies the challenge of working with survival data. Survival analysis also explores, through the use of specialized modeling techniques, the role that variables play in hastening or extending the time to failure. Survival analysis has been used extensively in the study of survival of patients following medical treatment and should be extremely useful in the prediction of corrosion. It enables the development of models to predict the influence of a variety of parameters using data from both components that have suffered corrosion and those that are still unattacked.

Logistic regression analysis is suitable when there is a "go/no-go" assessment, such as life or death and corrosion or no corrosion. In this method the presence or absence of corrosion is used as the response variable rather than the time to the event (as in survival analysis). The multiple logistic regression model estimates the probability of an outcome of interest (such as corrosion) given a set of suspected "risk factors." Through this approach, it is possible to select, from many potential predictors, those that are most highly related to corrosion.

Successful application of both survival analysis and logistic regression analysis requires a reasonable foundation in statistics. Artificial neural networks (ANNs) are much more accessible to statistical laymen but are still extremely useful for recognizing complex relationships between input and output data. ANNs are interconnected mathematical processing elements based on biological nervous systems. The result of the model is similar to what is obtained by logistic regression analysis. However, in contrast to a logistic regression approach, which often involves considerable subjectivity in the modeling process, ANNs develop predictive relations automatically through a training and validation process. Since ANNs operate by recognizing complex relationships among data, they are very powerful for modeling complex physical phenomena where a comprehensive deterministic understanding does not yet exist. For this reason, they are well suited for make predictions of damage accumulation due to corrosion, stress corrosion cracking and corrosion fatigue. ANNs have been used to predict corrosion behavior and their use will likely increase in the future.

Smart Coatings and Surface Engineering

"Smart coatings" is a buzzword phrase for futuristic corrosion protection. A wide range of coating intelligence has been promised by "smart coaters," even including the incorporation of nanomachines to somehow enable physically rebuilding of damaged coatings. The eventual extent of coating intelligence is debatable, but there is no doubt that coatings will get smarter.

Actually, CCCs are already rather smart. They store an inhibitor, release it into aggressive solutions in which it migrates to an active site and irreversibly reduce to quench corrosion attack. Even duplicating the efficacy of CCCs is a considerable challenge. Self-healing properties have been documented for chromate-free coatings, although the extent of inhibition was not equivalent [17].

Smart coatings will be able to do more than release active corrosion inhibitors. Sensing of corrosion, either the direct product of corrosion such as metal cations [18] or indirect products such as hydroxyl associated with the cathodic reaction [19], has already been studied, though practical embodiments have not yet been achieved. It is also possible to use x-rays to sense structural changes of a pigment added to an organic primer coating as an indicator of the presence of moisture in that layer [20]. Of course, the presence of moisture is necessary, but not sufficient evidence that corrosion is occurring. Ion-exchange compounds used as pigments can also provide added functionality by removing aggressive anions such as chloride from the coating or from a blister under the coating and replacing them with beneficial inhibiting anions [21]. Finally, color change on demand for camouflage purposes is a property that could reasonably be achieved by different technologies. Smart coatings are definitely in their infancy, and will be a hot topic of research and development in the future.

Related to smart coatings is surface engineering, which is a term that implies a more classical surface science approach to surface modification. It is clear that corrosion happens at surfaces, so it is possible to retard corrosion by controlling surface properties. For instance, corrosion under organic paint coatings occurs when the coating disbands or delaminates. Improvement in the metal/coating bonding is a very practical approach for improving corrosion protection. One needs to understand the oxide formed on the metal substrate, the nucleation and growth of sacrificial layers such as galvanizing, the oxides formed on top of these layers, the effects of surface treatments, the interaction of organic adhesion promoters with the surface and with a bulk pigmented organic coating, and the functionalization of polymer surfaces. To understand these interactions requires careful experimentation using surface analytical tools. A fundamental understanding developed by surface science approaches should enable the design and development of improved coating systems.

Infrastructure

A study on the cost of corrosion in the US published in 2001 was based on analyses of industrial sectors [22]. A remarkable finding of that study is that the sector with the highest cost is not defense or motor vehicles. The cost associated with corrosion of drinking water and sewer systems, $36B/yr, vastly exceeds any other sector. When other infrastructure sectors are included, such as highway bridges, electric utilities, oil and gas transmission pipelines and local gas distribution piping, the cost is a staggering $63B/yr. Certainly, known engineering fixes are all that is required for most of these corrosion problems. However, the magnitude of the problem necessitates that new and innovative solutions be sought. Governments should assemble a large, multidisciplinary team including both engineers and scientists to do just that.

Computation and instrumentation

Advanced computational power and instrumentation will continue to affect and improve corrosion science. Electrochemical measurements are extremely easy and inexpensive relative to even 10 years ago, which greatly enhances the productivity of corrosion scientists and engineers. Commercially-available multichannel potentiostats allow for up to 100 simultaneous measurements. If used with appropriate samples containing arrays of electrodes, this equipment allows for incredible parallel processing and reduction of experimental time. Such advances will continue to facilitate the activities of corrosion science.

Another aspect of computation that will have a big impact on corrosion science and engineering in the future is the application of thermodynamic databases to predict speciation and alloy stability. Commercial products [23] are already providing capability that far exceeds what was available 10 years ago, the Pourbaix Atlas. Such tools are incredibly useful for engineering applications in complex environments, such as those used in the chemical process industry. For corrosion scientists, this type of analysis should improved understanding of situations like the environment in pits and crevices.

Funding

The future of corrosion research will depend to a great extent on available resources, so a good question to ask about any predictions of the future is "Who's going to pay for it?" Research in universities will be on subjects for which funding is available. Another important fact about the present status of corrosion science in the US is that it is driven largely by funding from the Department of Defense. The Navy has traditionally been a strong supporter of corrosion science. As mentioned, the Air Force has taken up the subject with some vigor over the last 8 years. Finally, the US Army has renewed interests in corrosion. The DOD has sufficient resources to set the agenda and to fund large activities, as was described above regarding the areas of aging aircraft and chromate replacement.

There should be concern for the future funding of corrosion research. Corrosion is not sexy and trendy. Contract monitors in funding agencies, even within DOD, must be provided with support for the cause. Corrosion problems will not vanish, but the impetus to fund them will dwindle unless corroders can show success in important areas, such as lifetime prediction, coatings, and infrastructure.

Summary

The future of corrosion science lies in teaming with other scientists and engineers to address large important problems. In particular, the areas of reliability and lifetime prediction, surface engineering and smart coatings, and infrastructure improvement and maintenance will attract attention.

Acknowledgements

The author gratefully acknowledges input from N. Hackerman, R.G. Buchheit, R.W. Staehle, R.L. McCreery, R.G. Kelly, and M. Stratmann on the issues discussed in this paper.

References

1. J. A. Gorman and R. W. Staehle, in *Chemistry and Electrochemistry of Corrosion and Stress Corrosion Cracking: A Symposium Honoring the*

Contributions of R. W. Staehle, R. H. Jones, ed., p. 397, TMS, Warrendale, PA, 2001.

2. G. M. Gordon, *Corrosion*, **58**, 811 (2002).

3. J. A. Beavers, T. M. Devine, Jr., G. S. Frankel, R. H. Jones, R. G. Kelly, R. M. Latanision, J. H. Payer, "Peer Review of the Waste Package Material Performance," Final Report of the Waste Package Materials Performance Peer Review Panel, February, 28, 2002.

4. N. Sridhar and G. A. Cragnolino, *Corrosion* **49,** 885 (1993).

5. D. S. Dunn, G. A. Cragnolino, and N. Sridhar, *Corrosion*, **56**, 90 (2000).

6. A. J. Hebert, *Air Force Magazine*, **86,** N. 1 (2003).

7. *Aging of U.S. Aircraft, Final Report*. 1997, Committee on Aging of U.S. Air Force Aircraft, National Materials Advisory Board, National Academy Press, Washington, D.C.

8. M. M. Altynova, R. G. Kelly, J . R. Scully, D. T. Peeler, "Engineering Corrosion Prediction Model For Aircraft Structures," 6th Joint FAA/DoD/NASA Aging Aircraft Conference, San Francisco, Sept.16-19, 2002.

9. Report by the Air Force Blue Ribbon Advisory Panel on Aircraft Coatings, November 1995.

10. G. S. Frankel and R. L. McCreery, *Interface*, **10**, 34-38 (2001).

11. G. S. Frankel, "Mechanism of Al Alloy Corrosion and the Role of Chromate Inhibitors," Final Report to AFOSR, MURI grant No. F49620-96-1-0479, January 24, 2002.

12. R. W. Staehle, "Status and Future of Predicting and Assuring Corrosion Performance," presented at the 2nd International Conference on Environment Sensitive Cracking and Corrosion Damage, Hiroshima University, Hiroshima, Japan, October, 2001.

13. R. W. Staehle, "Future and Benefits of Corrosion Research," presented to the 12th Asia-Pacific Corrosion Control Conference, Corrosion Science Society of Korea, Seoul, Korea, October, 2001.

14. D. W. Hosmer and S. Lemeshow, Applied Logistic Regression, John Wiley, & Sons, New York, 1989.

15. D. W. Hosmer and S. Lemeshow, Applied Survival Analysis, John Wiley, & Sons, New York, 1999.

16. A.C. Ramamurthy, M. Uriquidi-Macdonald, Paper 932337, Proceedings of the 6th Automotive Corrosion Prevention Conference (P-268), SAE International, Warrendale, PA October (1993).

17. R.G. Buchheit, S. B. Mamidipally, P. Schmutz, H. Guan, *Corrosion*, **58,** 3 (2002).

18. R.E. Johnson, V.S. Agarwala, *Materials Performance*, **33** 25 (1994).

19. J. Zhang and G. S. Frankel, *Corrosion*, **55,** 957-967 (1999).

20. F. Wang and R.G. Buchheit, The Ohio State University, unpublished research (2003).

21. N. McMurray and G. Williams, Paper 327, The 203rd Electrochemical Society Meeting, Paris, April, 2003.

22. "Corrosion Costs and Preventive Strategies in the United States", Federal Highway Administration Report FHWA-RD-01-156, September 2001, http://www.corrosioncost.com/.

23. See for example http://www.olisystems.com/