PART I

BASICS OF CORROSION SCIENCE AND ENGINEERING
A. Introduction

Are failure analyses useful? The answer is an emphatic Yes. There are many reasons to perform a failure analysis; the most common one is to help prevent future failures. To ensure that corrective actions will be effective, it is necessary to understand why failures have occurred in the first place. Otherwise, any design or manufacturing changes that are implemented may not be effective or simpler ways to prevent future failures may be overlooked. Another common reason for performing a failure analysis is to establish responsibilities for the mishap. For instance, an insurance company may want to determine if an event is covered by the policy or not or financial responsibilities must be established for the resolution of a lawsuit.

There is always value in performing some level of failure analysis, even if it seems that it would be better to try something new rather than finding out exactly what went wrong. A tremendous amount of information can be gleaned from understanding how things fail, and this knowledge is invaluable in making things (equipment, machines, and processes) work better in the future. There is a natural tendency to move past the setback of a failure, maybe to avoid dwelling on unpleasant facts or assuming that nothing can be learned from something that did not work out. However, much can be learned from understanding what went wrong, and a good learning opportunity should not be thrown away with the failed parts.

The end point of a failure analysis depends on the specific circumstances and the type of answers needed. In some cases, it may be enough to rule out a specific failure mode, rather than establishing exactly what happened. In an industrial setting, the goal may be to understand the failure enough to be able to identify corrective measures or to determine if a product recall is required. Finally, in serious accidents an exhaustive failure analysis may be necessary for insurance, legal, or safety reasons.

B. Failure Analysis Procedures

The analysis of corrosion failures is not fundamentally different from any other failure analysis. Although some
unique techniques may be used and the failure modes are specifically related to corrosion, the methodology used is much the same for every type of failure analysis. Failure analysis follows the scientific method. Typically there is a question to be answered, such as “How or why did this failure occur?” Hypotheses are proposed to answer the question or questions. The hypotheses are checked against facts, experiments, and analyses. In the end, some hypotheses are ruled out and others are confirmed.

In practice, there may be many hypotheses put forward to explain a failure, some likely and others very unlikely. Conducting an efficient failure analysis means that most effort is spent proving the hypothesis that ultimately turns out to be the correct explanation while dismissing early (but with good reason) those hypotheses that turn out to be unfounded. Thus it is important to identify the relevant information early on, even though one cannot be sure of what information is ultimately going to be relevant. Performing a failure analysis results in an interplay between hunches, developing likely hypotheses, testing them rigorously, dismissing other hypotheses for good cause, and keeping an open mind for other possible scenarios if the ones that appeared likely at first turn out to not fit all of the facts.

C. GENERAL APPROACH FOR CONDUCTING A FAILURE ANALYSIS

There is no firm set of rules to conduct a correct failure analysis, but the following approach will help. Gather some general information, formulate hypotheses, and then use these hypotheses to gather more targeted information. Use this targeted information from observations, testing, and analyses to validate or rule out the hypotheses.

C1. Gather General Information

The first step of a failure analysis should be to understand the role of the failed component and its environment. Is the failed part available for examination? Does a cursory examination provide some clues as to why it failed? By definition, the failure was not desired, so were any steps taken in the design or operation to prevent it? Was the part or equipment that failed a recent design, had it been modified recently, or did it have a long history of good service? Does the manufacturer, designer, operator, eyewitnesses, or end user have any hypotheses about the cause of this failure? All these questions will help orient the investigator at the start of a failure analysis.

C2. Formulate Hypotheses

It is important to formulate hypotheses early in a failure investigation, because they will guide the collection of further information. Without some hypotheses, relevant information may be overlooked, or to the contrary too much information will be gathered in an effort to be inclusive, which may also impair getting to the truly important facts. One should also think about hypotheses that have to be considered even if they may be ruled out in the end. For instance, if the corrosion failure involves dissimilar metals, galvanic corrosion should be investigated because it is an obvious possibility, even if other aspects of the situation make it unlikely.

C3. Gather Further Information

The hypotheses will help the investigator gather relevant information. It is important to collect facts that may tend to disprove a given hypothesis as well as those that may support it. One of the traps to be avoided is to bias the information collected toward proving one particular scenario.

The Royal Society’s motto Nullius in verba, roughly translated as “Take nobody’s word for it,” is a valuable principle to follow when gathering information. Reported observations, hearsay (“Joe told me that...”), and sweeping generalizations (“This has never happened before”) should be noted but not considered reliable until they have been checked for accuracy. Often the simple act of verifying information will separate fact from fiction and considerably clarify a picture that may have appeared confused at first.

C4. Validate or Reject Hypotheses

It is very important that hypotheses be tested or validated in some fashion; without this step they are nothing more than speculation. The validation may be very simple in some cases or it may require extensive analysis in other cases, but this step should never be overlooked. The validation process must be based on physical and engineering principles, not merely on a process of elimination based on commonalities and differences. Sometimes a failure analysis proceeds by listing common factors and differences between failures and instances of successful operation. This method may be useful as a guide to formulate hypotheses (although not as useful as trying to understand the physical factors affecting a failure), but it should not be used as the exclusive means to validate or reject any hypothesis.

The validation of hypotheses must not be biased in favor of a specific scenario. It is not always easy to recognize that a hypothesis that looked promising at first should actually be rejected or modified, but one should remain alert to this possibility if the validation does not turn out as expected.

D. TECHNIQUES TYPICALLY USED TO INVESTIGATE CORROSION FAILURES

Corrosion failures often involve the use of some specific information or techniques. Several guidance documents
suggest checklists or procedures that are specific to corrosion failures, for instance the American Society for Testing and Materials (ASTM) has issued a Standard Guide for Corrosion-Related Failure Analysis [1]. These guides supplement the general failure analysis process and adapt it to corrosion failures. A few topics that recur regularly in corrosion failures are discussed here, but the reader may wish to consult some of the extensive literature on failure analysis [1–14].

D1. Sampling and Collecting Corrosion Evidence

Sampling and collection of corrosion evidence are often key steps in corrosion failure analysis. Sampling should be done carefully because corrosion products and deposits often contain valuable information that can be easily damaged or contaminated. For example, if microbial activity is suspected, samples should be collected in sterile containers under appropriate conditions to avoid contamination by other microorganisms. These live samples should be analyzed promptly. If the pH or dissolved oxygen level of the aqueous environment may help to explain the corrosion, field measurements should be made of these parameters as they can change rapidly during storage. Samples should be protected from contamination by other debris and stored such that they will be protected from further corrosion damage.

In addition, samples must be representative. In many cases a few well-chosen samples will be enough. The investigator may easily choose a few “typical” samples from the affected and nonaffected areas. However, in cases where one must assess the condition of a large number of items (e.g., to assess the extent of damage), a statistically valid sampling method must be used. There is no sampling method that always produces a “statistically valid” sample, so the sampling must be defined for each case with the help of a competent statistician.

D2. Determining Corrosion Rates

A question often arises about the timing of some corrosion event. For instance, one may want to know for how long some corrosive conditions have been present or how long before some corrosion will result in a leak or vessel rupture. Unfortunately, corrosion rates are notoriously variable, and in some cases it is nearly impossible to make precise predictions. However, corrosion rates have been published for many combinations of materials and environment and they can be useful if their limitations are understood. These rates are typically averages over many samples or observations; although the performance of any single sample may deviate significantly from the average, in aggregate these rates can be useful. In general, corrosion rates tend to slow down with time, so it is usually important to know the time period over which the rate was measured because linear extrapolation cannot be used in most cases.

Direct measurements of corrosion rates in the laboratory usually take a long time, which may not be practical in the context of the failure analysis. Where this is not possible, accelerated corrosion tests are sometimes performed; however, it is generally quite difficult to determine the acceleration factor over the actual environment. When possible, long-term monitoring of the corrosion process in service is the best way to obtain relevant rates, and this monitoring should be started as soon as possible after the equipment, product, or process is placed in service.

D3. Characterizing the Form of Corrosion

Various types of corrosion have been defined, based generally on morphology or mechanism. Authors differ on this classification, but generally some variation of the following eight categories of corrosion are used: (1) uniform, (2) galvanic, (3) crevice, (4) pitting or localized, (5) intergranular, (6) dealloying, (7) erosion–corrosion, (8) environmentally assisted cracking (EAC), or stress corrosion cracking (SCC) [15]. Other named forms of corrosion such as microbiological-induced corrosion (MIC), filiform corrosion, and liquid-metal embrittlement are typically covered as subcategories of these types. In this chapter we discuss corrosion failures of various types and illustrate them with case histories where applicable.

D3.1. Uniform Corrosion. Uniform corrosion, also known as general corrosion, is a very common corrosion type where the metal is corroding more or less uniformly. Most often, this type of corrosion is easily investigated, since it occurs whenever a susceptible metal is in contact with an aggressive environment: Leave a nail in water and it will corrode. Questions that are more difficult to answer may include the rate at which the corrosion damage occurred, for instance, why the corrosion was particularly rapid in a specific case. In other cases, the key may be to find out how the environment came into contact with the susceptible metal. Finally, questions may arise regarding the effect of corrosion on the strength or other properties of the corroding material.

D3.1.1. Corrosion Rates. Although corrosion rates are extremely variable, they are useful to indicate the average behavior of many samples. They are also useful as a broad indicator of the intensity of corrosion: In cases where the observed rates are far different from the published ones, there should be some explanation of the difference.

Case Study: Corrosion Rates Indicate That Product Is Not Suitable for Intended Use. A company decided to manufacture a copper-covered stainless sheet to make roof panels, gutters, and flashing products. In this process the stainless steel was electroplated with copper on both sides: 10 μm on the side expected to be exposed to the weather and
3 \mu m on the other (see Fig. 1.1). Atmospheric exposure tests performed by the manufacturer and others indicated a corrosion rate of the order of 1 \mu m per year for coastal marine atmospheric environments. At this rate, the copper coating would have been consumed in about 10 years (or 3 years if the wrong side of the sheet is exposed to atmospheric corrosion), well short of the 30-year life that was contemplated for this product and somewhat shorter than the time to form a patina. Once the copper layer is removed, the roof looks like stainless steel rather than the intended copper patina, and furthermore the now-exposed stainless steel may pit. Although this material may perform well in dry and noncoastal marine climates, it was clearly not suitable for general use under all outdoor atmospheric corrosion conditions.

The field experience indicated that after less than one year of service there were complaints of excessive corrosion. The copper layer was completely removed from areas of severe exposure, such as in chimney flashings exposed to the acidic flue gases or from the water runoff from wood shakes (see Fig. 1.2). Even though most of the installations had not failed after a few years, the occurrence of several early failures corroborated the reported corrosion rates and indicated that the coatings were too thin for this application. By comparison, a similar product with 50 \mu m of copper roll bonded to both sides of stainless steel sheet has demonstrated good performance for more than 20 years of service.

Case Study: Extraordinarily High Corrosion Rates. Dilute nitric acid can be extremely corrosive to carbon steel, but concentrated nitric acid passivates carbon steel. This passivation is temporary and can be reversed. A well-known experiment illustrates this behavior: A nail is placed in a test tube and concentrated nitric acid is added to cover about half the nail. Nothing happens because the nail is passivated by the acid. Water is added slowly so that it forms a separate layer on top of the nitric acid. Nothing happens at first, but after a minute or so, corrosion starts at the interface where water dilutes the nitric acid. The passivation breaks down and the corrosion reaction becomes extremely violent.

This experiment was repeated unwittingly inside a nitrogen tetroxide (N\textsubscript{2}O\textsubscript{4}) tank car through a series of errors [16]. The carbon steel tank car was used to carry N\textsubscript{2}O\textsubscript{4} that was being used in a paper plant. The N\textsubscript{2}O\textsubscript{4} will react with water to form nitric acid. This N\textsubscript{2}O\textsubscript{4} tank car had been involved in an earlier incident in which a significant amount of water had entered it undetected. Sometime later, the presence of water was detected and it was decided to drain the car of the nitrogen tetroxide and nitric acid that had formed. After draining some material, the car was erroneously thought to be nearly empty and water was added to dilute what was thought to be a small “heel” of liquid but was in fact a significant amount of nitric acid and nitrogen tetroxide. The operation was repeated twice in the following days, every time with the same result. Each time, a complicated process of mixing and diluting was taking place inside the car: The inflow of water may have stirred the car’s content, but water, concentrated nitric acid, and nitrogen tetroxide tended to separate in layers because of their different densities. The result was unpredictable and at some point the carbon steel passivation broke down. Very rapid corrosion occurred, a massive release of nitrogen oxides overwhelmed the venting capacity of the pressure relief valve, and the tank car ruptured. There were three distinct corrosion bands on the inside of the car where severe loss of material had occurred in a matter of hours or days.

D3.1.2. Cosmetic Corrosion Failure. Sometimes, uniform corrosion does not affect the structural properties of the corroding part and the only effects are cosmetic. Whether or not this represents a failure depends on the circumstances.
If the appearance of the part is of no concern, a slight corrosion may be acceptable; otherwise corrosion may be deemed a serious concern well before any structural failure may occur.

**Case Study: Atmospheric Corrosion on the Underside of Roofing Panels.** The roof of a California building was made of steel panels with a thick coating on the external side. The underside, which was exposed to an attic space, was left with a thin shop primer coating because there were no concerns about its appearance. After a few years in service, the structural performance of the panels was called into question, in part because the underside had visibly corroded. Some atmospheric corrosion had appeared in spite of the shop primer. Cross sections of the corroded areas demonstrated that the depth of corrosion was minimal and that, at the observed rate, perforation of the roofing panel would not occur during the expected lifetime of the building. Consequently, this was an instance where corrosion was not a failure.

**Case Study: Atmospheric Corrosion of Terne-Coated Roof.** In two buildings, one located in Alaska and the other in Louisiana, roofs made from lead–tin (terne)—coated stainless steel became severely discolored instead of developing the dull gray appearance typically associated with lead roofs. Metals such as copper and lead used for roofs develop a patina or surface film on exposure to the atmosphere; the patina for terne is usually dull gray. However, in these two instances, the roofs developed irregular patterns of reddish-yellowish corrosion patterns (Fig. 1.3). Our investigation showed that the discoloration of the terne-coated roofs was not caused by rusting of the stainless steel substrate. Rather, it resulted from the normal patination of the terne coating being disrupted due to adverse environmental conditions. The sequence of patina formation is orthorhombic lead oxide (PbO, yellow) → basic lead carbonate → normal lead carbonate → lead sulfite → lead sulfate. If access to the air is restricted, there may not be enough carbon dioxide to form the basic lead carbonate, so the yellow lead oxides remain. There was no attack of the stainless steel substrate and no risk of leaks from the roof corrosion, so this was purely a cosmetic failure. However, this is an example where the appearance of the roof was important—the terne coating had been chosen for its color—so this was indeed a corrosion failure.

**D3.2. Galvanic Corrosion.** Galvanic corrosion is a common failure mode. It occurs where a less noble metal is in electrical contact with a more noble metal in an electrolyte. ASTM standard G71 provides a test procedure to evaluate the potential for galvanic corrosion [17].

A related failure mode, but not strictly galvanic corrosion, occurs when the source of potential difference results from a difference in the electrolyte composition between two zones. For instance, differences in oxygen concentration can accelerate corrosion of the area depleted in oxygen. Yet another source of potential differences may be electrical currents generated by some external cause, for instance, stray ground currents from large electrical equipment.

Typically, galvanic corrosion results in fairly rapid attack. But potential differences may be used to protect a piece of metal by forcing the corrosion to occur on a sacrificial anode. This, of course, is the principle of cathodic protection. However, the cathodic protection may not perform as anticipated, leading to corrosion failures.

**Case History: Ineffective Cathodic Protection.** In some small ships, the propeller shafts are enclosed in stern tubes that are part of the hull. The inside of the stern tubes is exposed to the seawater whereas the outside is dry, being in the hold of the ship. In a specific model of ships, the propeller shafts are made of stainless steel while the stern tubes and the hull are made of low-carbon steel. The shafts are supported by three bearings in the tubes: one aft, one midlength of the tubes, and one that is part of the forward end of the tubes. The hull is painted and there are zinc anodes on the hull and propeller for cathodic protection. However, severe corrosion was observed after less than one year in service on the inside of the stern tubes, particularly at their forward end, which is the farthest from the aft opening of the tubes (Fig. 1.4).

The corrosion pattern was typical of painted low-carbon steel exposed to aerated seawater without cathodic protection. Potential measurements on a boat in service confirmed that the steel was not cathodically protected in the forward region of the stern tube. This is not surprising: There were no zinc anodes inside the tubes and the “throwing power” of the anodes on the outside of the hull was simply not enough to reach the inner surface at the forward end of the tubes, especially given the shaft bearing supports that are in the way. Further, the stainless steel shaft, sealing flange, and
rotating seal were likely to have anodically polarized the steel tubes, accelerating the corrosion. Under these conditions, any small defect or holiday in the paint coat (and the inside surfaces of the tubes are difficult to paint) would lead to the observed corrosion. It was recommended that zinc anodes should be placed on the inside of the tubes for effective cathodic protection.

Case History: Thermogalvanic Corrosion. A relatively uncommon source of potential difference between two electrodes is a difference in temperature. The electrode potential of a metal piece in an electrolyte depends in part on the temperature, but temperature effects are usually small and negligible. However, in some cases these temperature differences lead to significant failures. A common occurrence is the potential difference between the hot and cold water lines in homes when the copper pipes are buried under a concrete slab. In several residential developments in the western United States, the hot and cold water lines were buried under the home cement slab foundation. The temperature difference between the hot and cold copper water lines provides a potential difference, which in some environments results in the hot line being anodic to the cold. The soil and soil moisture provide the electrolyte. The result is pitting corrosion on the outside of the hot water lines. This failure mode happens more often on homes with hot recirculation pumps. These pumps keep hot water circulating constantly in the lines, so that there is almost instantly hot water at the faucets when they are open. The result is that the lines are hot 24 hours a day, whereas without recirculation pumps the lines would be cold most of the time.

In this situation, statistical methods can be used to predict future leaks based on prior experience. The Weibull distribution is commonly used to model failures. In a particular development, the number of leaks in homes with recirculation pumps could be modeled accurately by a three-parameter Weibull distribution (Fig. 1.5) whereas the homes without recirculation could not be easily characterized without accounting for home location or hot water usage.

D3.3. Crevice Corrosion. Crevice corrosion is a type of localized corrosion at an area that is shielded from full exposure to the environment. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. This form of corrosion is sometimes also called deposit or gasket corrosion [15]. ASTM provides a guide for evaluation of the crevice corrosion resistance of stainless steel and nickel-based corrosion-resistant alloys in chloride-containing environments [18].

Crevices are formed in a variety of design situations. For instance, aircraft skin panels are joined by lap splice joints, where moisture and corrosive atmospheric gases can become trapped between the two panels, resulting in crevice corrosion [19, 20]. This mechanism was blamed for the 1988 Aloha Airline accident in which a 20-year-old Boeing 737 lost a major portion of the upper fuselage at 25,000 ft [19, 21, 22]. In this particular instance, crevice corrosion resulted in the formation of voluminous hydrated aluminum oxides which acted to separate the two skin panels, stressing the rivets and resulting in fatigue failures.

D3.4. Pitting. Alloys that maintain their resistance to corrosion through the formation of a protective passive layer, such as stainless steels, aluminum alloys, and titanium alloys, generally do not suffer from uniform corrosion; rather they will usually corrode as a result of the localized breakdown of a small region of the passive film. Corrosion occurs rapidly at this defect compared to the surrounding material covered with the passive film, resulting in the formation of a pit. ASTM has a standard that helps to characterize the nature of pitting [23].

Case History: Pitting Corrosion of Aluminum Due to Copper-Containing Fungicides. Irrigation pipes used in several California farms suffered from rapid pitting corrosion starting on the inside of the pipe. The pipes are used to irrigate crops and spray fungicide and other chemicals. The pipes that experienced severe pitting were used to spray copper-based fungicides.

A literature review indicates that dissolved copper (in the form of copper hydroxide, the active ingredient of the fungicides) is not enough to promote severe pitting of aluminum alloys; there must be some chlorine and bicarbonate ions as well. The pitting mechanism has not been identified in detail, but it probably involves penetration of the aluminum oxide layer by chloride ions, plating of copper on the exposed aluminum surface, and starting the formation of corrosion products nodules over the corroding areas. Once
the nodules are formed, they set up concentration cells and severe pits grow under the nodules.

Experiments confirmed that all three ions were necessary for severe pitting. Aluminum pipes exposed to fungicide dissolved in deionized water were slightly attacked, with few shallow pits forming. Similarly, pipes exposed to farm water (containing bicarbonate hardness as well as about 9 ppm chlorides) without fungicide experienced mild pitting. Only the combination of farm water and fungicides caused severe pitting, comparable to the damage observed in the irrigation pipes on the farms (Fig. 1.6).

D3.5. Dealloying. Dealloying (also known as selective dissolution) includes two commonly occurring phenomena known as graphitic corrosion of cast irons and dezincification of brasses. These are two related corrosion modes, in which one of the components of an alloy leaches out selectively, leaving behind a spongy and weak matrix. In dezincification, zinc leaches out of the brass, leaving behind a copper matrix. In graphitic corrosion of cast irons, the iron corrodes away, leaving behind a porous and weak graphite matrix.

This dealloying corrosion may not be easily recognized by a simple visual examination; frequently the matrix does not look appreciably different from the intact material. A metallographic cross section may be required to identify this type of corrosion and determine its extent.

Case History: Graphitic Corrosion of a Sewer. A fire protection water main at a restaurant failed. As part of the repairs, slurry comprised of cement and pea gravel was pumped under the restaurant foundation to fill the void that was created from water gushing out of the ruptured

FIGURE 1.5. Three-parameter Weibull distribution fits very well the cumulative failure distribution of homes with recirculation pumps (left), but homes without pumps cannot be characterized with a two- or three-parameter Weibull distribution without accounting for geographic distribution or other effects such as hot water usage (right).

FIGURE 1.6. Pitting observed on the inside surface of an aluminum irrigation pipe (left) and cross-section of a pit in a laboratory sample of aluminum pipe exposed to copper-containing fungicide (right).
fire main. The contractor performing the repairs then found that the sewer line was plugged with this slurry. Further inspection found the sewer line was corroded and the contractor thought that perhaps his cement had corroded the pipe. The insurance for the restaurant ordered an investigation into the cause of the sewer line failure. The piping is shown in Figure 1.7.

It was immediately clear that pumping the slurry was not likely to have corroded the sewer line, as cement is not corrosive to ferritic materials. Inspection of the gray cast iron sewer line showed severe graphitic corrosion: substantial wall thinning, holes, and selective leaching of iron from the cast iron matrix. The corrosive attack was primarily on the sewer pipe inner surface, with little or no corrosive attack from the outside. The graphitic corrosion was extensive, indicating that the sewer may have been leaking for a long time, probably years. The most severe corrosion, including holes in the sewer line, was near the foundation on the south side of the restaurant where the fire protection water main entered the building. Examination of the fire main showed that it had failed due to weakening of the pipe wall from external corrosion. Thus, it is likely that the sewer line leak was the source of moisture that caused the external corrosion damage to the fire protection water main.

D3.6. Erosion–Corrosion. Some metals corrode more rapidly when exposed to flowing water. A good example is copper: Corrosion is much accelerated when exposed to water flowing at more than about 1 m/s past the surface. These conditions may be found in home plumbing systems with hot recirculation lines, as shown below.

Case History: Erosion–Corrosion of Copper Hot Recirculation Lines. Some homes have hot recirculation lines; that is, the hot water lines form a loop in which a small pump keeps a constant flow of water. This allows hot water to flow almost instantly from any tap in the home. However, the constant flow and high temperature could lead to severe corrosion. In a recent residential development where these loops were installed in fairly small homes, the available pumps were oversized with respect to the pipes, resulting in a constant high-velocity flow of hot water. Localized corrosion developed in a few years at areas where the flow was disrupted, such as elbows and tees. The corrosion pattern showed deep, well-defined eroded areas looking like sand dunes or river erosion patterns, indicative of erosion–corrosion (Fig. 1.8).

D3.7. Environmentally Assisted Cracking. EAC/SCC is a frequent cause of corrosion failures because it tends to be unexpected. Many early corrosion failures occurred in situations where SCC was unknown or unexpected at the time. For instance, the Silver Bridge at Point Pleasant, West Virginia, was designed in 1927 at a time when SCC was not known to occur under rural atmospheric conditions in the classes of bridge steels used for construction [24–26]. Yet SCC developed in an eyebar suspension link and led to the catastrophic collapse of the bridge after 40 years in service. Similarly, the Flixborough explosion of 1974, which killed 28 people in Great Britain when 50 tons of cyclohexane was released in a chemical plant, was (in part) a result of nitrate SCC and liquid metal embrittlement [27, 28].

Generally, SCC requires a specific combination of stress, material, and environment. Since the fundamental mechanisms for SCC are not always well understood, new combinations that can cause SCC are unfortunately found by accident.

Case History: Room Temperature Transgranular SCC of Austenitic Stainless Steel. Austenitic stainless steel, such as type 304 or 316, is known to be susceptible to transgranular SCC (TGSCC), but it was thought that this required exposure to concentrated chloride environments above 60°C. However, there have been several recent reports of such SCC at room temperature. For instance, SCC has been observed in permanent anchors used for rock climbing in Thailand (Fig. 1.9), in limestone formations at sea level [29].

After a few years, some of the anchors developed extensive cracking, to the point that they broke under normal climbing loads. Examination of the broken pieces showed
pervasive intergranular SCC and the fracture surfaces contained a high concentration of magnesium, rather than the sodium that would be expected in a marine environment. Review of the known cases of room temperature transgranular SCC showed that the climbing anchors are in an environment that combines known promoters of TGSCC. Essentially, this type of SCC requires that the steel be exposed to very high concentrations of chlorides, which are promoted by salts such as magnesium or calcium chlorides, and by low relative humidity (a high relative humidity tends to dilute any salt water film on the metal). The climbing cliffs are located on tower karsts, which get their characteristic steep sides because of very active dissolution and redeposition of the limestone. Thus the climbing anchors can be exposed to calcium and magnesium salts as well as sodium chloride from the ocean. Although the environment is usually very humid, there are times where the relative humidity is fairly low, concentrating any solution that has formed on the stainless steel. Thus the climbing anchors are exposed to an environment that is extremely severe for transgranular chloride SCC.

D4. Complex failure analysis

Sometimes the incident under investigation is particularly complex or involves significant costs, either human or financial. In these instances, it is more important than ever to perform the failure analysis in a careful manner, separating various issues that may be involved and thoroughly validating hypotheses before coming to final conclusions. Such an example is described here.

Case Study: Chlorine Release at a Manufacturing Facility. A massive amount of chlorine gas was released to the atmosphere at a chemical plant making chlorine from calcium chloride [30, 31]. In the plant, the chlorine gas is liquefied before transport by railcar. In the liquefaction process, the chlorine gas is first compressed, then cooled down in a shell-and-tube heat exchanger, in which the chlorine flows inside tubes while chilled calcium chloride brine at about −23°C (−10°F) circulates on the outside of the tubes. The liquefied chlorine is sent to a storage tank via a long transfer pipe containing several tees and elbows. The release
occurred through a large corrosion hole in an elbow in the transfer line between the liquefier and the storage tank.

Early indications showed that the hole in the elbow was due to severe general corrosion on the inside surface. Dry chlorine is not corrosive to the steel elbow, but addition of water to the chlorine could make the mixture extremely corrosive. Potential sources of water included the chlorine liquefier: If there was a leak in the tubes, brine solution could enter the chlorine stream. The liquefier was pressure tested and several tubes were found to be leaking.

The liquefier was cut open to expose the leaking tubes. To the general surprise, an old rag was found stuck in the shell of the liquefier, right at the brine inlet piping. It appeared that the rag had been there for a long time, most probably from the time of installation of the liquefier, some 25 years earlier. The rag partially blocked the brine flow path, resulting in accelerated flow in the areas that remained unobstructed. The leaking tubes were found in the area of accelerated brine flow.

With these early findings, the following scenario was hypothesized: The rag had been in the liquefier since installation, leading to increased brine flow rates over some tubes. This eroded the tubes, and, after about 25 years, one or more tubes were perforated. The brine flowed into the chlorine, creating a very corrosive mixture that corroded through the elbow in the transfer line within a few days, before the water contamination of the chlorine could be detected. Each step in the scenario was validated with tests and analyses.

1. **The rag increased the flow rate over some tubes in the bundle.** A fluid flow finite-element analysis of the liquefier inlet section was performed. With the cloth, the brine velocity in the area of the holes was about 3.94 m/s, whereas without the cloth it would have been only 1.27 m/s, or about one-third.

2. **This increased flow rate led to through erosion of the tube in about 25 years.** The observed corrosion rate of the tubes in areas where the brine flow was not accelerated by the cloth was very slow, about 10 μm per year. At this rate, it would take over 200 years to puncture a tube, so the design and operation of the liquefier were not the cause of the tube leak. The corrosion rate of the tube material exposed to brine flowing at high velocities was measured in a test bed in which chilled brine of various pH values was flowed over dummy tubes at various velocities. For a brine solution at its natural pH (no chemical additions), flowing at about 4 m/s, the interpolated corrosion rate would lead to through-wall erosion in about 22 years, very close to the actual service life of 25 years.

3. **Once the tube was perforated, brine flowed into the chlorine stream.** This conclusion was actually not immediate, because both the brine and chlorine systems were pressurized to roughly the same value. A careful pressure drop analysis of both the chlorine and the brine systems, coupled with review of plant data and some actual measurements made on a mock-up of the brine system, confirmed that the brine pressure was likely higher than that of the chlorine, so that brine would be entrained into the chlorine stream.

4. **The transfer line elbow corroded mostly from the inside out.** This was not immediately obvious, as both the inside and the outside of the elbow were severely corroded. The outside surface may have suffered from underinsulation corrosion during its life, and perhaps more rapid corrosion had occurred during the incident, when liquid chlorine was released from the leak site, but the extent of damage on the inside and outside needed to be compared accurately. A cross section of the failed elbow was traced over the outline of an undamaged elbow; this illustrated clearly that most of the corrosion had occurred on the inside surface (Fig. 1.10).

5. **The corrosion rate at the elbow was high enough to lead to a leak in a few days.** It is likely that the brine leak in the chlorine liquefier occurred relatively shortly before the incident, because it is likely that small amounts of water in the chlorine would have been detected prior to distribution. The best estimate of the start of the brine leak was a few days before the incident. The elbow was about 5.3 mm thick originally, so the corrosion rate would have to be extraordinarily high for through-wall attack in a few days. A related observation that required explanation was that the corrosion at the leak site was much more severe than

![FIGURE 1.10. Erosion–corrosion wall loss of liquefied chlorine run down elbow compared to exemplar elbow.](image-url)
elsewhere in the transfer line, even though the line contained at least one other elbow. This was investigated by a combination of tests and analysis. The failed elbow happened to be located immediately after a T fitting, so that the flow went through two changes of direction in rapid succession. A computer fluid dynamics (CFD) model showed that the flow velocity and the shear rate in this elbow were much higher than in the other elbow in the transfer line, explaining why the corrosion was so much more severe at the leak point (Fig. 1.11). Actual corrosion rate measurements with several mixtures of brine and chlorine, both static and flowing, showed very high corrosion rates, but not quite high enough to achieve penetration in less than seven days. However, given the variability of the measured rates and the uncertainty about the flow conditions and the composition of the corroding mixture, it was concluded that the elbow most likely corroded in a few days after the tubes had started leaking.

The hypothesized scenario was thus validated step by step. This was a very serious incident, in which the stakes were high enough that a thorough failure analysis had to be performed, and the resources were available. Most failure analyses cannot be this detailed, but the basic steps must be the same: gather initial information, formulate hypotheses, and, most importantly, validate these hypotheses with the level of detail appropriate for the conclusions to be reached.

REFERENCES


