Select Corrosion References with Application to Geothermal Power Production

Materials and Treatment Technologies

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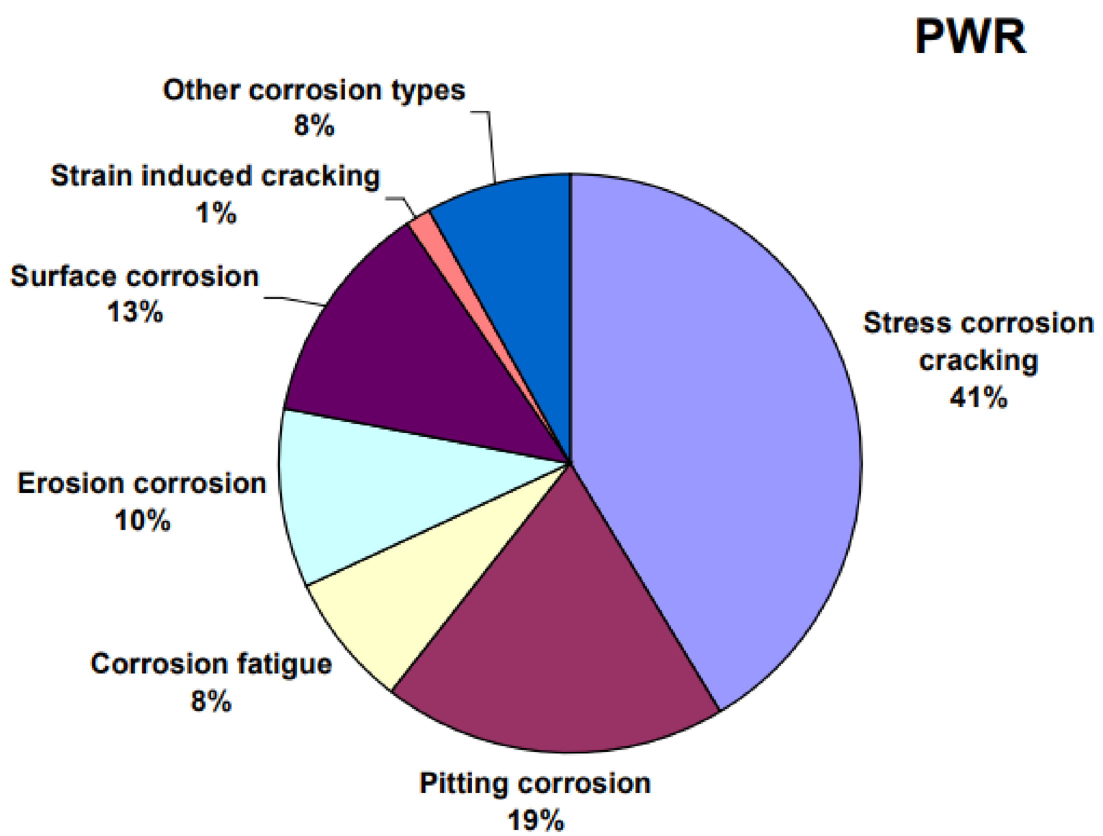

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Technical Update, February 2018

EPRI Project Manager

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ABSTRACT

To support the development of new technologies for managing corrosion in geothermal systems, this report provides a select bibliography of corrosion references from geothermal, thermal, and nuclear generation technologies. A previous EPRI Technology Innovation report (3002007966, 2016) identified and compared chemical data from past and present research in a variety of geothermal fields, including the Geysers in northern California, whose temperatures approached 400°C. The review also identified the causes, types of damage, and mitigation practices associated with corrosion in these reservoir systems. References from other generation technologies are cataloged because conventional thermal plants are more prevalent in the generation mix and fund more corrosion research. Unlike thermal facilities in which fluid compositions are rigorously controlled, geothermal fluid compositions vary widely depending on the geologic setting, within individual fields, among wells within a field, and even within individual wells. Evaluating corrosion mitigation practices from conventional hydrocarbon or nuclear-fueled facilities can identify potential crossover applications for the more chemically complex geothermal environment.

Keywords
Corrosion mitigation
Enhanced geothermal systems
Geothermal fluids
The Geysers

要約

本報告書では、地熱系における腐食管理のための新技術発展を支援するため、地熱、火力、原子力発電技術より抜粋した腐食参考文献の目録を提供する。以前のEPRI技術革新報告書（3002007966,　2016）では、カリフォルニア北部の400℃近いガイザースを含む、さまざまな地熱地帯の過去および現在の研究から化学データを調べて比較した。また、このレビューでは、こうした貯留層における腐食の原因、損傷の種類、関連する緩和措置の調査も行った。他の従来型発電所は発電ミックスの中でも普及率が高く、腐食研究への投資も多いため、こうした発電技術からの参考文献も目録化している。流体組成を厳密に管理する発電所とは異なり、地熱流体の組成は、地質環境によって、各地熱地帯、地熱地帯内の地熱井、さらには各地熱井内でも大きく変動する。従来の炭化水素燃料や核燃料施設の腐食緩和措置を評価することで、より化学的に複雑な地熱環境のための、潜在的に分野横断的な応用を特定することができる。

キーワード
腐食の緩和
増産地熱系（EGS）
地熱流体
ガイザー

EXECUTIVE SUMMARY

Dealing with corrosive fluid geochemistry can be one of the most difficult challenges in developing and producing geothermal systems. Early in the development history of geothermal resources, conventional hydrothermal systems produced relatively benign geothermal fluids. Corrosion problems have become more prevalent as more geothermal systems are discovered, developed, and produced for long periods of time. Mitigating corrosion in existing geothermal fields can become an urgent need as resource production progresses and reservoirs begin to produce increasing volumes of superheated steam.

Deeper drilling, exploration in near-magmatic volcanic environments, and projected deep enhanced geothermal system (EGS) resource development have shown that volatile hydrogen chloride (HCl) and other corrosive conditions can occur in geothermal areas all over the world. Research efforts were motivated in part by the increasing importance of mitigating corrosive geochemical environments and the recognition of the energy potential of deep, near-magmatic systems. The feasibility of deep high-temperature EGS projects—or drilling into near-magmatic, highly corrosive environments as contemplated in the Icelandic Deep Drilling Project—depends directly on addressing potential corrosion problems.

Funding for academic research into geothermal corrosion declined after the 1990s, but the geothermal industry has continued to evaluate cost-effective corrosion mitigation options. Carbon steel has been commonly used for geothermal production wells and gathering lines because of its low cost and availability, but it corrodes easily when exposed to acidic geothermal fluids. Materials choices for well casings are critical because the casing materials and cements used in completing geothermal wells are projected to last for the project life and replacing them is difficult compared to work on surface facilities. Although many metals adequately survive corrosive conditions, the cost of some materials is so high that it significantly impacts geothermal development costs and project economics. In several geothermal fields, chemical injection to adjust the fluid chemistry is the most cost-effective solution to corrosion. Sodium hydroxide (NaOH) injections increase pH and can improve operating conditions to reduce the immediate need for corrosion-resistant alloys.

Conventional thermal (hydrocarbon or nuclear-fueled) facilities are a dominant part of the electrical generation mix. Consequently, corrosion mitigation efforts for these generation technologies are continually well funded, and the volume of academic/industry studies from the sector far outweighs those for geothermal corrosion research. Select references from thermal facility corrosion studies were included as part of this effort because of the potential to identify crossover corrosion mitigation measures or new material or alloy combinations that could be cost-effective and applicable to more chemically complex geothermal settings.

エグゼクティブサマリー

腐食性流体の地化学を扱うことは、地熱系の開発や生産におけるもっとも困難な課題の一つである。地熱資源の開発史初期における、従来の熱水系が生み出す地熱流体は、比較的無害なものだった。長期間に、より多くの地熱系が発見、開発、生産されるにつれて、腐食の問題もより一般的となった。　既存の地熱地帯での腐食緩和は、資源開発が進展し、地熱貯留層から発生する過熱蒸気の量が増え始めると、差し迫って必要になる可能性がある。

より深層の掘削、近マグマ火山環境の探査、深層の高温岩体地熱発電（EGS）資源の開発計画により、世界各地の地熱地帯において、揮発性炭化水素（HCl）その他の腐食状態が発生する可能性のあることが明らかとなった。研究努力は、地化学的な腐食環境の緩和の重要性が増していたこと、および、深層の近マグマ系のエネルギー潜在力に対する認識に動機づけられたものである。アイスランド深層掘削計画で想定されているような、深層の高温EGSプロジェクトや近マグマの腐食性の強い環境での掘削の実現可能性は、潜在的な腐食問題の対策に直接左右される。

地熱腐食の学術研究への出資は1990年代以降減少したが、地熱産業では費用対効果の高い腐食緩和策の評価を続けてきた。炭素鋼は、コストの低さや入手しやすさから、地熱生産井や輸送ラインで一般的に使われてきたが、酸性の地熱流体に晒されると容易に腐食する。地熱井の仕上げに使われるケーシング材やセメントは、プロジェクトの寿命が終わるまで存続することが想定されており、地表施設の工事に比べると改修が難しいため、坑井ケーシング用材の選択は非常に重要である。腐食状態においても十分に耐えられるいくつかの金属もあるが、材料の中にはコストが非常に高く地熱開発コストやプロジェクトの経済に顕著な影響を与えるものもある。地熱地帯によっては、化学薬品の注入によって流体化学を調整することが、腐食に対するもっとも費用対効果の高いソリューションとなる。水酸化ナトリウム（NaOH）を注入するとpHが高くなって運転条件を改善することができ、耐食合金の差し当たりの必要性が軽減される。

従来型（炭化水素燃料もしくは核燃料による）発電所は、発電ミックスの主要部分を構成している。そのため、こうした発電技術のための腐食緩和策に対しては潤沢な資金提供が続き、このような部門からの学術/産業研究の量は地熱腐食研究の量よりはるかに多くなっている。本取組みには、費用対効果が高くより化学的に複雑な地熱環境に適用できる、腐食緩和策や新材料・合金の組み合わせを特定できる可能性があるため、従来型発電所の腐食研究から抜粋した参考文献も含む。

LIST OF TERMS

Al	aluminum
Al_2O_3	aluminum oxide
Cl	chloride
Cl^-	chloride ion
ClO_2^-	chlorite
ºC	degrees Celsius
Cr	chromium
CVD	chemical vapor deposition
DOE	U.S. Department of Energy
EGS	enhanced geothermal system
FAC	flow-accelerated corrosion
Fe	iron
H_2S	hydrogen sulfide
HCl	hydrogen chloride or hydrochloric acid
HTZ	high-temperature zone
IDDP	Iceland Deep Drilling Project
m	meter
Mg(OH)	magnesium hydroxide
$MgSO_4$	magnesium hydroxyl sulfate
NaOH	sodium hydroxide
Na_2SO_4	sodium sulfate
NCG	noncondensible gas
Ni	nickel
PVD	physical vapor deposition
SCC	stress corrosion cracking
SO_2	sulfur dioxide
SO_3	sulfur trioxide

SPE	Society of Professional Engineers
SSC	sulfur stress cracking
Ti	titanium
TiO_2	titanium oxide
U.S.	United States
Zr	zirconium

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1 INTRODUCTION

Geothermal electricity production provides a renewable source of energy and baseload power that other renewables, including wind and solar power, cannot provide. Conventional geothermal power is produced in areas with naturally occurring hydrothermal reservoirs or in stimulated dried-out geothermal reservoirs. Exploration in deeper and hotter environments has revealed highly corrosive fluids that present a significant challenge for common mitigation methods. Finding reasonably priced materials to minimize corrosion in fluid production and power systems is a significant constraint faced by project developers as exploration extends to these more challenging environments. At the same time, producing conditions in maturing developed geothermal fields are changing as superheating becomes the dominant reservoir condition, resulting in corrosion problems that affect project economics.

Compiled references include EPRI studies of thermal (hydrocarbon and nuclear-fueled) facilities. Geothermal environments are quite different compared with these more common generation methodologies, but many materials used in early geothermal resource development were adapted directly from thermal power plant applications. Conventional geothermal systems generate electricity by using lower temperatures and pressures than most thermal or nuclear facilities. They require an extensive array of wells and surface gathering facilities to deliver fluid to turbines. Unlike thermal facilities in which fluid compositions are rigorously controlled, geothermal fluid compositions vary widely and, depending on the system, may include an array of heavy metals, salts, and dissolved gases that contribute to its corrosive nature and cause significant fatigue and failure of metal components. Fluid chemistries can vary greatly between different sections of an individual field, among wells in a single field, and even within individual wells where the chemical composition of steam or water inflows can vary dramatically. Fluid compositions also change over the life span of a geothermal field. Water of varying compositions is also reinjected back into a geothermal reservoir to replace produced mass and to mine additional heat from the rocks. The injection process introduces fluids with different compositions, resulting in complex fluid interactions and dynamic chemistries. Although these factors make geothermal production unique compared with more common thermal or even nuclear generation methodologies, corrosive conditions are still a concern. Corrosion references from other power generation systems are included in this report because these systems are a predominant part of the generation mix, and the research to address corrosion issues in conventional generation facilities can still have applications in geothermal settings.

2 GEOTHERMAL CORROSION REFERENCES

In support of the development of new technologies, EPRI (2016) reviewed and compiled published references for corrosion in geothermal systems. That report discusses the causes and occurrence of corrosion in geothermal systems, corrosion-resistant materials, chemical treatments to mitigate corrosion, and corrosion in high-temperature geothermal environments. Mitigating corrosion has become more important as higher temperature conventional geothermal resources are identified, developed fields mature, and reservoirs begin to produce more superheated steam. Highly corrosive conditions related to near-magmatic temperatures may limit the future development of deeper, hotter resources or high-temperature enhanced or engineered geothermal systems (EGSs). The results are summarized and select references included in the bibliography.

Causes and Occurrence

Corrosion of production wells, gathering lines, and turbomachinery by geothermal fluids (steam and water) has been a problem with some geothermal reservoirs since the industry's inception and can be a significant impediment to project development. EPRI Technology Innovation report 3002007966 (2106) provides references to the high variability in composition of geothermal fluid and the wide array of heavy metals, salts, and dissolved gases that contribute to corrosion, fatigue, and failure of metal components. Fluid chemistries vary among specific geothermal fields, among wells in a single field, and even within individual wells where the chemical composition of steam or water inflows can vary dramatically. Two-phase conditions can exist as initial reservoir conditions in conventional geothermal resources and can develop over time as reservoir pressures decline. In two-phase systems, the flash point may change over time and can be a particularly corrosive environment for steel well casings. Fluid compositions also change over the life span of a geothermal field. Sustaining geothermal production depends on injection to replace mass and to mine additional heat from the reservoir. Injection introduces fluids of different compositions, resulting in complex fluid interactions and dynamic shifts in geochemistry. Deeper wells drilled to evaluate field limits or deeper, higher temperature resources introduce further complexity with lower pH values and higher salinities.

Fluid pH is a dominant geochemical influence on corrosion in geothermal systems. There are several major causes of geothermal fluid acidity. Volcanic gases containing hydrogen chloride, sulfur dioxide (SO_2), and sulfur trioxide (SO_3) may infiltrate a benign geothermal fluid system, resulting in drastic shifts in pH. Acid-sulfate fluids may develop in shallower two-phase portions of a system from the reaction of oxygen in meteoric water with hydrogen sulfide (H_2S). Acidic brine has been noted in some island geothermal systems where reservoir fluids are predominantly seawater at ≥300°C, causing precipitation of magnesium hydroxide ($Mg(OH)_2$), chlorite (ClO_2^-), and/or magnesium hydroxyl sulfate ($MgSO_4$), resulting in pH declines.

Hydrogen chloride (HCl) is a severely corrosive chemical species in high-temperature geothermal systems or systems that have developed significant amounts of superheat and steam-dominated two-phase conditions. The EPRI report (2016) provides references to several fields in which the chemistry of relatively neutral fluids changed as production progressively dried out, became superheated, and began generating hydrogen chloride. Hydrogen chloride occurs in superheated volcanic fumarole discharges, and outgassing magmatic heat sources for geothermal systems are likely sources of volatile chloride. The EPRI report (2016) also provides reference to direct partitioning of hydrogen chloride from acidic, hypersaline Salton Sea geothermal brine; however, partitioning hydrogen chloride from brine has not been documented in natural geothermal systems in which there is no direct influence from volcanic gases. Depending on well completion design, low-pH corrosion can cause severe damage, rapidly affecting casing integrity. Chloride concentrations measured in dry, superheated steam produced by wells at the Geysers range from less than 0.010 ppm to 200 ppm. Corrosion damage from volatile chloride at the Geysers includes extensive well casing corrosion, casing head perforation, and surface piping failures. Volatile chloride conditions should be anticipated as deeper and hotter geothermal wells are drilled around the world. In most cases, acidic conditions can be treated by steam scrubbing, desuperheating, or injecting pH-modifying chemicals at the surface or downhole.

Mitigation

Materials planning and selection for a geothermal generation facility can be a major challenge in corrosive environments. The EPRI report (2016) focuses on references to the difficulties in predicting how various materials will perform under dynamic reservoir conditions. Early geothermal development had some guidance from thermal power plant technology for surface piping and turbines, and a larger database of materials performance has developed over time as more resources are developed. Carbon steel has been commonly used for production wells and gathering lines because of its low cost and availability, but it corrodes easily when exposed to acidic geothermal fluids. Materials choices for well casings are critical because the casing materials and cements used in completing geothermal wells are projected to last for the project life and replacing them is difficult compared to work on surface facilities.

The EPRI study (2016) includes several references to research on material failures in geothermal environments; for example, the Geothermal Task Force of the International Energy Agency (IEA) initiated research in the mid-to-late 1990s that included laboratory and field testing to evaluate corrosion at high temperatures in geothermal wells and materials for geothermal power production. In general, research has shown that corrosion is the most common failure mechanism in geothermal environments. Academic funded research has declined, but the geothermal industry has continued to work on finding cost-effective alloys for geothermal applications. More recently, failures have been recorded and root analyses performed to determine corrosion mechanisms and prevention options. Geothermal power stations inspect their equipment more frequently than conventional thermal generation facilities—and detailed failures have been studied in greater detail to identify specific locations in the system and pieces of equipment that are being degraded.

Although many metals and alloy combinations offer corrosion protection, these materials are blends of high-cost metallic elements, and the costs remain prohibitive. The EPRI study (2016) identifies several options in the literature reviewed. Austenitic stainless steels are not as corrosion resistant as the titanium (C-276) and nickel (625) alloys, but they are more affordable. Titanium and high-nickel alloys are currently too expensive for most deep-seated geothermal targets, and the price volatility of these specialty metals further complicates project cost estimations. Composite coatings, spray application, electrochemically deposited, and explosion cladded materials have been successful in laboratory testing, but there is little published information on their use in large-scale projects at temperatures typical of high-enthalpy geothermal systems. Furthermore, some coatings may require thicker applications to resist corrosion in low-pH environments. In some geothermal power stations, chemical injection to adjust fluid chemistry is the most cost-effective solution to corrosion. The EPRI report (2016) references an example from differing parts of the Geysers field where an operator failed to anticipate and plan for low-pH conditions while another operator developed proactive treatment strategies that resulted in the successful development of a separate portion of the field. Sodium hydroxide injections increase pH and can improve operating conditions to reduce the immediate need for corrosion-resistant alloys.

Unconventional Geothermal Systems

Corrosion problems have become more prevalent as more geothermal systems are discovered, developed, and produced for long periods. Initial state conditions in most conventional geothermal systems commonly reflect conditions for saturated steam—roughly 235°C—although most developed steam fields identified zones of superheat in which temperatures exceed saturated conditions. As resource depletion progresses, pressures decline and liquid saturation in reservoir fractures approaches zero, yielding increased superheat and increased levels of corrosion.

Developing unconventional hotter resources or high-temperature EGS systems specifically targets very high temperatures or supercritical reservoirs with temperatures approaching 374°C (supercritical conditions for pure water) because of the potential of producing very high-enthalpy fluids. Supercritical conditions often exist in the deep roots of volcanic-hosted conventional geothermal systems. At least 25 wells in or around conventional geothermal fields have encountered temperatures approaching or exceeding supercritical conditions and have even penetrated magma. These systems have encountered more corrosive conditions related to near-magmatic temperatures or contributions of magma-derived volatiles. The feasibility of deep high-temperature EGS projects or drilling into near-magmatic highly corrosive environments such as the Icelandic Deep Drilling Project (IDDP) directly depends on addressing potential corrosion problems.

EPRI has sponsored geothermal corrosion research in the past, and independent Japanese research has evaluated deep or corrosive geothermal environments. The IEA sponsored fundamental research on corrosion in deep geothermal systems between 1997 and 2001, led by Japanese research groups including the New Energy and Industrial Technology Development Organization (NEDO), the Geothermal Energy Research & Development Co. Ltd. (GERD), the National Institute of Advanced Industrial Science and Technology (AIST), the Geological Survey of Japan (GSJ), and the National Institute for Resources and Environment (NIRE).

EPRI (2015) reviewed a cooperative EGS demonstration project in the northwest Geysers that evaluated the potential for increasing permeability within a high-temperature (750ºF [400ºC]) portion of the reservoir. EGS technology offers the possibility of stimulating relatively impermeable rocks in regions of elevated heat flow to allow the circulation of working fluids through a sufficiently permeable volume of hot rock to produce fluid to the surface and generate electricity. The project goal was to identify reservoir management and enhancement methodologies at the Geysers that might be applied in Japanese geothermal fields, such as Yanaizu-Nishiyama in Fukushima Prefecture, and potentially at other project sites in Japan. The experiment successfully enhanced steam deliverability in producing wells. Injection reduced high amounts of NCG common to that part of the reservoir; however, corrosive hydrogen chloride (HCl) remained a problem. Deeper drilling and exploration in near-magmatic volcanic environments elsewhere have also shown that volatile chloride (that is, HCl) can occur in geothermal fluids all over the world. Research efforts in the late 1990s were motivated in part by the increasing importance of mitigating corrosive geochemical environments and the recognition of the energy potential of deep near-magmatic systems. The feasibility of deep high-temperature EGS projects or drilling into near-magmatic highly corrosive environments, such as the IDDP, directly depends on addressing potential corrosion problems.

3
THERMAL CORROSION REFERENCES

Because of the complexity and variety of each thermal plant environment, corrosion is a serious problem and can directly influence the operation and lifetime of a facility. Many thermal plant components corrode because of either poor material selection or lack of corrosion awareness. Thermal energy–generating plant components are typically subjected to corrosion when they are not in operation as a result of maintenance or during low seasonal power demand. During these shutdown periods, ambient air containing varying amounts of water vapor may contact metal surfaces. The amount of water vapor—and therefore the severity and rate of corrosion—depends on the air temperature and pressure.

Causes and Occurrence

Gaseous environments that contain oxygen, sulfur, and carbon are the primary cause of corrosion and rapid material degradation in thermal plants. Coal plants contain varying quantities of sulfur and a substantial fraction of noncombustible mineral constituents, commonly called *ash*. Combustion of coal produces corrosive media near the superheater tubes of the boilers. In the boiler tubes suffering from fireside corrosion, sulfate salts concentrate at the deposit/scale interface, becoming partially fused because these salts contain alkali metals of sodium and potassium. Sodium and potassium volatized in combustion systems react with the sulfur oxides (SOx) released from coal to form sodium sulfate (Na_2SO_4) vapors that then condense together with fly ash on the superheater and reheater tubes in the boiler.

Corrosion in thermal plants typically occurs through the following sequence:

1. The release of the corrosion-relevant substances from the fuel in the furnace
2. The reaction of the compounds formed from the flue gas and flue gas deposits
3. The reaction of the corrosive medium on the surface of and with the metallic materials

Effect of Sulfur

Sulfidation of the steel is the principal corrosion mechanism in the presence of reduced sulfur species, mainly H_2S and SO_2 in flue gas. In reducing conditions, iron sulfide or mixed iron sulfide/iron oxide scales are formed. These are less adherent and more prone to spalling than iron oxide scales and result in high corrosion rates. H_2S also has adverse effects on copper and copper/nickel alloys and increases the likelihood of hydrogen bubbling.

Effect of Chloride

Chloride ions are the main contributors to breakage of the passivation layer, resulting in pitting and stress corrosion cracking (SCC). Although elevated chloride levels are not as common in thermal plants compared to geothermal plants, several studies have found material degradation in metal components due to the presence of chlorides in thermal generation environments.

Pitting Corrosion

Pitting corrosion is a form of localized attack in which pits develop in the metal surface. This usually occurs because of the breakage of the passivation film commonly facilitated by high concentrations of chloride and hydrogen ions. Pitting corrosion is initiated when the rate of metal dissolution is momentarily higher at one point compared to the surrounding surfaces. Pitting is a cause of major concern because of the unpredictability of the beginning of pit formation and the rate of deepening.

Hydrogen Embrittlement

Hydrogen embrittlement is a process related to the introduction and diffusion of hydrogen ions in the metal vacancies, causing the metal to become brittle and fracture. The diffusion of hydrogen ions also causes a bubbling effect in which the surface of the metal detaches from its main component, allowing entrance of other chemicals and further damage.

Hot corrosion and erosion corrosion are two other main types of corrosion affecting thermal energy–generating plants.

Hot Corrosion

Hot corrosion (also called *dry corrosion*) is an oxidation reaction between a metal and air or oxygen at high temperature in the absence of water or an aqueous phase. The rate of oxidation at high temperature depends on the nature of the oxide layer that forms on the metal surface. Oxidation may be accelerated when metals and alloys are coated by a thin film of fused salt (such as from the presence of Na_2SO_4) in an oxidizing gas.

Erosion Corrosion

Erosive, high-temperature wear of heat exchanger tubes and other structural materials in coal-fired boilers is recognized as being the main cause of downtime at thermal power–generating plants. Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid surface velocities. In addition, erosion corrosion is often the result of the wearing away of a protective scale or coating on the metal surface and may be enhanced by particles (solids or gas bubbles). Solid particle erosion (SPE) is the progressive loss of original material from a solid surface as a result of mechanical interaction between that surface and solid particles. Erosion corrosion is a serious problem in many engineering systems, including steam and jet turbines, pipelines, and valves used in slurry transportation and fluidized bed combustion systems.

High-temperature oxidation and erosion by impact of fly ash and carbon particles are the main problems in thermal plants, especially in regions in which the component surface temperature is above 600ºC. Therefore, research on the development of wear and high-temperature oxidation protection systems in industrial boilers is extremely important and is continually being tested. Degradation of materials is, however, a function of many property parameters such as particle (size, shape, velocity, impact angle, and hardness), target (hardness, ductility, and corrosion resistance), and the environment (temperature and partial pressure). As a result, a material that is corrosion resistant in one environment may not be in another.

Mitigation

An EPRI report in 1998 compiled a materials guideline for gasification plants and lists recommended metals for each component as well as corrosion prevention procedures. A case study by Prakash et al. reported that 25–30% of annual corrosion-related costs could be saved with optimum corrosion prevention and control strategies. To prevent hot corrosion, options include changing of metal to super alloys, use of inhibitors, and use of coatings. Super alloys such as Cr and Al—common alloying elements that can improve the hot corrosion resistance of materials—often have negative effects on mechanical properties at high temperatures. Alloying elements with better mechanical properties at higher temperatures, such as Ni and Ti, are expensive and not often used because of cost constraints.

Coatings and thermal sprays are other commonly employed corrosion prevention measures. The three methods in current use to deposit coatings are chemical vapor deposition (CVD), physical vapor deposition (PVD), and plasma spraying. Plasma-sprayed ceramic coatings are used to protect metallic structural components from corrosion, wear, and erosion. The most common coating in thermal plants is Al_2O_3 containing 13wt% TiO_2. Recent studies are also being conducted on nanostructured coatings; they have been shown to be effective, but more laboratory testing is required.

Many coal-fired plants use both wet and dry scrubbing technologies. Both technologies use slurries of sorbent and water to react with SO_2 in the flue gas, producing wet and dry products. Most scrubbers use limestone mixed with water. The limestone effectively captures the sulfur and “pulls” it out of the gases, reducing the chance of sulfur-based corrosion mechanisms.

Geothermal Corrosion Applications

As stated previously, critical or supercritical geothermal environments can be acidic with high concentrations of HCl. Therefore, knowledge of how thermal plants mitigate chlorine-induced corrosion could be applicable. Although thermal sprays in thermal plants have proven effective in reducing corrosion rates, these same coatings may be impractical in geothermal well casings because of the variety of particulates in the geothermal fluids that cause erosion corrosion. Coatings can, however, still be applied on above-surface geothermal components. Scrubbing technologies are already in use in many geothermal plants, such as the Geysers, to capture volatile chloride and have proven effective in reducing corrosion rates.

4
NUCLEAR CORROSION REFERENCES

A nuclear reactor is a complex system of different connected materials that must behave in unison to ensure safe operation of the plant. Corrosion in nuclear plants is unique in that the materials are often exposed to radiation. Irradiation effects weaken the material properties and expose it to more detrimental corrosion of all types. Therefore, although radiation effects are unique to nuclear plants, knowledge of how to identify and mitigate the resulting corrosion effects may also be applied to geothermal facilities—both are subjected to analogous forms of corrosion.

Common materials used in nuclear reactors are austenitic CrNi steel and other nickel-based alloys, in particular, Inconel-600 ($NiCr_{15}Fe$). However, some Inconel-600 has been shown to be susceptible to cracking corrosion because of insufficient thermal treatment in the manufacturing process. Other materials used are the stainless steel-300 ASTM series, Zr alloys (cladding for fuel rods), low-alloy steels, copper alloys (condenser tubes and heat exchangers), and Ti alloys.

Causes and Occurrence

Most nuclear plants experience corrosion mechanisms similar to those of other thermal power plants. The exception is that these corrosion mechanisms are amplified by irradiation. Because irradiation is not typically applicable to geothermal environments, irradiation effects are not fully discussed here.

Figure 4-1 summaries the distribution of corrosion types in pressurized water reactors (PWRs) from a German study. Inadequate coatings are also a major contributing factor in nuclear corrosion and SCC susceptibility.

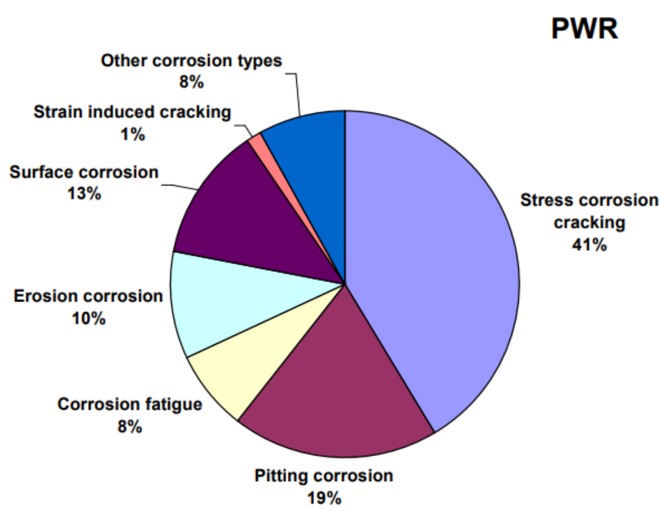

Figure 4-1
Distribution of corrosion types in PWRs (Berg 2009)

Stress Corrosion Cracking

SCC, the most prevalent form of corrosion in nuclear plants, occurs as a result of a combination of actions from specific chemicals (usually chloride ions) and tensile stress. The presence of oxygen and high temperatures increases the severity of attack. This type of corrosion is dangerous because it can permeate through passivation layers or coatings on material surfaces, making it difficult to detect or fully determine the extent of damage. A variation called *sulfur stress cracking* (SSC) results from the combination of tensile stress and environments involving hydrogen sulfide.

Creep and Growth

All metals will exhibit creep over time when exposed at high temperatures and operational stresses. Thermal creep is a diffusion-based migration of atoms and vacancy sites within a metal lattice initiated above some minimum temperature, usually >0.3 T_m, the melting temperature of the metal. Because diffusion is the primary mechanism at play for thermal creep it typically increases exponentially with increasing temperature following an Arrhenius law.

Galvanic Corrosion

Galvanic corrosion occurs by the electrical conduction of two different metals through a medium. Considering the galvanic series endurance list is a must in material selection; however, changes in the chemical systems and temperature may influence the endurance list.

Corrosion Fatigue

Components in nuclear plants are often exposed to wide-ranging steam or water temperatures that can destroy or damage metal parts due to periodic expansion and contraction of the material. In a corrosive medium, this leads to corrosion fatigue. Although the load cases that lead to corrosion fatigue are plant-specific, Figure 4-2 provides an overview of the various factors involved in corrosion fatigue.

Erosion Corrosion

Erosion processes or mechanisms can be categorized as follows:

- **Shear stress erosion.** The surface of a material gets destroyed in a single-phase flow at high velocity by the effects of shear stresses and the variations in fluid velocity.
- **Liquid impact–induced erosion.** Occurs in two-phase flow by the impingement of liquid droplets entrained in flowing gases or vapors. This type of corrosion damages power plant condenser tubes, elbows, and turbine blades. The wear process can be avoided through a combination of making improvements in plant design, drying the steam, and using more corrosion-resistant steels.
- **Flashing-induced erosion.** Occurs when spontaneous vapor formation takes place because of sudden pressure changes. Typically occurs in drain and vent lines downstream of control valves.
- **Cavitation erosion.** Caused by repeated growth and collapse of bubbles in a flowing fluid as a result of local pressure fluctuations. In regions of higher pressures downstream, the sudden collapse of gas bubbles results in pressure spikes that may erode nearby material.

Flow-Accelerated Corrosion (Erosion Corrosion)

Flow-accelerated corrosion (FAC) is a unique and dangerous type of erosion corrosion common in carbon and low-alloy steel piping systems in nuclear plants; it has been responsible for many shutdowns and accidents (for example, the Surry PWR in the United States in 1986 and the Mihama 3 PWR in Japan in 2004). The basic mechanism of FAC is dissolution and wearing of the protective film of magnetite that develops on corroding steel in high-temperature water. This wearing is exacerbated by fluid flow, particularly turbulence. Corrosion mechanisms include soluble iron production at the oxide/water interface or transfer of the corrosion products to the bulk flow across the diffusion boundary layer.

Conditions for FAC include the following:

- **Flow.** Both single- and two-phase water/steam flow at temperatures of >95°C and flow velocity greater than zero.
- **Chemistry.** Potential differences between the liquid and the carbon steel pipe wall that lead to dissolving the protective oxide layer in the flowing stream.
- **Material.** Carbon steel or low-alloy steel pipe material. FAC is effectively inhibited if the steel components are made to contain at least 0.1% chromium.
- **Flow geometry.** Flow-restricting or redirecting geometries downstream causing FAC at an orifice, a sudden contraction, an expansion, an elbow, or at reducers.

Mitigation

Corrosion in nuclear facilities is closely monitored because of the severity of nuclear disasters related to a material failure. Figure 4-2 provides an overview of the root causes of various corrosion mechanisms, the developed corrosion types, and the preventive measures being implemented in nuclear power plants.

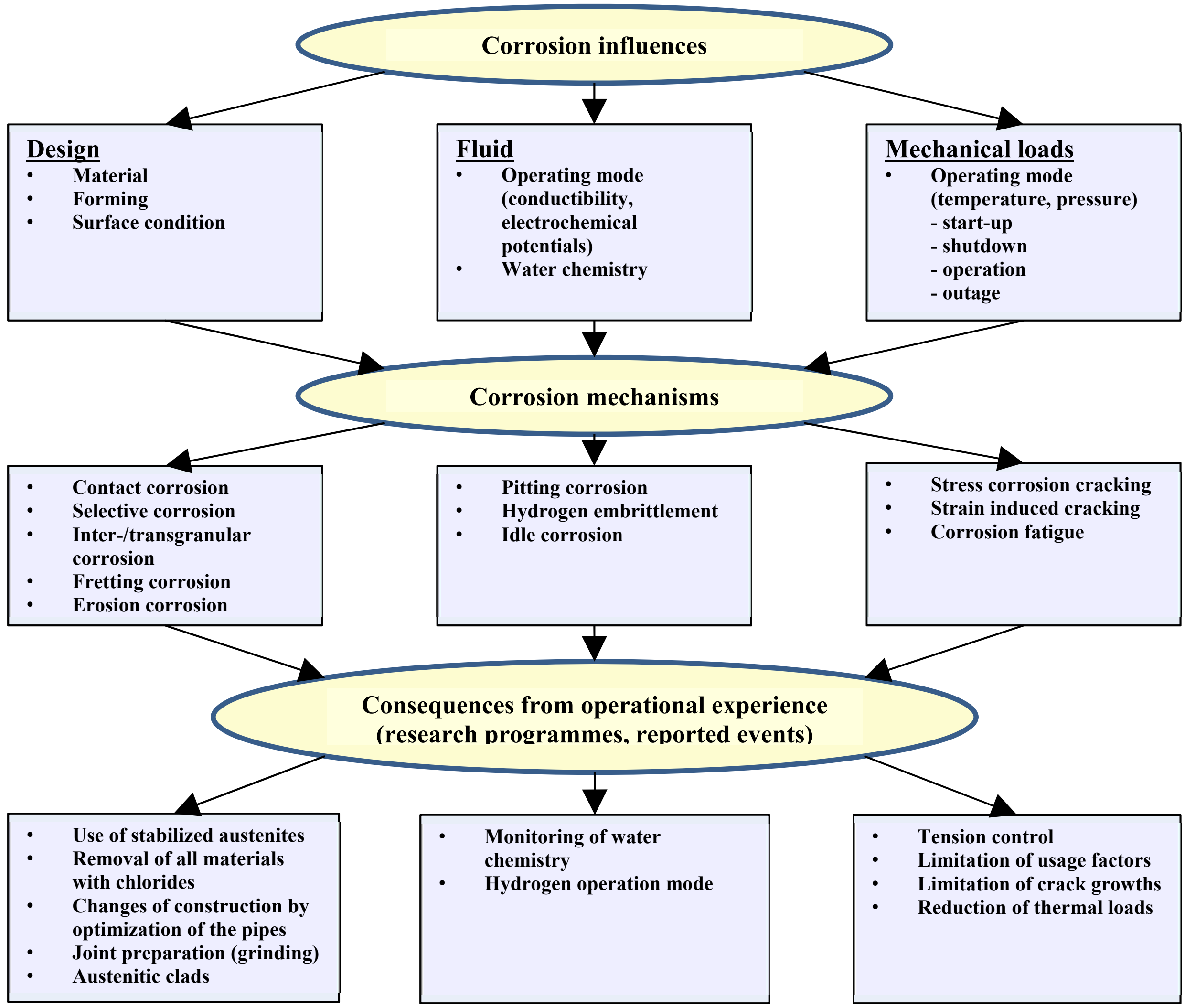

Figure 4-2
Root causes of corrosion, corrosion types, and preventive measures (Berg 2009)

Material selection is also an important part of corrosion mitigation. CrNi, Inconel-600, and Inconel-800 are the primarily used materials in nuclear plants because of their corrosion resistance, particularly to cracking corrosion. Recurrent in-service inspections are strong methods for preventing further (or the onset of) corrosive damage to metallic materials. A list of commonly employed test procedures is provided in Table 4-1.

Table 4-1
Inspection types, procedures, and techniques (Berg 2009)

Type of Test	Test Procedure	Test Technique
Examination with regard to cracks in the surface or in near-surface regions	Magnetic particle flaw detection	Magnetic particle examination, magnaflux examination
	Liquid penetrant examination	e.g. dye penetrant examination
	Ultrasonic examination procedure	e.g. surface waves, mode conversion, dual search units with longitudinal waves, electromagnetic ultrasonic waves
	Eddy-current examination procedure	Single frequency, multiple frequency
	Radiographic examination procedure	X-ray Radioisotope
	Selective visual examination	With or without optical means
Volumetric examination	Ultrasonic examination procedure	e.g. single probe technique with straight (ES) or angle beam scanning, tandem (angled pitch-catch) technique, mode conversion
	Radiographic examination procedure	X-ray Radioisotope
	Eddy-current examination procedure for thin walls	Single frequency Multiple frequency
Integral examination	Integral visual examination	—
	Pressure test	—
	Functional test	—

Methods of reducing FAC include using transition metals (copper, molybdenum, and especially chromium) in the carbon steel. Studies have shown that even small concentrations of Cr reduce FAC rates drastically (~60% FAC rate reduction with steels containing 0.001–0.019% Cr). Software applications, such as CHECWORKS developed by EPRI, are often used to accurately predict the corrosion rates resulting from FAC in piping systems. EPRI has also developed a set of guidelines for improving the flow water chemistry to slow damage.

Cathodic protection methods, such as using a sacrificial anode or an impressed current, are also employed to alter the electrochemical condition of the corroding interface and prevent external corrosion and SCC.

Geothermal Corrosion Applications

Many of the monitoring methods and tests used in the nuclear industry can be applied to monitor corrosion rates and onset in geothermal plants. The ASTM handbook provides a detailed list of currently employed coatings for the nuclear industry; some, specifically the high-temperature coatings, may be applicable for downhole geothermal pipes. Material selection is also key, and materials such as Inconel-600 have been used in various geothermal components.

5
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