Corrosion of Materials Used in Geothermal Power Production

Review of Materials and Treatment Technologies

3002007966

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Technical Update, April 2016

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ACKNOWLEDGMENTS

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This report describes research sponsored by EPRI.

This publication is a corporate document that should be cited in the literature in the following manner:

Corrosion of Materials Used in Geothermal Power Generation: Review of Materials and Treatment Technologies. EPRI, Palo Alto, CA: 2016. 3002007966.

PRODUCT DESCRIPTION

Corrosion can quickly render newly installed geothermal well casings useless, causing damage in the multimillion-dollar range. Mitigating corrosion has become more important as conventional geothermal resource depletion progresses 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). To support the development of new technologies for managing corrosion in geothermal systems, this report provides critical information about environmental chemical conditions that corrode equipment in high-chloride (Cl), low-pH, and high-temperature geothermal environments. It reviews laboratory and field testing of corrosion resistant materials and chemical treatments that mitigate corrosion.

Background

Geothermal systems are an established renewable energy resource with a long history of adaptable, reliable baseload generation. Long-term production withdrawals, changing temperature and pressure conditions, and differing fluid sources can alter reservoir chemistry over time to yield more corrosive fluids. Expanding exploration to include intensely active volcanic systems, deeper resources, and deep EGS stimulation experiments is purposely targeting more challenging reservoir conditions at greater depths and higher temperatures. Operations such as deep drilling in Kakkonda, Japan; magma drilling in Iceland; step-out drilling in Larderello, Italy; and EGS stimulation experiments at The Geysers in northern California in the United States have already experienced reservoir characteristics that far exceed the temperatures and geochemical conditions common to conventional, convecting hydrothermal systems.

Because geothermal fluid chemistry varies considerably, even within individual fields, a wide array of heavy metals and salts may contribute to metallic decay (corrosion). Reservoir conditions contributing to corrosion depend on depth: conditions between the surface and a depth of 5 kilometers (km) vary greatly, while these conditions may contrast sharply with those at a depth of 10 km. Conditions in a production well may be single-phase (water- or steam-dominated), or two-phase (transitioning from water- to steam-dominated). In a two-phase system, the water flashes to steam (at the flash point) as it rises to the surface. Conditions in a production well can be most challenging near the surface as pressures initiate phase changes or minor amounts of condensation occur near the well head creating a chemical environment particularly hospitable to corrosion.

Carbon steel has commonly been used as a corrosion-resistant material in geothermal applications because of its low cost and availability. But in lower-pH geothermal fluids, alternate materials or coatings are required to prevent material degradation and failures. During the 1980s and early 1990s, various studies evaluated the causes of material failures in geothermal environments to improve geothermal power production. Laboratory and field testing revealed a pattern of corrosion resistance among high-alloy materials, and rapid degradation of low-alloy materials or plain carbon steel. In field testing, commercially available carbon steel, low-alloy or chromium-molybdenum (Cr-Mo) steels, martensitic and ferritic stainless steels, high-nickel (Ni) alloys, and titanium (Ti) were evaluated in geothermal production settings at high temperatures (> 260 °C).

Only field testing under actual production conditions can validate the reliability of a given material in a geothermal environment. But, no two geothermal wells have exactly the same chemistry. In response to this fact, Wilson and Lichti (1982) proposed standardized materials testing. Since then, corrosion resistant materials have faced increasing challenges as geothermal wells are drilled deeper to obtain maximal heat output and power generation. Deeper wells also tend to have lower pH and higher salinity.

Objectives

- To review chemical data from past and present research in a variety of geothermal fields with temperatures approaching 400 °C to assess comparative conditions in high-temperature environments.
- To review technologies, downhole chemical treatments, and metal alloys used for casings in these reservoir systems from 1990 to the present.

Approach

A literature review identified the causes, types of damage, and mitigation practices associated with corrosion of metals in geothermal applications.

Results

This review updates open source information on the development and testing of traditional and innovative geochemical mitigation and monitoring methods. Managing the geochemistry of geothermal fluids plays an important role in mitigating materials degradation in differing geothermal environments. In sections of a field that produce the most corrosive superheated steam, caustic (sodium hydroxide or NaOH) and condensate are injected at the wellhead to control corrosion. This technique has also been used successfully to minimize corrosive effects downhole. Available logging and sampling tools have been used in wells at temperatures reaching about 330 °C, but tools suitable for use at 400 °C are still needed to monitor downhole conditions and identify zones of corrosive fluid production in the hottest wells.

Applications, Value, and Use

The results of this research can be used to assess the unique geochemical conditions of corrosive geothermal reservoirs under construction, especially in Japan and Indonesia, and under development in Latin America. It offers a basis for comparing corrosive conditions at The Geysers with superheated high-temperature conditions in other geothermal reservoirs. This work also points out the need for more analysis of the environmental and chemical attributes associated with the transition from a normal hydrothermal reservoir to a superheated steam reservoir. Additional studies may be needed to model high-temperature zones at EGS sites, with expanded evaluation of the mechanisms of chloride generation operating at high temperatures.

Keywords

Engineered geothermal systems (EGS)
Hydrothermal
Chlorides
Corrosion
Nickel-alloys

ABSTRACT

Corrosion can quickly render newly installed geothermal well casings useless, causing damage in the multimillion-dollar range. Mitigating corrosion has become more important as conventional geothermal resource depletion progresses 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). To support the development of new technologies for managing corrosion in geothermal systems, this report provides critical information about environmental chemical conditions that corrode equipment in high-chloride (Cl), low-pH, and high-temperature geothermal environments. It reviews laboratory and field testing of corrosion resistant materials and chemical treatments that mitigate corrosion.

A review of published studies 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 metal corrosion in these reservoir systems from 1990 to the present.

The results show that managing the geochemistry of geothermal fluids plays an important role in mitigating materials degradation in differing geothermal environments. In sections of a field that produce the most corrosive superheated steam, caustic (sodium hydroxide or NaOH) and condensate are injected at the wellhead to control corrosion. This technique has also been used successfully to minimize corrosive effects downhole. The choice of corrosion resistant materials involves tradeoffs between effectiveness, as demonstrated in laboratory and field tests, and cost. Chemical injection combined with materials of lower cost and decreased corrosion resistance is currently the best option. Available logging and sampling tools have been used in wells at temperatures reaching about 330 °C, but tools suitable for use at 400 °C are still needed to monitor downhole conditions and identify zones of corrosive fluid production in the hottest wells. The results of this research can be used to assess the unique geochemical conditions of geothermal reservoirs where sources of actual or potential corrosion require identification and mitigation.

EXECUTIVE SUMMARY

Geothermal systems are an established renewable energy resource with a long history of adaptable, reliable baseload generation. Dealing with corrosive fluid geochemistry can be one of the most difficult challenges in developing and producing geothermal systems. Corrosion and scaling issues have been addressed in a limited number of hydrothermal settings; however, the majority of conventional hydrothermal systems initially produce 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 produce increasing volumes of superheated steam.

An enhanced or engineered geothermal system (EGS) attempts to access and utilize geothermal heat by drilling into hot dry rock at depth. Development and implementation of successful EGS technologies has the potential to expand the geothermal industry by siting geothermal power plants in more locations and expanding the world's potential geothermal resources. The creation of an EGS involves hydraulically fracturing the deep rock to extract its geothermal heat for power generation. Subsurface injection wells are drilled to allow the injected fluid to heat up and transfer the maximum heat from the hot rock before being extracted by a production well.

Deeper drilling, exploration in near-magmatic volcanic environments, and projected deep EGS resource development have shown that the presence of volatile hydrogen chloride (HCl) and other corrosive conditions can occur in geothermal areas 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 as contemplated in the Icelandic Deep Drilling Project—depends directly on addressing potential corrosion problems.

Research is ongoing to find cost-effective alloys for geothermal well casings. Although many metals adequately survive corrosive conditions, the cost of some materials is so high that they significantly impact geothermal development costs and project economics. Austenitic stainless steels are not as corrosion resistant as titanium (Ti) and nickel (Ni) alloys such as Hastelloy C-276 and Inconel 625, 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 estimates. Although composite coatings, spray applications, and electrochemically deposited or explosion cladded materials have been successful in laboratory testing, there are few published studies on their use in large-scale projects at temperatures typical of high enthalpy geothermal systems, and some coatings may require thicker applications to resist corrosion in low-pH environments.

In many 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. Chemical injection combined with a lower cost and decreased corrosion resistance is currently the best option, until nickel and titanium costs moderate enough to justify manufacturing clad or solid piping. Material and treatment technologies should be chosen based on laboratory and/or field testing at conditions similar to those at a specific field, or even well site, if practical.

LIST OF TERMS

Al	aluminum
(aq)	aqueous phase
bar	unit of pressure
bara	unit of absolute pressure
Ca	calcium
$Ca(OH)_2$	calcium hydroxide (hydrated lime)
Ca^{2+}	calcium ion
$CaCl_2$	calcium chloride
$CaCO_3$	calcium carbonate (limestone or calcite)
CaO	calcium oxide (lime)
$CaSO_4$	calcium sulfate
CCPA	Central California Power Agency
Cl	chloride
Cl^-	chloride ion
$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2\cdot(Mg,Fe)_3(OH)_6$	chlorite
CMFs	corrosion mitigation facilities
C-N	carbon-nitrogen (bond)
CO_2	carbon dioxide
CO_3^{2+}	carbonate
Cr	chromium
CRA	corrosion resistant alloy
Cr-Mo	chromium-molybdenum
Cu	copper
DHS	downhole sampler
DOE	U.S. Department of Energy
DSS	dry steam scrubbing
EGS	enhanced geothermal system

F^-	fluoride
Fe	iron
$FeCl_2$	ferrous chloride
FRP	fiberglass reinforced plastic
(g)	gas phase
g/mol	grams per mole
H_20	water
H_2S	hydrogen sulfide
HCl	hydrogen chloride or hydrochloric acid
HTZ	high-temperature zone
IDDP	Icelandic Deep Drilling Project
K	potassium
K_2CO_3	potassium carbonate
KCl	potassium chloride
kg/m s	kilograms per meter per second
kg/m^3	kilograms per square meter
kg/s	kilograms per second
$KHCO_3$	potassium bicarbonate
kJ/kg	kilojoules per kilogram
kJ/mol	kilojoules per mole
km	kilometer
KOH	potassium hydroxide
kPa	kilopascal
lph	liters per hour
$2MgSO_4 \cdot Mg(OH)_2$	magnesium hydroxide sulfate
m	meter
m/s	meters per second
Mg	magnesium

$Mg(OH)_2$	magnesium hydroxide
mg/kg	milligrams per kilogram
mil	one-thousandth of an inch
mm	millimeter
MMT	montmorillonite
Mo	molybdenum
MPa	megapascal
Na	sodium
Na+	sodium ion
$Na_2B_4O_7 \cdot 10H_2O$	sodium borate
Na_2CO_3	sodium carbonate (soda ash)
NaCl	sodium chloride
n-alkyl	normal-alkyl
NaOH	sodium hydroxide
NCG	noncondensible gas
NH_3	ammonia
NH_4^+	ammonium ion
NH_4Cl	ammonium chloride
Ni	nickel
n-octadecyl	normal-octadecyl
O_2	oxygen
ºC	degree Celsius
OH^-	hydroxide
(org)	organic
ppb	parts per billion
ppm	parts per million
ppm_w	parts per million by weight
PPS	polyphenylsulfide

$(R)_3(R)NH_2$	tertiary-alkyl primary amine
$(R)_3(R)NH_3^+ Cl^-$	tertiary-alkyl primary amine chloride
(s)	solid phase
SiO_2	silicon dioxide or silica
$SiO_2 \cdot nH_2O$	silicic acid
SO_2	sulfur dioxide
SO_3	sulfur trioxide
t-alkyl	tertiary-alkyl
Thermochem	Thermochem, Inc.
Ti	titanium
U.S.	United States
Zn	zinc
$Zn_3(PO_4)_2$	zinc phosphate
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. Conventional geothermal systems are being explored in deeper and hotter environments where handling corrosive fluids is challenging. 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.

An enhanced or engineered geothermal system (EGS) attempts to access and utilize geothermal heat by drilling into hot dry rock at depth. Development and implementation of successful EGS technologies have the potential to expand the geothermal industry by enabling geothermal power plants to be built in more locations, thus enlarging the world's potential geothermal resources. The creation of an EGS involves drilling deep injection wells and hydraulically fracturing the rock in order to circulate fluids needed to extract the geothermal heat for power generation. Subsurface injection wells are drilled to allow the injected fluid to absorb the maximum heat from the hot rock before the fluid is extracted by a production well. Wells in recent EGS experiments are typically between 2,000 and 3,500 meters (m) in depth, but scientists and engineers are looking to drill deeper to reach higher temperatures and produce more power [1]. EGS technology could be the future of geothermal energy; according to the U.S. Department of Energy (DOE), if enough plants are successfully established in the United States, geothermal energy could support 10% of U.S. energy consumption [2].

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 is a significant impediment for project developers to overcome. 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. The industry has turned to alternate, more expensive corrosion resistant materials—or coatings and treatment technologies in some cases—to mitigate rapid material degradation and failure.

Geothermal fluid is highly variable in composition, as shown by the wide array of heavy metals, salts, and dissolved gases that contribute to its corrosive nature and cause significant fatigue and failure of metal components. A wide variation in fluid chemistries has been observed among different 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. Fluid compositions have been known to change over the life span of a geothermal field, while injection of water for mass replacement introduces fluids with different compositions, resulting in complex fluid interactions and dynamic geochemistries. Reservoir conditions can be single-phase (water- or steam-dominated) or two-phase. In the case of two-phase, the flash point—where the water “flashes” to steam as it rises to the surface in the well and pressure is reduced—can be a particularly corrosive environment for steel well casings. Furthermore, as time has passed, the geothermal industry has drilled deeper to obtain maximum heat output and power generation, revealing a new set of challenges. In addition to higher temperatures, deeper wells tend to have a lower pH and higher salinity.

The combination of highly variable fluid compositions, temperatures, pH, and dynamic reservoir conditions makes it difficult to predict material performance *a priori*. Therefore, the geothermal industry has developed field-, and in some cases, well-specific solutions to corrosion, taking complex site conditions into consideration when selecting materials and treatment strategies. This report summarizes a review of the open literature on corrosion resistant materials and treatment technologies deployed by the geothermal industry. Section 2 identifies geothermal reservoir conditions leading to metal corrosion at The Geysers field in northern California in United States, and other locations. Section 3 reviews corrosion mechanisms, identifies corrosion resistant materials including solid and cladded piping, and summarizes costs. Section 4 identifies effective chemical treatment technologies that have been used to mitigate corrosion, including the treatment of highly corrosive geothermal fluids at The Geysers that result from the co-production of acid gases like hydrogen chloride (HCl). Section 5 summarizes the findings and makes recommendations for future research.

2

ACIDIC GEOTHERMAL FLUIDS

Causes and Occurrence

There are several major causes of geothermal fluid acidity, but hydrogen chloride is the most prevalent and severely corrosive chemical species found in geothermal fluids associated with high-temperature geothermal systems. Volcanic gases containing hydrogen chloride, sulfur dioxide (SO_2) and sulfur trioxide (SO_3) may infiltrate a benign geothermal fluid system, causing the liquid to become highly acidic. For this and other reasons, development of geothermal reservoirs with strong volcanic influence is typically avoided. Immature geothermal systems may contain residual acidic fluids of volcanic origin that have yet to be completely neutralized by the rock. These systems have been avoided in most commercial developments.

Acidic brine may be caused by the influx of shallow acid-sulfate fluids into a deeper, benign geothermal reservoir. The acid-sulfate fluid is often formed by the reaction of oxygen in meteoric water with hydrogen sulfide (H_2S), or by water contacting acidic minerals. The associated corrosion of geothermal wells often manifests as external casing corrosion when the exterior portion of a well is exposed to the shallow acidic fluids. These shallow fluids may or may not directly affect the produced fluids, depending on the well completion design and casing integrity.

Acidic brine is also created by heating seawater to temperatures of 300 degrees Celsius (°C) or more. At these temperatures, magnesium in seawater precipitates as magnesium hydroxide ($Mg(OH)_2$), chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$), and/or magnesium hydroxide sulfate ($2MgSO_4 \cdot Mg(OH)_2$), causing the pH to drop. This process was believed to be responsible for low-pH brine produced in early wells at Puna, Hawaii and at Reykjanes, Iceland.

In most cases, acidic brine can be treated by downhole injection of sodium hydroxide (NaOH), in the same manner (described later in this report) as hydrogen chloride is treated downhole. Downhole injection has been successful at several fields in the Philippines, but the only field where acidic brine is currently being treated downhole is at Miravalles in Costa Rica [3].

Volatile chloride—in the form of hydrogen chloride and/or ammonium chloride (NH_4Cl)—is commonly produced from vapor-dominated geothermal fields such as The Geysers in the United States and Larderello in Italy, and is typically associated only with superheated steam wells. Severe corrosion problems related to volatile acid-chloride species in geothermal power facilities have occurred at these fields. At Larderello, 1–10 ppm (parts per million by weight, or mg/kg) chloride in steam has etched turbine components—mostly at the base of stationary and moving blades in the wet stages of the machines—while 10–100 ppm chloride in contact with condensate has caused severe corrosion of carbon steel steam lines. 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 due to volatile chloride at The Geysers includes extensive well casing corrosion, casing head perforation, well surface piping failures, and gathering system piping perforations. The corrosion products exfoliated from wellbores and gathering systems impact power plant equipment by plugging steam strainers and eroding turbine blades; in some cases these impacts are more severe than direct corrosion of the components.

Geothermal steam containing volatile chloride has been reported in other fields throughout the world, including Tatun, Taiwan; Krafla, Iceland; Saint Lucia, Windward Islands; Coso, United States; and the Salton Sea, United States. Geothermal systems producing volatile chloride vary greatly in reservoir characteristics; they may be vapor-dominated, liquid-dominated, or volcanic-related fields. However, all of these fields have produced measurable levels of chloride (Cl) in dry steam from certain wells without associated quantities of alkali metals such as sodium (Na) and potassium (K), or alkaline earth metals such as calcium (Ca) and magnesium (Mg). In Krafla, Iceland, hydrogen chloride in steam was first suspected 35 years ago in well KG-4. In the 1980s, well KG-12 was reported to produce about 100 ppm chloride in dry superheated steam, while results from 2008 show chloride levels above 800 ppm in steam condensates from well KG-36. The presence of hydrogen chloride fluids appears to be widespread throughout the Krafla field [4–7]. The IDDP-1 well drilled in Krafla—as part of the Icelandic Deep Drilling Project (IDDP)—with the target of reaching near-magmatic conditions and supercritical fluids, produced superheated steam containing 100 ppm hydrogen chloride from a 400 °C subcritical reservoir. Continued encounters with hydrogen chloride are expected as deeper and hotter geothermal wells are drilled around the world.

It be conclusively stated for only a few geothermal systems that hydrogen chloride is the volatile chloride species, although the presence of hydrogen chloride has been well documented for high-temperature volcanic gases. In the condensate of chloride-bearing steam at The Geysers, there are usually more ammonium ions (NH_4^+) than chloride, making it unclear whether the chloride was initially hydrogen chloride that reacted with ammonia (NH_3) in solution, or was transported as ammonium chloride in the vapor phase.

Several existing mechanisms can produce the observed range of volatile chloride in geothermal steam. Hydrogen chloride does not partition significantly from hot (300–350 ºC), high-salinity (~2 molal), near-neutral sodium chloride (NaCl) brines [8, 9]. For most geothermal reservoirs that are not in direct contact with volcanic fluids, hydrogen chloride is most likely generated from superheated steam by reaction with chloride salts, quartz, and silicates upon brine dry out [10]. An example of this occurred at Coso Geothermal Station in central California in the United States, where a neutral brine-producing well that dried out and became superheated due to low permeability and silica scaling began generating hydrogen chloride at 10 ppm. The reservoir temperature was 270 ºC, brine salinity was 10,000 ppm and pH was 6 [11]. Simonson [12] has shown conclusively that only about 8 ppm hydrogen chloride can be generated from pH 4 brine containing 70,000 ppm chloride ion (Cl^-) at 300 to 350 ºC, and less than 1 ppm hydrogen chloride can be generated under the same conditions at pH 5. These values are an order of magnitude lower than the values proposed by Truesdell and Haizlip [13] based on a deep boiling brine theory for The Geysers.

Since hydrogen chloride is ubiquitously found in superheated volcanic fumarole discharges, it is likely to be of volcanic origin for geothermal wells in contact with volcanic systems and outgassing magma. Direct partitioning of hydrogen chloride from acidic, hypersaline brine is known to occur at the Salton Sea, where brine (4 molal sodium chloride) is deliberately acidified to pH 3–4 for silica-scale control, generating up to 50 ppm hydrogen chloride in steam at 220 °C.

But to our knowledge, partitioning of hydrogen chloride from brine has not been documented in natural geothermal systems where there is no direct influence from volcanic gases.

Occurrence of Hydrogen Chloride in Steam at The Geysers

Early production from The Geysers reservoir consisted entirely of saturated steam with generally low concentrations of noncondensible gas (NCG) that varied systematically throughout the field [14, 15]. Production of saturated steam was not associated with corrosion problems in well casings and surface piping. As The Geysers underwent rapid development during the 1980s, reservoir pressure began to decline and superheated conditions developed in the reservoir. Corrosive steam with relatively high concentrations of volatile acid chloride has been produced from many wells since the reservoir steam transitioned from saturated to superheated conditions in the latter half of the 1980s. Hirtz et al. [16] noted that it is unclear whether the volatile chloride is transported in the vapor phase as ammonium chloride or as hydrogen chloride. Simonson [9] later demonstrated that ammonium chloride transport can occur, with ammonium chloride partitioning (up to 100 ppm chloride) from near-neutral, high-salinity brines at 350 ºC.

Haizlip and Truesdell [17] and Walters et al. [18] reported that steam from the high-temperature zone (HTZ) in the northwest Geysers tends to have elevated NCG and volatile chloride concentrations. The top of the HTZ is defined by a temperature at or above 260 ˚C, measured during drilling. Hirtz et al. [16] reviewed the various origins proposed for volatile chloride that include reactions involving concentrated brine and/or solid chloride phases at temperatures above 300 ºC. Since hydrogen chloride gas is a well-documented component of many high-temperature fumaroles in volcanic environments [19], hydrogen chloride in The Geysers steam may emanate directly from a magmatic heat source. Whatever the origin of the volatile chloride, its occurrence in produced steam signifies a dry (i.e. superheated) path from its source to the production wellbore. Otherwise, the volatile acid chloride—whether ammonium chloride or hydrogen chloride—will ionize, form acid, and react with rocks in the reservoir.

Calpine Corporation, the operator of most of The Geysers wellfield and 16 of the 19 operating power plants, has collected steam samples from wells producing high-chloride steam using a downhole sampler (DHS) designed by Sandia National Laboratories and Thermochem, Inc. [20]. The DHS employs a eutectic material with a high heat of fusion to condense steam and allow collection of a significant volume of both condensate and NCG gas. Samples collected with the DHS show higher concentrations of chloride when the sample is taken in the wellbore immediately above the deepest steam entries. The high-chloride steam is believed to emanate from the HTZ. Production of high-chloride steam from wells that do not penetrate the HTZ is an indication of vertical permeability connecting the HTZ with the normal reservoir. Figure 2-1 shows, in a southwest-to-northeast cross section, the distribution of steam entries (short red "ticks" crossing wellbores and representing steam-bearing fractures) for producing wells in the areas of Unit 5 and Unit 6. The surface concentrations of chloride in steam produced from these wells are shown adjacent to their bottom-hole locations in the cross section. In this area of the steam field, although wells have a wide range of depths and steam entries, none are believed to penetrate the HTZ. The cross section indicates that, in general, the concentration of chloride is controlled by an upwelling dome of high-chloride steam in the vicinity of the SB25 well. None of the shallow wells in the area surrounding the SB25 production well produce steam with high chloride. The implication is that high-chloride steam is migrating upward from the HTZ along a steep fracture zone [21].

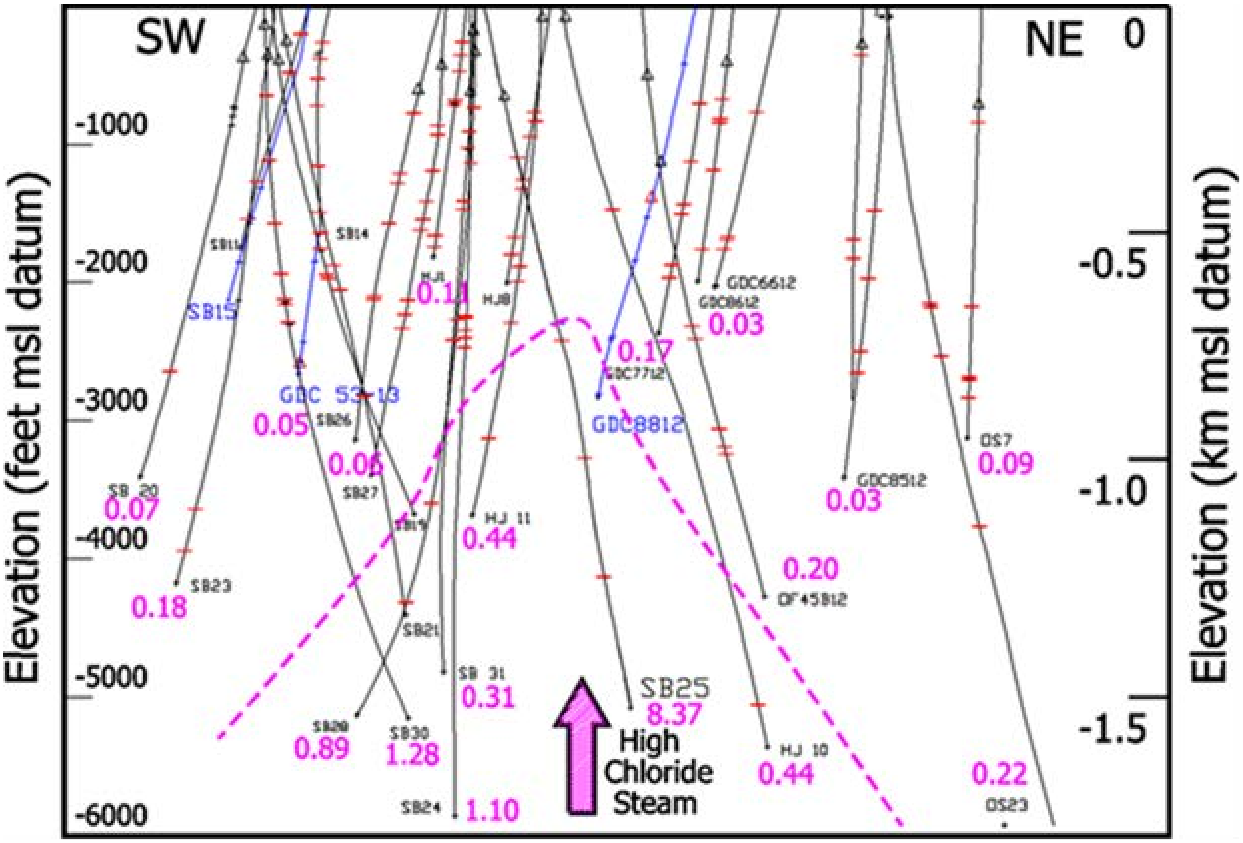


Figure 2-1
Southwest-to-northeast cross section through the areas of Units 5 and 6 at The Geysers. Red ticks represent steam entries to wells. Produced chloride concentrations are shown next to bottom-hole locations of wells. Dashed line represents an upwelling of high-chloride steam originating in the HTZ.

3

CORROSION RESISTANT MATERIALS

Studies began in the 1980s to determine how and why materials were failing in geothermal applications, so a solution to the corrosion problem in geothermal fields could be developed. Wilson and Lichti [22] recognized a need to standardize materials testing because no two geothermal wells had exactly the same chemistry. Laboratory and field testing revealed an obvious pattern of superior corrosion resistance among high-alloy steel and rapid degradation of low-alloy and plain carbon steel. However, results were still too irregular to make any unanimous claims about the overall best material for geothermal well construction. Carbon steels, low-alloy or chromium-molybdenum (Cr-Mo) steels, martensitic and ferritic stainless steels, high-nickel (Ni) alloys, and titanium (Ti)—all of which are commercially available alloys—were evaluated in geothermal brine at high temperatures (260 °C). [23]

The Geothermal Task Force of the International Energy Agency initiated research in the mid-to-late 1990s, including laboratory and field testing, to evaluate corrosion at high temperatures in geothermal wells and materials for geothermal power production [24]. Task Force Subtask C focused on materials research in two areas: (a) collecting data and information on materials, and (b) laboratory and field testing to investigate failure mechanisms. Principal organizations participating in Subtask C included Materials Performance Technologies, New Zealand (high-temperature corrosion and deep-seated geothermal wells developed in New Zealand and proven to have integrity and reliability); Tōhoku National Industrial Research Institute, Japan (materials for geothermal wells); and the New Energy and Industrial Technology Development Organization (NEDO), United States office in California (geothermal well casing and pipelines) [25].

Failure Mechanisms

This section provides a brief overview of the most commonly observed corrosion mechanisms related to materials used in geothermal applications; it is not intended to be a complete treatment of the subject.

Materials issues range from general corrosion (uniform material loss) to more complicated failure mechanisms like stress corrosion cracking and hydrogen embrittlement—but may also include scaling and sludge deposition, as well as biological damage from algae or microbes [26]. In the 1990s, a survey [49] across seven companies found general corrosion to be the most common failure mechanism in geothermal power plants. Corrosion occurs because of a difference in chemical potentials of metals that encourages the transfer of electrons—it is more energetically favorable for an electron to migrate from the anode, where it is at a higher potential (more reactive), to a lower potential at the cathode. The greater the difference in this potential energy is between two metals (or between a metal and an oxide), the faster the rate of corrosion will be for the more active (less noble) metal.

For electrochemical activity or galvanic corrosion to occur, an anode, a cathode, an electrolyte, and a metallic pathway must be present. In the case of high-salinity brines found in many geothermal systems, the electrolyte consists of naturally occurring salts. Many geothermal fluids have high concentrations of dissolved ions, including sodium (Na^+), calcium (Ca^{2+}), chloride (Cl^-), and silica (SiO_2) that contribute to the total dissolved solids content of the fluid and electrical conductivity of the solution. The total dissolved solids content of the geothermal fluid plays an important role in the transfer of electrons leading to material corrosion. Elevated levels of dissolved solids contribute to erosion in addition to corrosion, synergistically interacting to degrade materials in geothermal generation stations. Erosion from high-salinity brine generally occurs at material bends or elbows. According to Povarov [27], typical damage in geothermal power plants is related to general corrosion, pitting corrosion, contact corrosion, erosion-corrosion wear, stress corrosion cracking, drop impact erosion, cavitation erosion, and abrasive erosion.

When the fluid has neutral pH, a passivation layer consisting of a thin film of sulfide or oxide will form on the surface of the metal, protecting it from corrosion. The passivation layer prevents geothermal fluids from coming in direct contact with the metal; instead they must diffuse through the passivation layer, slowing the rate of corrosion. Oxygen (O_2) destabilizes the passivation layer, causing further corrosion [28]. Tests performed in aerated and de-aerated environments have shown that an aerated environment accelerates general corrosion and pitting for carbon steel and brass [29]. The worst corrosion to materials in geothermal steam occurs when the system is exposed to air, creating an oxidizing environment. Although geothermal operators do their best to control these conditions, they are not always successful. Aeration may occur during startup or shutdown, result from a packing leak, or occur for a number of other reasons [30].

Geothermal fluids may also contain high levels of acidic or noncondensible gases—such as carbon dioxide (CO_2), hydrogen sulfide, chlorides, and ammonia—that lower the pH of fluids in a water- or vapor-dominated geothermal system. Low-pH water increases the solubility of the sulfide or oxide film, exposing fresh metal to the corrosive effect of the geothermal fluid, thus increasing the rate of corrosion. The presence of gases and the phase of the geothermal fluid, therefore, play an important role in corrosion [27].

Stress corrosion cracking is a common failure mechanism that occurs when metals are under tensile or residual stress in the presence of chlorides, sulfides, or fluorides (F^-) found in geothermal brines. Corrosion and pitting may occur in any location, but areas with high residual stress, such as heat-affected zones or areas directly adjacent to a weld, are particularly susceptible to stress corrosion cracking in the presence of sulfides or chlorides [31]. Since most welds impose an irregular geometry, irregular flow patterns will be created that may lead to higher localized corrosion rates. To avoid this problem, welds may be ground flush to the base metal; however, this may not be an option on the inside diameter of geothermal well casings, making welds the weak link in geothermal equipment integrity [32].

Four common mechanical failure modes in geothermal well casings result from four unique load conditions: buckling, collapse, shear, or tensile failure. Euler buckling has the potential to affect shorter sections of unsupported well casing that are under compressive stress induced by strain from thermal expansion of the casing material. Although well casings should be supported laterally by annular cement, shale shrinkage due to desiccation, a poor cement job, or a void that has been washed out by fluid flows may cause sections of well casing to be unsupported. Wagg et al. [33] stated that at 550 megapascals (MPa) for 178-millimeter (mm) casing in a 254-mm borehole, an unsupported length of approximately 5 m is required to allow elastic Euler buckling.

Longer sections of casing may buckle in a helical fashion. It is possible to reduce these types of failures by calculating the strain from thermal expansion and selecting a material with a higher yield stress than would be induced by the calculated strain. Collapse is a failure mechanism that results from a difference in fluid pressure between the outside and inside of the well casing—a high ratio between external and internal pressures causes the well casing to implode [33]. To protect against mechanical failure such as buckling, a standard known as the Code of Practice for Deep Geothermal Wells (NZS 2403:2015) has been developed by Standards New Zealand® [34]. Once material parameters in particular conditions are understood and more research is performed, setting standards will become easier.

Wright [35] and De Waard and Milliams [36] concluded that various compositions of carbon steels in anaerobic, CO_2-dominant, moderately acidic solutions had variable corrosion results depending on the phases within the metal or the presence of inclusions. Wright [35] lists extensive research indicating that localized corrosion, or pitting, occurred due to multiple phases within the material exhibiting different electrochemical potentials that create galvanic couples. The greater the difference in potential is, the higher the rate of corrosion will be. Galvanic couples are present in steels due to the different electrochemical potentials of cementite—the carbide-rich phase of austenitic steel, which acts as the cathode—and ferrite, which acts as the anode. At elevated temperatures, carbides may diffuse out of the crystal grains, causing a reduction in corrosion resistance in regions with a high concentration of carbide precipitates [14]. When some alloys come in contact with another corroding material, the metallic alloy may become charged with hydrogen, which induces hydrogen embrittlement [37]. In some wells where the reservoir fluids contain high concentrations of heavy metals, galvanic corrosion may occur beneath the metal scale precipitating on the casing surface, causing the underlying base metal of the casing to corrode. This complexity illustrates the importance of considering geothermal fluid chemistry and treating the range of conditions as dynamic parameters that inevitably change with temperature and pressure variations or with the addition of injection fluids.

Materials

Corrosion protection is the most important damage mitigation mechanism for geothermal well casings and pipelines [38]. Early proposals for corrosion protection included the use of polymer coatings and austenitic high-alloy nickel-free chromium manganese steels [39]. Metallic zinc and aluminum sacrificial coatings were also tested, since the cost of manufacturing hundreds to thousands of feet of piping made from corrosion resistant alloys was not an economically viable option at the time. Various application methods were used, including galvanic, vacuum, thermal diffusion, and spray coating. Zinc- and aluminum-based coatings were applied to pipes, which were then field tested in high-temperature water and steam. Zinc (Zn)- and aluminum (Al)-based coatings were recommended as an economically viable solution to corrosion [39]. Polymer and polymer matrix composite coating systems were tested, in combination with metallic zinc phosphate [$Zn_3(PO_4)_2$] compounds or nickel-aluminum alloys, as an intermediate layer to increase abrasion resistance. The only drawback to using these coatings is that they may not meet the thickness requirements for corrosion resistance in low-pH geothermal conditions.

Thermal spray coatings provide corrosion resistance; however, they are typically applied to a thickness of a couple mils (a couple thousandths of an inch). Based on corrosion rates observed by Lichti et al. [40] in the extreme near-magnetic environment of White Island, New Zealand, well casings in severe geothermal environments would require a very thick (e.g., several hundred mils) coating of high-nickel alloys, such as Inconel 625 and Hastelloy C-276, to achieve a service life of 25–30 years typically seen in developed geothermal fields. Solid pipe would be a better choice under these conditions. In addition, applying a thick thermal spray coating may create residual stresses within the coating, leading to cracking and subsequent failure of the casing.

In the mid-to-late 1980s, powder metallurgy offered another option for metallurgically bonding (cladding) a corrosion resistant alloy to a mild carbon or low-alloy steel well casing. Clad steels are generally classed as roll bonded, explosion bonded, and overlaid or laser clad [41]. Roll bonding uses pressure to deform and bond the metals, and sometimes involves heating the two metals to bond them together. Explosion welding creates a strong bond between the corrosion resistant alloy (CRA) cladding and the base metal, which is generally a carbon or low-alloy steel [42]. The bond is created by chemical explosives that fuse the cladding and base material together. In laser cladding or overlay cladding, a powder coating is applied and fused to the surface of the base materials with a laser. During laboratory testing, alloy 625 cladding performed better than other materials in terms of strength and corrosion resistance [43].

From the 1980s on, carbon steel was commonly used in steam gathering systems and power plant piping because it made economic sense. However, chromium-manganese steel performed better during corrosion testing in thermal mineralized waters when alloyed with molybdenum (1%–2%), copper (Cu) (1.5%), and silica in low-temperature geothermal fluids (60 °C) [12]. In Kurata's 1992 survey [44] of seven geothermal power generation companies, wells and pipelines were either replaced, exchanged for a higher grade material, or patched with undefined other material. Few companies reported patching pipes, but 25%–30% of the companies replaced, exchanged, or took other action.

From these data, Kurata et al. [44] developed an equation to calculate corrosion rate based on variables for pH, temperature, and activation energy. According to experimental data collected from the Fushime, Matsukawa, Hatchobaru, Kurokawa, and Onikoube geothermal fields in Japan, actual measured corrosion rates exceeded calculated corrosion rates. Further research through the mid-1990s led Lichti [45] to develop a computer-based program for materials selection based on environmental input parameters, such a temperature and pH. These analyses have the greatest potential for successful materials selection for geothermal environments because geothermal fluids have unique, highly variable chemistries and parameters such as pH, salinity, temperature, and dissolved gas concentrations that must be taken into account when selecting materials. Additional research is needed to enable the use of these tests and their outcomes as data points in a computer-based materials selection program. Recently, Kurata's corrosion resistance equation was revised to reflect environmental parameters of a well in Indonesia, where materials were selected for testing based on equation predictions [38].

Current Research for Deep-Seated Geothermal Wells

From early 1990s research, Lichti et al. [30] determined that for fluid pH less than 3 and temperatures greater than 300 °C, pipe material mass should be more than 30% chromium—potentially requiring duplex stainless steel or high-nickel alloys. More recent testing has been done on high-chromium, nickel, and/or molybdenum materials, all of which aid in corrosion protection. Flow velocities also influence corrosion rate of various materials. At a pH of 3, low-alloy and carbon steels showed a direct relationship between fluid velocity and corrosion rate, while Type 304 and Type 316 stainless steels did not. At a pH of 2, stainless steels (and even some high-alloy stainless steels) had corrosion rates over a hundred times greater in flowing fluid than in a static fluid. Hastelloy C-276 and titanium were found to have low corrosion rates under both static and flowing conditions, making them acceptable materials for corrosion reduction [46]. Sanada et al. [46] identified gaps in geothermal materials research that need to be addressed before the industry can make headway with deep-seated geothermal wells, as shown below in Figure 3-1 [25].

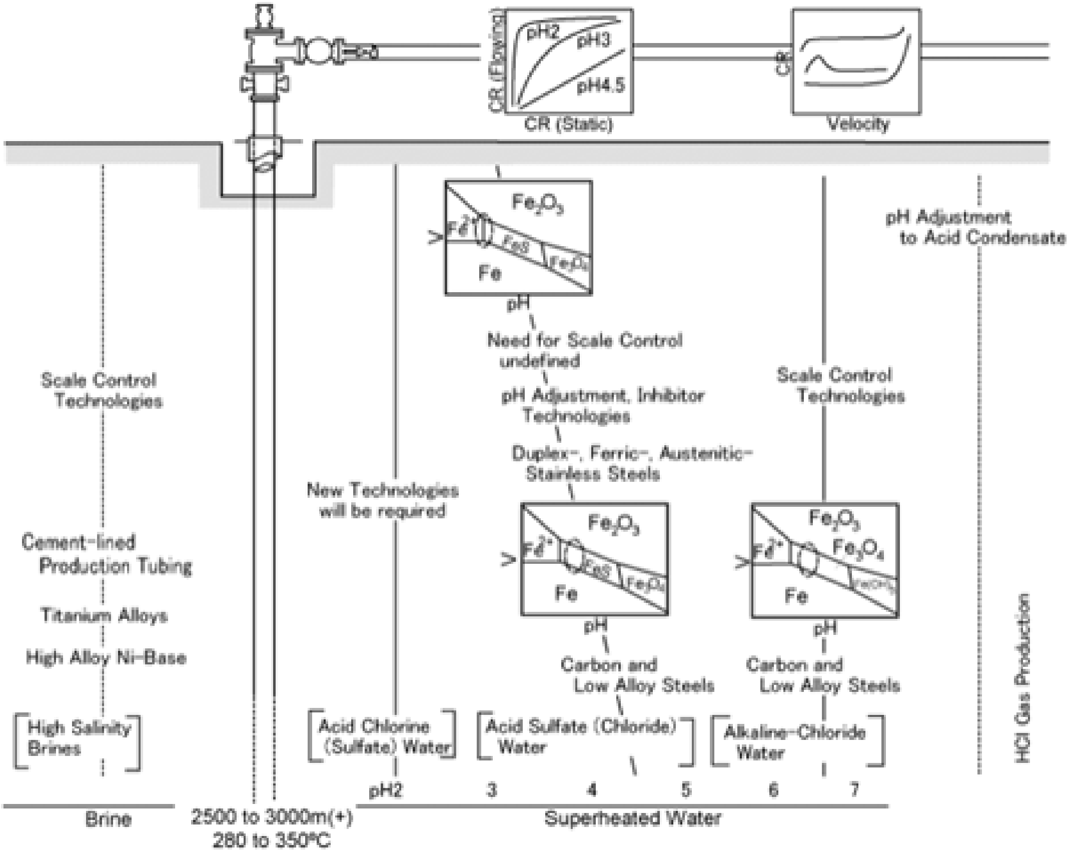


Figure 3-1
Schematic showing gaps in geothermal materials research [25]

Deep-seated geothermal investigations are underway in Italy, Japan, Mexico, Indonesia, New Zealand, the Philippines, and the United States. The DOE has compiled a database on materials performance under different geothermal conditions as part of the Geothermal Legacy Collection, a searchable public access platform on the Office of Scientific and Technical Information website (http://www.osti.gov/geothermal/) [31]. The database was compiled to increase information exchange and to aid scientists and engineers in selecting the optimal material(s) for a geothermal well, based on unique reservoir conditions.

Corrosion may also be prevented by using corrosion inhibitors that interfere with corrosion processes by forming a thin coating (with no effect on heat transfer), or by coating pipes with a “polyethylene coating, epoxy coal tar, or fiberglass reinforced plastic (FRP)” [26]; however, FRP does not hold up well in extreme thermal conditions. Newflex pipeflex, or other anti-corrosion coating materials may also have a future.

Steam washing is used to help prevent corrosion in the steam turbines. Corrosive chemical species are minimized by injecting alkaline solutions and caustic soda into the header [26]. Chemical injections of sodium hydroxide that affect the pH of geothermal fluids have recently had great success in reducing corrosion. Cost-effective injection of chemical additives has been demonstrated to help control corrosion in geothermal reservoir fluids with pH of approximately 2 [47].

Coatings have not been researched as extensively as cladding or solid alloys. On their own, polymer coatings do not have the wear-resistance to endure geothermal conditions and their melting point is generally too low for high-enthalpy geothermal conditions [48]. Brookhaven National Laboratory researched geopolymers, composite materials made from clay particles and polymers [49]. These composite materials provide better wear and corrosion resistance. In laboratory testing at 300 °C in a simulated hot geothermal brine environment, the polyphenylsulfide (PPS) with montmorillonite (MMT) filler was discovered to provide adequate corrosion protection. This composite material had improved mechanical properties, a higher melting point than PPS alone, and increased crystallization energy. Instances of hydrothermal oxidation related to sulfide-sulfite linkage transformations were eliminated for this composite material [49]. Tests of geopolymer compounds also found that the coating adhered better when an intermediate layer of zinc was applied. Multi-layer coating systems are often necessary for successful corrosion protection. In some cases, combining multiple layers enhances the properties of the coating system, as with self-advancing coatings demonstrated by Sugama [50]. These self-advancing coating systems—which are a combination of styrene acrylic latex and calcium aluminate cement—exhibited good corrosion resistance in laboratory testing of the conductivity of corrosive electrolytes in an autoclave at 250 °C.

Geothermal power stations inspect their equipment more frequently than is customary at conventional thermal generation facilities. Baseline data collected during these inspections help power plant engineers and inspectors track the corrosion rate of a material and assess the condition of the material over time [51]. In more recent years, failures have been recorded and root analyses performed to determine the corrosion mechanism and to find a way to prevent corrosion in the future. Recently, failures have been studied in greater detail to identify specific locations in the system and pieces of equipment that are being degraded. By using computer-based technology to estimate the dynamic environmental parameters in geothermal wells, well models can predict the areas of highest corrosion where casing strings designed with CRAs are deemed necessary.

Cost of Materials

Material costs for corrosion resistant alloys are high because these materials generally are a blend of high-cost metallic elements. Plain carbon steel is comparatively inexpensive and has commonly been used in geothermal plants. But its poor corrosion resistance makes it a cost-ineffective choice, as more corrosive surface system conditions are encountered or geothermal reservoir conditions become more corrosive over time. The service life of a geothermal well is typically 25–30 years, so well casing materials should have a similar life expectancy. Even though the cost of corrosion resistant alloys can be anywhere from 3 to 7 times the cost of carbon steel, their improved corrosion resistance could pay for itself compared with plain carbon steel that requires replacement after only a few years of service.

Typically, cladding would be the most cost-effective way to manufacture well casing with corrosion resistant characteristics without paying for an expensive CRA. However, market variance for specialty metals pricing has currently brought the price of nickel down to a six-year low, making it more cost-effective to manufacture well casing entirely out of a CRA, instead of cladding the interior of a carbon steel pipe. The current price is a reflection of market variability and may change rapidly to higher values, making it difficult to develop long-term plans for projects that require nickel-based alloys [52]. Blakely and Olivas [42] suggest that significant cost savings could be achieved if a thin clad stainless steel, monel, zirconium (Zr), or titanium were applied to piping. Thin titanium cladding is impractical because of problems with metal workability, while high-nickel (alloy 625 or C-276) cladding is supposedly more expensive than manufacturing the same length of solid alloy pipe [53].

Research performed on CRA for vessels and tanks for geothermal power plants shows similar pricing of materials (Table 3-1) [54].

Ashland Engineering recently compared price ratios between alloy 2205 duplex stainless steel and alloy C-276 (Table 3-2) [52, 55]. These values were originally compared to prices for fiber-reinforced plastics, which provide great corrosion resistance but cannot be used in high-temperature applications.

Table 3-1
Cost comparison of materials for fabrication of pressure vessels and heat exchangers

Alloy	316L	2205	Titanium Grade 2	Titanium Grade 12	825	625	C-276	Zirconium 702
Cost Factor	1.0	1.01-1.2	1.16-1.5	1.43-1.6	2.2	1.92-3.6	2.04-3.6	4.0

Table 3-2
Price comparison of stainless steel plate and carbon steel plate clad with C-276

Material	Cost	Cost Ratio
Mild carbon steels (P110, N80, P235GH, P265GH) > 97.5% Fe		1
Stainless steel (430F) 16–18% Cr		1.7
Alloy 2205 (9.5-mm steel plate)	\$1,050/m^2	1.9
Alloy C-276 clad carbon steel plate	\$1,548/m^2	2.9
Duplex (318LN) 21–23% Cr, 4.5– 6.5% Ni, 2.5–3.5% Mo		7.1
Stainless (Alloy 316L) 16.5–18.5% Cr, 10–14% Ni, 2–2.5% Mo		8.3
Titanium alloy (Grade 2) 99.2% Ti		16.2
Special Austenite (Alloy 914L) 19–21% Cr, 24–26% Ni, 4-5% Mo, < 2% Cu		19.4
Superduplex (Alloy 31) 26–28% Cr, 30–32 %Ni, 6–7% Mo, < 1.4% Cu		33
Fe—iron Cr—chromium Ni—nickel Mo—molybdenum Cu—copper		

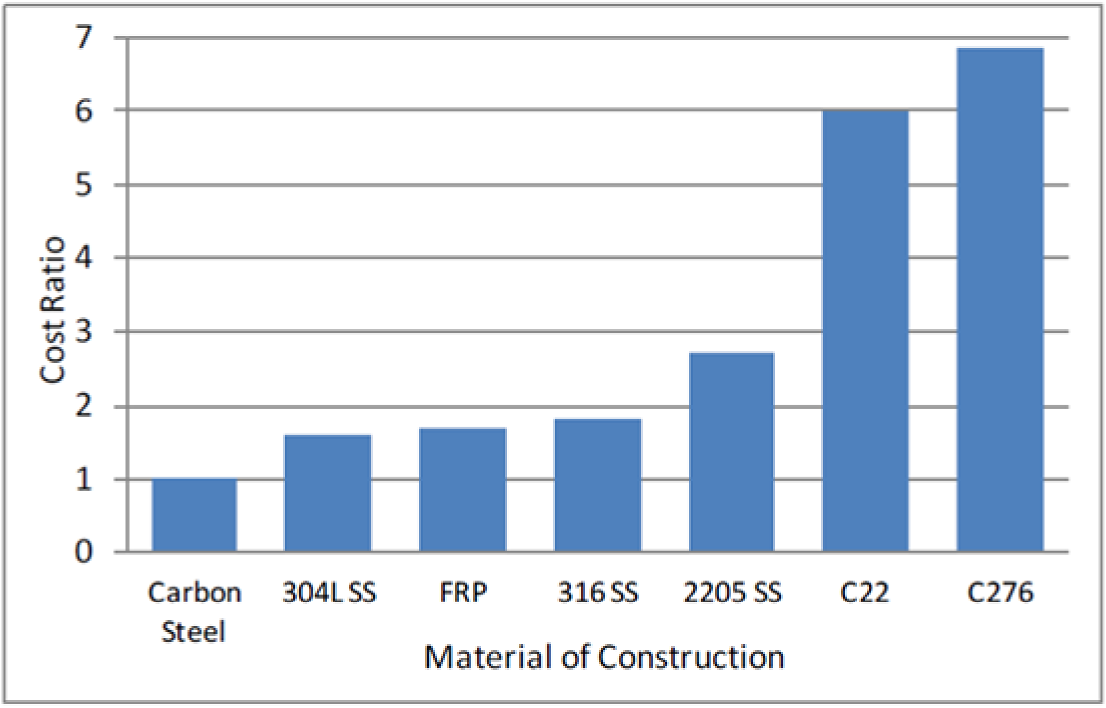


Figure 3-2
Cost comparison of materials for tank construction as performed by Ashland Engineering in their 2015 report [52]

Ashland Engineering also provided data for cost comparison of materials for tank construction, which show the drastic increase in price difference between carbon steel and high-nickel alloys, such as alloy C-276 (Figure 3-2).

Love et al. [56] calculated that, over a 30-year period, the cost of carbon steel pipe would be more than five times that of Beta-C titanium because of the frequent replacement of carbon steel required by rapid corrosion rates of 1,000 to 2,000 mils per year.

4

CORROSION MITIGATION TECHNIQUES

The Geysers has more than 350 producing wells, most of which produce noncorrosive steam containing less than 0.5 ppm chloride. About 20% of the wells produce steam with 1.0 ppm chloride or more; these wells are corrosive if not sufficiently superheated. A few wells currently produce steam containing as much as 100 ppm chloride, and several wells have produced steam with up to 200 ppm chloride. This steam can be corrosive at a superheat of 25 °C or more, due to the dew point effect of ammonia. An excess of ammonia relative to chloride in steam lowers the vapor pressure of volatile chloride, requiring much higher superheat to prevent initial condensation compared with pure hydrogen chloride in steam. Corrosion of casings, wellheads, and pipelines occurs where hydrogen chloride-bearing steam encounters films of moisture on steel surfaces or surfaces sufficiently cool to initiate dew point deposition of ammonium chloride. At those points, hydrogen chloride (or ammonium chloride) partitions from the steam and concentrates in the moisture, transferring up to thousands of ppm chloride into the liquid.

Liquids collected from pipelines at The Geysers have contained 40,000 ppm ferrous chloride ($FeCl_2$), the product of hydrogen chloride reacting with steel well casings and pipelines. Typically, the excess of ammonia relative to chloride in most chloride-bearing steam condensates results in pH above 5 at 20 °C, although systems without excess ammonia may produce condensates below pH 2 at 20 °C. Ammonia is a very weak base at steam line temperatures (~175 °C); therefore, the measured pH of condensate containing ammonia at ambient temperature can be much higher than the measured pH of condensate in the pipeline at high temperature. Condensate films with high-chloride contents and excess ammonia typically have a pH of about 4 at steam line temperatures, sufficient to cause the very high corrosion rates observed at The Geysers.

Early Volatile Chloride Corrosion Mitigation Techniques

High-chloride steam is handled in several ways to prevent corrosion. Many moderate-chloride wells (~10 ppm) that are superheated (≥ 20 ˚C) flow to pipelines that are also superheated. In this case, all the steam can be passed through the gathering system and scrubbed immediately upstream of power plants by desuperheating and steam washing using hotwell condensate. In these steam lines carrying high-chloride, high-superheat steam, prevention of cold spots is critical at pipeline heat sinks such as valves, rupture disks, and pipe anchors. In some cases, cold spot prevention is impractical because a few wells feeding the same part of the gathering system may be saturated, effectively quenching the superheat needed to carry the steam safely to the plants.

Many wells have been damaged when conditions required curtailing the flow of the steam field. Lower flow rates allow wellhead pressures to rise, thereby decreasing superheat. Slower steam flow through wellbores and pipelines also allows more conductive heat loss, increasing the probability of dew point conditions along the flow path. A partial solution to this problem at The Geysers is to preferentially curtail wells that have low chloride while keeping high-chloride wells as close to full flow as possible. This requires monitoring well chloride levels to identify which wells can be safely curtailed.

The first full-scale, volatile chloride corrosion mitigation system at The Geysers was designed and operated by Thermochem, Inc. (Thermochem) at the Aidlin project in 1989 [57]. This system, still in use today, involves water and caustic (sodium hydroxide) injection at each production wellhead with subsequent liquid removal by vertical separators, and a final two-stage steam wash system at the plant inlet. Although steam washing with dilute sodium hydroxide has been used successfully for many years at The Geysers and Larderello to protect steam gathering and power generation equipment [16], it causes a reduction in steam utilization efficiency. The wash water quenches steam superheat and condenses steam, reducing the total enthalpy and mass flow rate. The efficiency loss in steam washing is greatest in vapor-dominated fields, due to the high levels of superheat typically present. For The Geysers, it is estimated that up to 5% of recoverable energy is lost as a result of steam quenching and increased steam utilization factors when steam washing is employed. For the IDDP-1 well in Krafla, a loss of about 10% is estimated with conventional steam washing [58].

Steam washing with sodium hydroxide is highly effective for corrosion control in pipelines and for protection of the steam turbine downstream. Typically, volatile chloride is reduced to less than 1 to 5 ppm at the outlet of the wellhead scrubbing process (95–99% removal efficiency), and to less than 0.1 ppm after a second-stage water wash at the plant inlet. In conventional fossil fuel and nuclear steam turbine power plants, chloride-induced stress corrosion cracking is considered to be one of the major problems in turbine reliability. These units operate at much higher inlet pressures and superheat than geothermal units, generating greater stresses on the machines and increasing the likelihood of salt deposition upstream of the Wilson line (condensation zone). Sodium chloride is often found in the turbine deposits of conventional units and is linked with stress corrosion cracking. Hydrochloric acid and ammonium chloride have also been identified in these turbine deposits and are considered highly undesirable due to their extreme corrosivity, in addition to their tendency to cause stress corrosion cracking.

The turbines in use at the Cerro Prieto geothermal field in Mexico are exposed to mechanically entrained sodium chloride, rather than volatile chloride, and have experienced negligible corrosion. The turbine blade material in use at these units is 12% chromium steel, similar to the blade material at The Geysers units. The Geysers' caustic scrubbing process for removing volatile chloride generates sodium chloride and sodium carbonate (Na_2CO_3), which are entrained in the turbine steam at trace levels, but have turbine impacts similar to those experienced at Cerro Prieto. Operating standards for steam purity at The Geysers require less than 0.1 ppm chloride at the inlet to the turbine for most plants. Although units have run for many years with volatile chloride in the range of 0.1 to 1.0 ppm, this concentration is not recommended for long-term operation due to the potential for cracking and pitting damage to the turbine alloys in use.

At The Geysers, wells producing high chloride or a combination of moderate chloride and low superheat such that corrosion has been identified as a problem are equipped with corrosion mitigation facilities (CMFs). Near the wellhead, enough sodium hydroxide solution is sprayed into the steam for desuperheating, as well as to absorb and neutralize the hydrogen chloride. A separator removes the spent liquid from the pipeline downstream. The amount of sodium hydroxide needed is stoichiometric with chloride, plus a slight excess, resulting in a separated water pH of about 8.5. The scrubbed steam flows to the main pipeline at saturation and serves to lower the superheat of the steam with which it is commingled in the gathering system. This raises the probability that volatile chloride in dry, superheated steam from non-CMF wells will mix with wet steam downstream of the CMF. Corrosion can then occur at the mixing point and beyond, so this situation is carefully avoided. In some parts of the field, parallel pipelines are in use—one carrying moderate-chloride superheated steam, the other carrying steam from CMF wells with very low chloride and saturated steam.

The 130-MW Coldwater Creek Power Plant, built by the Central California Power Agency (CCPA), was located in the northwest Geysers, where chloride and NCG concentrations are the highest and the HTZ is the shallowest. The plant never ran at full load and was shut down in 1994 after only six years of operation, primarily because of corrosive steam. Much of the steam produced to the CCPA plant originated in the HTZ. Although high-NCG steam was problematic, chloride corrosion proved to be the terminal problem. Wellhead mitigation was eventually used on all wells, but extensive gathering system damage and casing corrosion downhole would have required an extensive replacement program that made the project uneconomical. However, near the CCPA plant in the northwest Geysers, the Aidlin Power Plant has been running for more than 25 years without corrosion problems. The Aidlin wells produce some of the highest-chloride steam at The Geysers, with one well at 160 ppm and another 200 ppm. The reason this project has been successful is that properly designed CMFs were installed before startup and diligently operated ever since, demonstrating that it is possible to utilize high-temperature corrosive resources.

Most wells in Larderello have high superheat (> 50 ºC) and low ammonia compared with wells in The Geysers, so volatile chloride can be allowed to pass through the gathering system and be removed by scrubbing with water and caustic at the power plant. One of the main drawbacks for wellhead water scrubbing in vapor-dominated fields is that each wellhead location scrubbed produces saturated, wet steam. When this steam combines with untreated steam from other wells, the superheat in the entire gathering system is reduced. Severe corrosion can occur when the steam from relatively low-chloride wells (1–3 ppm), which previously did not require scrubbing, mixes with the wet steam from treated wells. Ideally, superheat throughout the gathering system is maintained at a maximum level to avoid the volatile chloride dew point.

Downhole Volatile Chloride Scrubbing and Neutralization

Steam washing has also been successfully employed downhole at The Geysers. Generally, a minimum of about 20 ºC superheat is required to prevent severe corrosion damage to casings and piping for wells at The Geysers producing a few ppm or more volatile chloride. Wells producing chloride at more than 2 or 3 ppm under nearly saturated conditions must be treated downhole or shut in. In some cases, steam from volatile chloride producing wells is saturated at the surface, and may contain significant fractions of liquid due to wellbore condensation or intrusion of shallow water through casing breaks and corrosion perforations. A solution of water and caustic is injected at depths of 1,000 to 2,000 m to mitigate pH and protect the casing and wellhead.

Mitigating downhole corrosion by injecting a water-sodium hydroxide solution through coiled tubing was successful at the CCPA project in the northwest Geysers, but such severe damage had already been done to the well casings, gathering system, and plant that the project was abandoned. At about the same time, the Aidlin project was brought on-line in the northwest Geysers. Downhole corrosion mitigation was also employed at Aidlin, but was not needed long term because injection was changed to return these wells to superheated conditions.

New Volatile Chloride Corrosion Mitigation Technologies

Alternatives to traditional steam washing for removal of volatile chloride from superheated geothermal steam have been conceived and demonstrated over the last ten years. These alternatives, termed Dry Steam Scrubbing (DSS), are designed to remove volatile chloride from steam without significant desuperheating and subsequent reduction in steam utilization efficiency.

Initially, Hirtz [59] discovered that solid-phase, alkaline compounds such as sodium carbonate (Na_2CO_3) and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) can absorb up to 90% of the produced hydrogen chloride from superheated steam in wellbores at The Geysers. This phenomenon was observed during testing of downhole hydrogen chloride mitigation systems (water washing with sodium hydroxide in the wellbore) after the downhole injection was shut off and the alkaline scale in the wellbore dried out.

Fisher and Jung [60] proposed dry scrubbing, oil washing, and hybrid cleaning as alternatives to traditional steam washing. Dry scrubbing consists of adsorbing or absorbing steam impurities with an agent, followed by separating the spent agent. The spent agent is reconditioned and recycled into the process. Oil washing consists of spraying oil into steam, separating oil from impurities, and recycling the oil. High-boiling point oils (that exist in equilibrium with highly superheated steam) can be used, so there is no heat loss due to vaporization of the scrubbing liquid. Hybrid cleaning is described as contacting steam with a liquid/solid mixture formulated to react with impurities in the steam pipeline. The active components are separated from the steam, regenerated, and recycled.

Gallup [61] investigated removing hydrogen chloride from steam by boiling a weak hydrogen chloride solution and passing the vapor through small columns containing various solids and liquids. The materials tested for hydrogen chloride removal included:

- Absorbents—calcium carbonate ($CaCO_3$), anhydrite ($CaSO_4$), sodium carbonate, and liquid anion exchange amines.
- Adsorbents—zeolites, hydrotalcite, silica gel, activated carbon, carbonaceous adsorbent, phenolic foam, and a solid anion exchange resin.

A U.S. patent was issued in 1999 on these process ideas (U.S. Patent No. 5,879,433) and a patent was also secured in Italy, but no other foreign patents were filed. Thermochem has the exclusive license to the U.S. patent, which covers many of the current DSS innovations.

Beginning in 2000, Thermochem conducted pilot testing at The Geysers, which demonstrated that calcium carbonate was an effective DSS agent with 98% removal efficiency in wells producing up to 160 ppm hydrogen chloride and 30 ºC superheat, the highest available test parameters at the time. Mixtures of amines and oil were also effective, but were more costly due to amine vapor-phase losses despite liquid-phase recycling and liquid-liquid regeneration [62]. A full-scale demonstration of DSS using calcium carbonate was conducted in 2008 on a well producing 100 ppm hydrogen chloride at 34 ºC superheat. Removal efficiency was in the range of 92%. The lower removal efficiency was attributed to flow channeling through the bed due to uneven distribution in the larger-diameter vessel (1,370 mm diameter in the full-scale demonstration vs. 305 mm diameter in the pilot test).

A commercial water treatment company has reported that a solution of amines and dilute potassium carbonate (K_2CO_3) [63] can be used to treat hydrogen chloride at The Geysers, with minimal loss of superheat. But the treatment scheme results in complete dry out and potassium chloride (KCl) salt deposition at superheat values above 16 ºC. In most cases, the volume of the liquid phase is insufficient to effectively remove hydrogen chloride at the wellhead. The process has some short-term applications where the reaction products of hydrogen chloride neutralization can be allowed to remain in the pipeline, but is not useful or cost-effective to treat steam with superheat above about 160 ºC.

Hydrogen Chloride Mitigation Strategies—Detailed Process Examples

The following section describes example process conditions and chemical data for treatment of hydrogen chloride produced by a subcritical, high-temperature, superheated geothermal well. These examples are intended generally to represent treatment of targeted production from deep-seated, high-temperature, and EGS-type reservoirs approaching 400 °C.

The example process design conditions are as follows:

Wellhead temperature:	380 °C,
Wellhead pressure:	22 bars,
Steam enthalpy:	3,200 kJ/kg,
Mass flow:	30 kg/s,
Hydrogen chloride concentration:	100 mg/kg.

Conventional Water and Caustic Scrubbing

As discussed above, water and caustic scrubbing has been successfully employed to treat volatile chloride at The Geysers and Larderello for many years. The main drawbacks of this treatment are loss of superheat, condensation of steam, and mixing of saturated steam with superheated steam from other wells with low to moderate levels of hydrogen chloride—resulting in corrosive conditions that did not previously exist when the entire gathering system remained superheated.

A water and caustic scrubbing process is shown in Figure 4-1 for the example well conditions listed above. With water at 40 ºC and 30% caustic (sodium hydroxide) used to scrub steam from the well at 8 bara (absolute pressure), 5.5 kilograms per second (kg/s) water and 31 liters per hour (lph) caustic (sodium hydroxide) would be needed to achieve a liquid fraction of 2% after desuperheating and a neutral-to-alkaline pH. This will result in 34.8 kg/s saturated steam at 170 ºC, while the 0.71 kg/s residual scrub water will be sent for disposal. The clean water must be oxygen-free (< 10 parts per billion [ppb]); the usual source for this process is hotwell condensate from a surface condenser, which is typically 40 ºC. Direct-contact condenser water is too high in oxygen and may contain undesirable treatment chemicals (oxidizing biocides) from the cooling tower. With good mixing design, only a 2% residual water fraction (after desuperheating) is typically required.

If the scrub water were preheated to 123 ºC using low-pressure brine in a heat exchanger, then 6.4 kg/s scrub water would be required, resulting in 35.7 kg/s steam (about 1 kg/s improvement over unheated scrub water), as shown in Figure 4-2. Given the low residual scrub water flow rates, additional heating using the 170 ºC scrub drain water results in a negligible increase in efficiency (0.05 kg/s).

For maximum energy recovery from this example well, it would be better to scrub the steam at 20 bara if the well can sustain the same flow of 30 kg/s at this pressure (Figure 4-3). At 20 bara, 5.9 kg/s scrub water, preheated to 123 ºC, is required to reach a 2% residual scrub water fraction. The caustic requirements would be the same as in the above cases. Under these conditions, 35.1 kg/s steam can be recovered at 20 bara. This is improved by only 0.1 kg/s if the scrub injection water is further preheated using the drain water at 212 ºC.

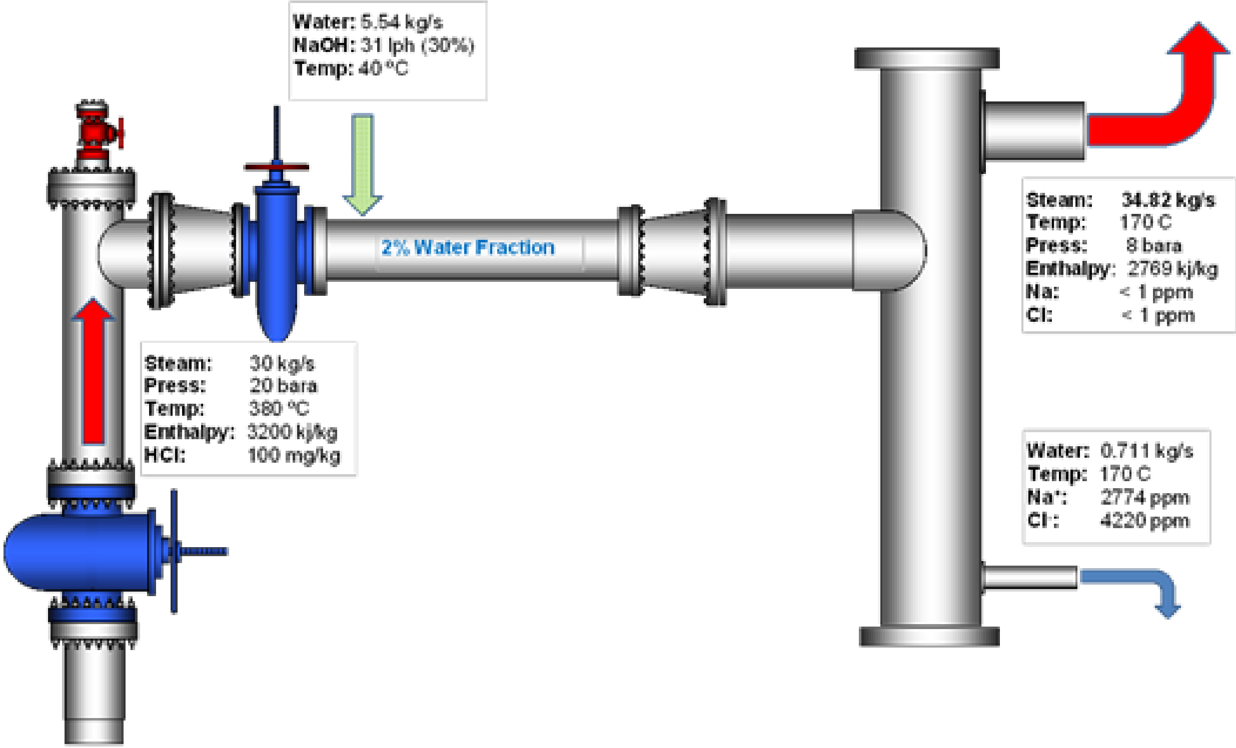


Figure 4-1
Water and caustic process flow diagram—8 bara

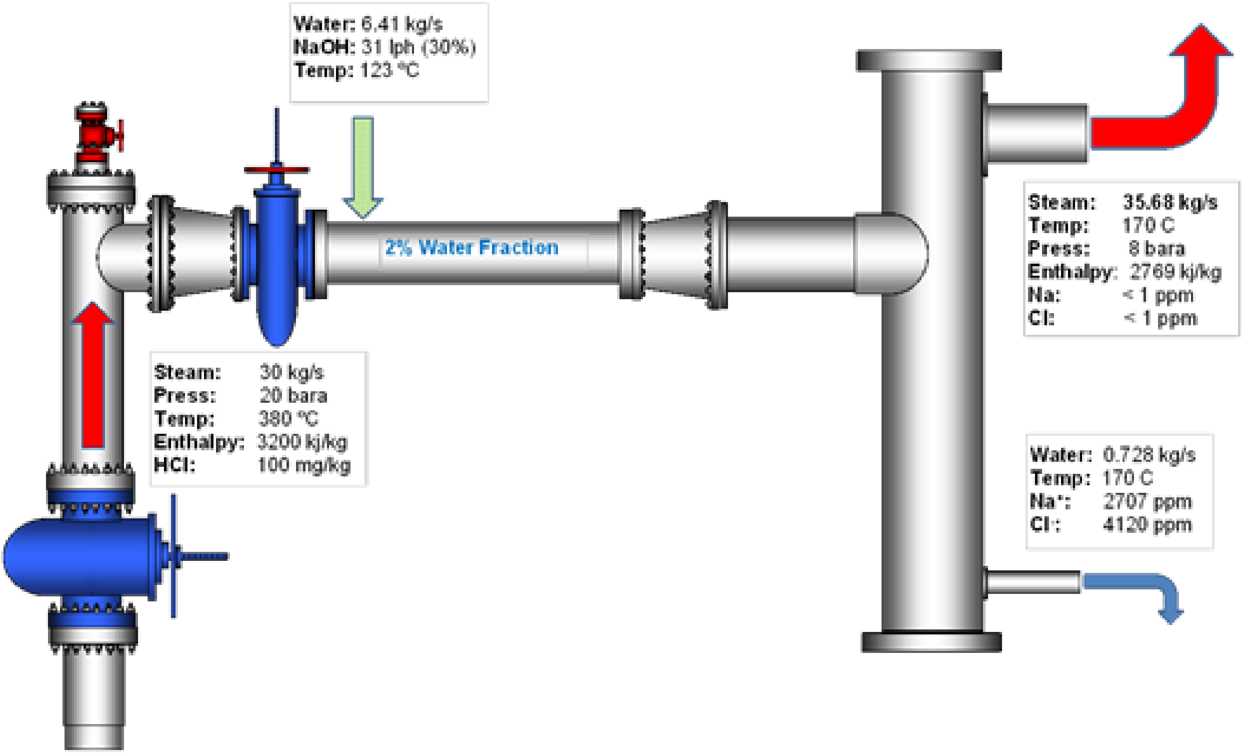


Figure 4-2
Water and caustic process flow diagram—8 bara, pre-heated scrub water

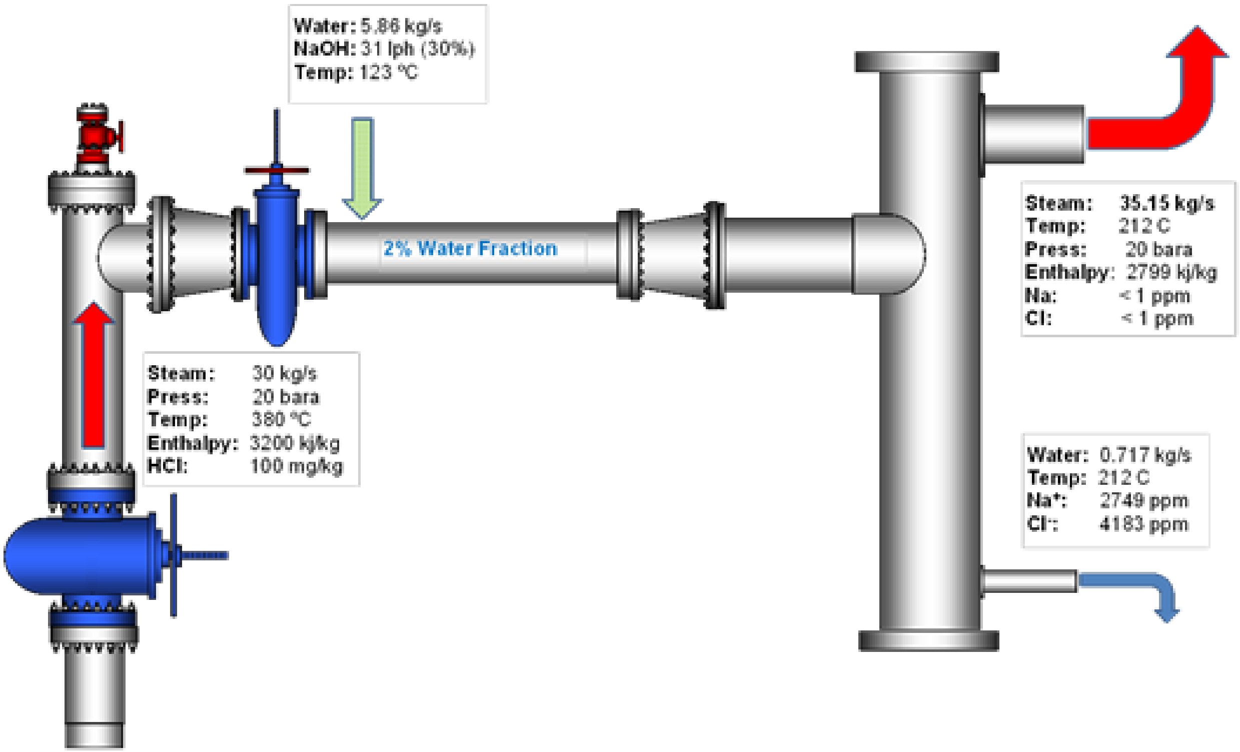


Figure 4-3
Water and caustic process flow diagram—20 bara

Water and caustic scrubbing is a very low-risk approach, as the technology is well understood and mature. The drained scrub water could be disposed of with the low-pressure injection brine with no significant impact on silica scaling. A clean, oxygen-free water source is needed, as well as a small heat exchanger to preheat the water using injection brine. The annual chemical cost would be roughly US$200,000 based on current bulk pricing in the United States. At this high level of superheat, a mixing run that is longer than normal would be required to desuperheat the steam and completely scrub the hydrogen chloride. The mixing spool must be fabricated from alloy 625, as discussed above. Typically, mixing spools are only 1 to 2 m long, but for this well a spool at least 10 m long would probably be required. Residual hydrogen chloride after scrubbing would be in the range of 0.1 to 1 ppm at the most; with careful mixing process design, the residual hydrogen chloride could be less than 0.1 ppm.

Severe corrosion can occur immediately upstream of the desuperheating point in the scrubbing process (the quench zone) due to conductive heat loss through the pipe. Condensation in the quench zone does not have the benefit of chemical neutralization by scrub water, and is extremely corrosive. The use of duplex stainless steel alloy 254 SMO for mixing spools has been considered. This material was tested at The Geysers in the bulk steam flow and drop pots of corrosive wells, but never in the quench zone [64]. Although 254 SMO performed well with respect to stress corrosion cracking and pitting corrosion resistance, super-duplex 2507 performed better. However, no alloy except 625 has survived the quench zone in wells at The Geysers. This is the only material routinely used in water and caustic mixing spools at The

Geysers. Wellhead tees and casing heads are also fabricated from alloy 625 for highly corrosive wells that are not sufficiently superheated.

Dry Steam Scrubbing

The removal of hydrogen chloride and/or ammonium chloride from geothermal steam has been thoroughly tested and demonstrated at The Geysers using calcium carbonate (calcite or limestone pellets, ~ 40 mm diameter) as the absorptive material [62]. Calcium carbonate consumption in the DSS process is governed by the reaction between calcium carbonate and hydrogen. This process can occur directly between the superheated gaseous phase containing hydrogen chloride and the solid calcium carbonate substrate, without the presence of liquid water:

$CaCO_3(s) + 2\,HCl(g) = CaCl_2(s) + H_2O(g) + CO_2(g)$

There are no known competing reactions that could occur in geothermal steam exposed to calcium carbonate, unlike caustic. Sodium hydroxide reacts rapidly with carbon dioxide to form sodium carbonate, but is still effective in neutralizing hydrogen chloride. Due to the very low solubility of calcium carbonate at high temperatures (retrograde solubility), virtually no calcium carbonate is dissolved when the material does become wet during wellfield operations or washing of the calcium carbonate bed to remove reaction products. This low solubility is important in maintaining the mechanical integrity of the bed material and properties such as reactive surface area, porosity, and permeability.

Reflux regeneration is the most effective means of removing reaction products from the calcium carbonate bed and maintaining long-term performance. In this case, the reactive surface is regenerated, but the calcium carbonate is still consumed in the process through reaction with hydrogen chloride. Regeneration is accomplished by shutting in the outlet pipe from the vessel for several hours while leaving the inlet open (pressurized with steam) and the drain valve partially open to allow a slow steam bleed and liquid drainage. Calcium carbonate bed regeneration is required about every 15 to 30 days, depending on inlet hydrogen chloride levels. The process can be accelerated through the use of a water wash, with nozzles spraying clean water down from the top of the vessel.

Previous research studies at The Geysers demonstrated that up to 160 ppm hydrogen chloride could be treated effectively by the DSS process. Wells producing 50 ppm or more hydrogen chloride were conservatively estimated to need a calcium carbonate bed depth of 1,800 mm. The first full-scale DSS vessel was designed to accommodate a bed depth up to 2,440 mm. The bed depth can be changed to optimize chloride removal and minimize pressure drop by simply adding or removing calcium carbonate pellets.

Volatile chloride concentrations are typically reduced down to about 2 ppm (± 1 ppm) regardless of the inlet chloride concentration range up to 160 ppm. This volatile chloride reduction is sufficient to prevent corrosion in gathering systems where at least 20 ºC superheat is maintained. This process has been tested to a maximum steam temperature of 210 ºC. Pressure drop through the beds at The Geysers is typically less than 30 kilopascal (kPa), with superficial steam velocities of 1 to 1.5 meters per second (m/s) through beds with a bulk porosity of about 50%.

The Ergun function [65] is used to predict the pressure drop as a function of steam flow, pressure, temperature, bed pellet size, depth, and diameter through the beds:

$$\frac{\Delta P}{L} = 150 \frac{\mu G}{kg\rho D^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} + 1.75 \frac{G^2}{\kappa g\rho D} \frac{(1-\varepsilon)}{\varepsilon^3}$$

where the variables represent the following parameters:

ΔP = pressure drop,

L = depth of the packed bed,

G = ρV = mass velocity,

V = superficial linear velocity,

ρ = fluid density,

μ = fluid viscosity,

D = effective particle diameter,

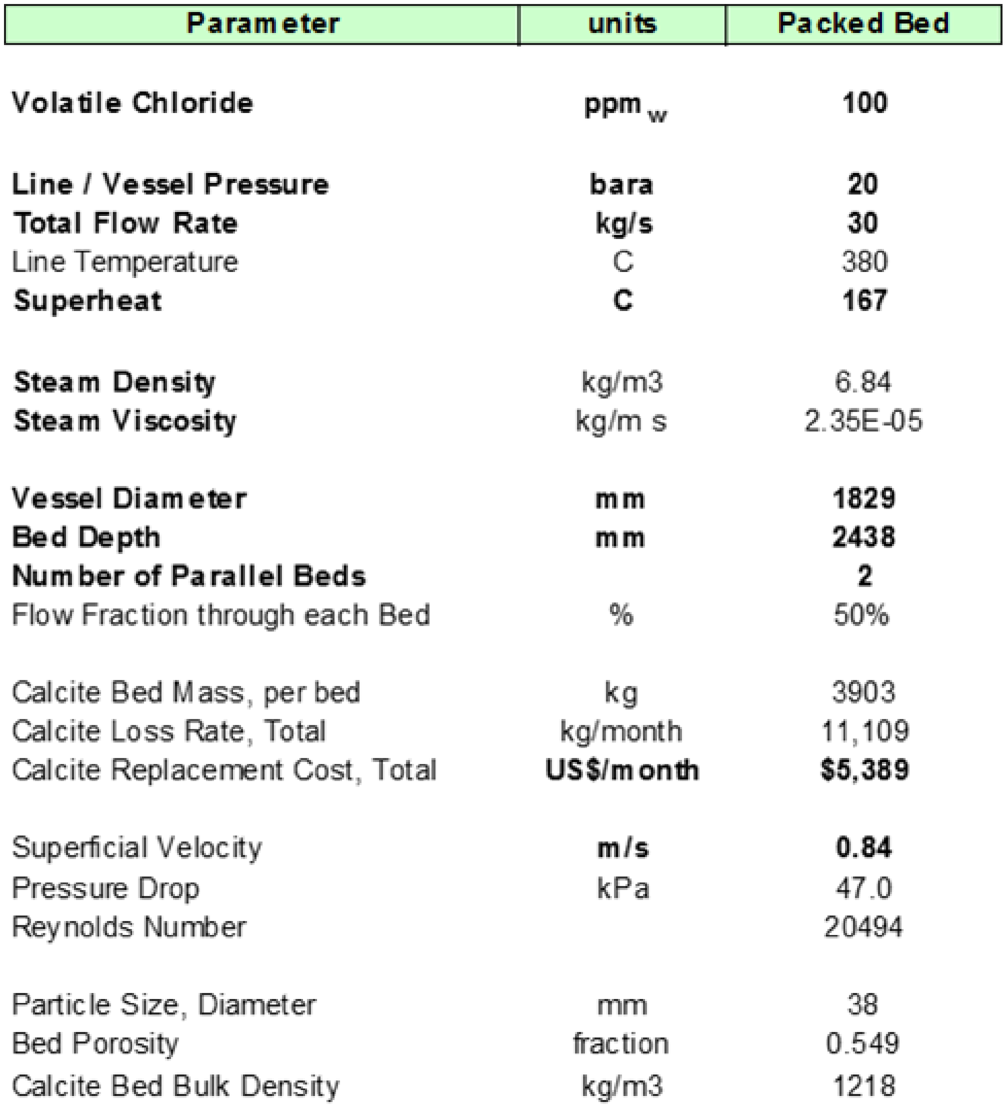
ε = inter-particle void fraction,

g = gravitational constant,

k = conversion factor.

Table 4-1 lists the initial design operating parameters for a calcium carbonate DSS bed installed on our example well; the basic process flow diagram is given in Figure 4-4. To minimize the diameter of the DSS vessels and facilitate maintenance, at least two vessels are employed in parallel for a well of this size. It would be possible to use four vessels, with a reduced diameter of 1,220 mm per vessel. To assess the relative value of these options, the cost of two large-diameter vessels versus the cost of four smaller-diameter vessels with the additional cost of piping would have to be determined and compared. For bed regeneration and refilling, it is best to have at least two vessels in parallel so that only one at a time has to be taken off-line for service. Multiple, smaller-diameter vessels may be more desirable as they would be easier to fill and wash, and less likely to encounter flow channeling due to uneven distribution of the bed packing.

Table 4-1
Calcium carbonate dry steam scrubbing bed design and operating parameters for example well



Parameter	units	Packed Bed
Volatile Chloride	**ppm $_w$**	**100**
Line / Vessel Pressure	**bara**	**20**
Total Flow Rate	**kg/s**	**30**
Line Temperature	C	380
Superheat	**C**	**167**
Steam Density	kg/m3	6.84
Steam Viscosity	kg/m s	2.35E-05
Vessel Diameter	**mm**	**1829**
Bed Depth	**mm**	**2438**
Number of Parallel Beds		**2**
Flow Fraction through each Bed	%	50%
Calcite Bed Mass, per bed	kg	3903
Calcite Loss Rate, Total	kg/month	11,109
Calcite Replacement Cost, Total	**US$/month**	**$5,389**
Superficial Velocity	**m/s**	**0.84**
Pressure Drop	kPa	47.0
Reynolds Number		20494
Particle Size, Diameter	mm	38
Bed Porosity	fraction	0.549
Calcite Bed Bulk Density	kg/m3	1218

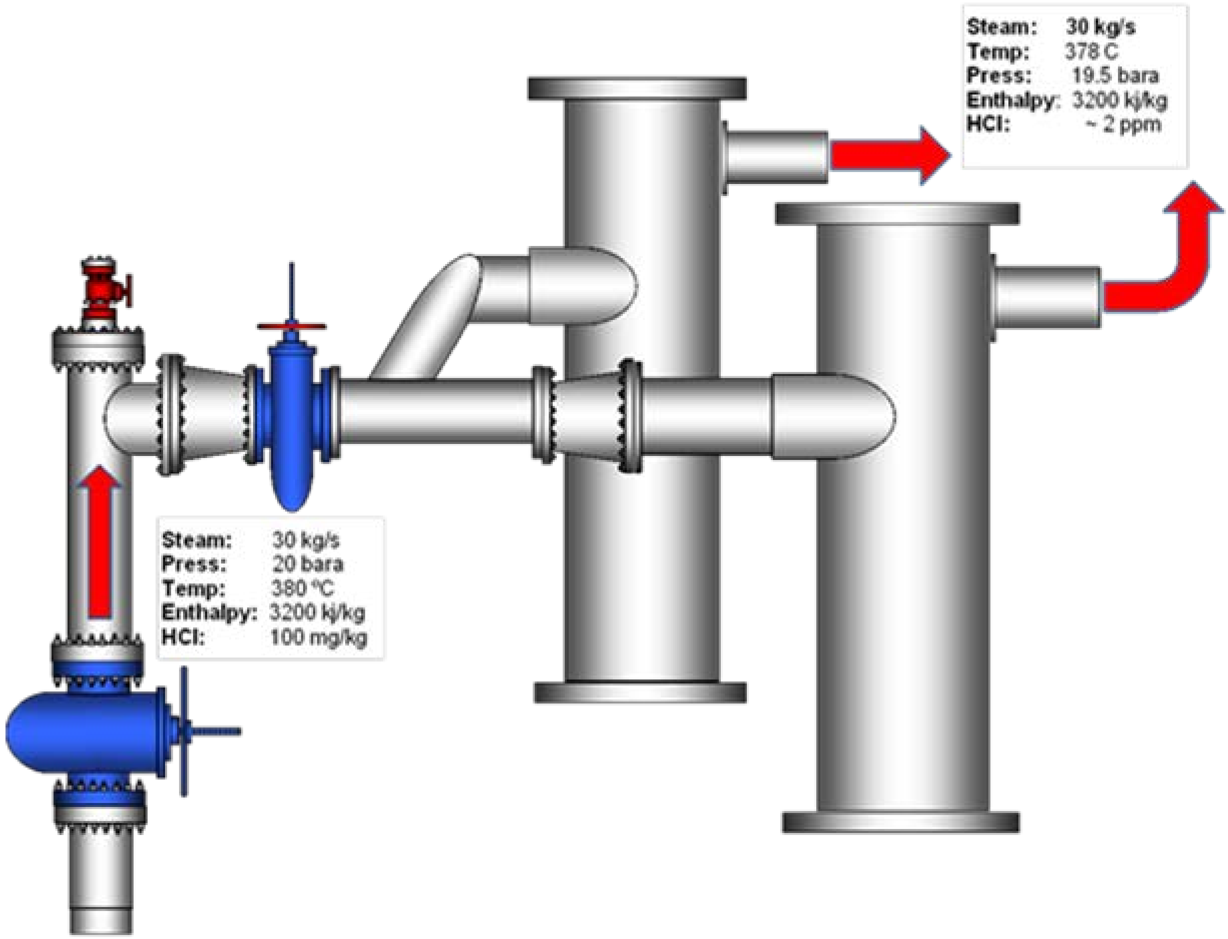


Figure 4-4
Calcium carbonate dry steam scrubbing process flow diagram—20 bara

A more advanced approach would be to use fluidized bed designs. The fluidized bed concept uses smaller-diameter calcium carbonate pellets that become suspended in the upward steam flow. Spent material would be separated by a conventional cyclone integral to the vessel, and the calcium carbonate would be replenished using a slurry pump and an aqueous calcium carbonate suspension for the feedstock. Fluidized beds can be highly efficient due to thorough contact between the gas and the solid, but it may be hard to maintain the optimal pellet size in the fluidization process during long-term operation. Computer modeling software is available to simulate fluidized bed designs, and pilot testing could be conducted to prove the solids handling and mechanical feasibility of the concept.

Based on a calcium carbonate (limestone) cost of US$0.50 per kilogram, the annual chemical cost for the DSS process on this well would be US$65,000 per year. The DSS chemical cost should be substantially less than that of the caustic scrubbing process.

The primary uncertainty in the calcium carbonate DSS process is the efficiency of hydrogen chloride removal at 380 ºC. The limiting factor in hydrogen chloride removal may be equilibrium vapor/liquid partitioning of hydrogen chloride from saturated films of aqueous calcium chloride ($CaCl_2$) on the surface of the calcium carbonate pellets, and/or sublimation of hydrogen chloride from solid calcium chloride. Highly concentrated (50% by weight) aqueous films of calcium chloride will exist in equilibrium with superheated steam at the conditions that have been tested. At temperatures up to 260 ºC, calcium chloride is soluble to 77% by weight. The calcium chloride will probably dry out completely in 380 ºC steam with 160 ºC superheat; it is not known what effect this will have on the process. Partial desuperheating of steam with clean water to 300 ºC or 275 ºC may be required if efficiency is poor at the full superheat temperature.

Partial desuperheating could involve water injection directly into the bed to eliminate any potential for dew point corrosion near the water injection point. However, it is known that dry limestone efficiently removes sulfur dioxide and hydrogen chloride from flue gas at temperatures of 300 to 1,200 ºC. Under these conditions, the relative humidity (water vapor saturation) is very low, suggesting that it may not be necessary to maintain a liquid film on the calcium carbonate in a highly superheated geothermal DSS process. This possibility can be tested under pilot conditions.

To date, the evaluation of dry sorbent materials for DSS processes has focused primarily on commodity chemicals and raw materials that don't require recycling in order to minimize cost and complexity. High-boiling point amine and oil mixtures were rigorously evaluated early on in the laboratory and at The Geysers. Given the cost of these chemicals, recycling is required for steam containing more than a few ppm hydrogen chloride. Recycling and regeneration of amines is effective using liquid-liquid extraction with sodium hydroxide in a continuous loop process. But the vapor-phase and entrainment losses on the order of 15% typically experienced at The Geysers make the process uncompetitive with other techniques. Losses would be greater at higher temperatures.

Crystalline molecular sieves, such as naturally occurring zeolite and activated carbon, have previously been proposed as potential DSS solids. These materials have been demonstrated to remove hydrogen from steam in qualitative laboratory experiments [61]. But it's not clear how the materials would be regenerated after saturation with hydrogen chloride, or what the cost might be for such a process given uncertain requirements for mass and surface area, as well as regeneration efficiency.

Other materials that have been considered, but not tested, for hydrogen chloride adsorption in a once-through DSS process are sodium carbonate (Na_2CO_3, soda ash) and calcium oxide (CaO, lime). Sodium carbonate should perform as well as, or better than, calcium carbonate in terms of hydrogen chloride adsorption. But soda ash is much more water-soluble than limestone, so it would cause problems with bed integrity during wet stages of operation such as startup and regeneration. Lime should be even more reactive than soda ash since it is a very strong base and also reacts with water to form calcium hydroxide [$Ca(OH)_2$, hydrated lime]. Under saturated steam conditions, lime would quickly convert to hydrated lime, which is still a solid. Under superheated conditions, lime may remain primarily as calcium oxide and maintain the mechanical properties needed for a packed bed. Lime is available in large lump (200-mm diameter) and pebble (6- to 60-mm diameter) form. If limestone is found to be inefficient at removing hydrogen chloride at temperatures above 300 ºC, then lime might be an alternate material for a dry packed bed process, and should be pilot tested.

Both soda ash and lime could be used in a spray-dry process, where a slurry of the powdered material, at roughly 70–80% by weight in water, is sprayed into the superheated steam. The water carrier is immediately vaporized and the solid particles (and possibly highly concentrated droplets) are carried with the steam to a separation device for removal. The particles would likely still contain active soda ash or lime that could be recycled back to the slurry. The superheat loss would be minimal as very little water is needed, but the mechanics of recovering the dry particles without deposition on piping and vessels could be challenging. Dry scrubbing using solid lime and spray-dry scrubbing with lime slurries is routinely performed in coal-fired power plants for sulfur dioxide and hydrogen chloride removal. These processes are also used in municipal waste-to-energy plants and secondary aluminum plants for hydrogen chloride removal. Process temperatures are often well above 400 ºC, but pressures are very low—which may facilitate solids handling (injection and recovery). Efficiencies are reported in the range of 95–99%, comparable to geothermal wet and dry scrubbing processes for hydrogen chloride.

Hybrid Steam Scrubbing

Hybrid process chemistries involving highly concentrated inorganic liquids that can exist at equilibrium with superheated steam have been demonstrated in the laboratory. The advantage of a hybrid process over DSS is that it eliminates vapor-solid contact issues, large vessels, pressure drop, regeneration, and mechanical systems for solids conveyance. A hybrid liquid scrubbing process involves a carrier liquid that can be injected and recirculated at sufficient liquid-to-steam ratios to provide good contact between liquid and vapor for hydrogen chloride mass transfer (1–5% by mass liquid fractions). The liquid must be high-boiling (exist in equilibrium with highly superheated steam) without drying out and/or precipitating solids. Finally the liquid must be kept sufficiently alkaline to allow high-efficiency mass transfer of hydrogen chloride to the liquid phase, and to minimize corrosion of steel or alloys in contact with the liquid. The following chemistries have been identified with the properties needed in a hybrid scrubbing process:

Potassium Hydroxide–Carbonate–Chloride system ($KOH–K_2CO_3–KCl$)

This process involves the injection of water and potassium hydroxide (KOH) into geothermal steam to generate potassium carbonate (K_2CO_3) and potassium bicarbonate ($KHCO_3$):

$$2\ KOH + CO_2 \rightarrow KHCO_3 + KOH^- \rightarrow K_2CO_3 + H_2O$$

At temperatures above 200 ºC, potassium carbonate solubility is at least 70% by weight, and the liquid phase can maintain a superheat of 70 ºC at a 300 ºC solution temperature. Hydrogen chloride from the vapor phase reacts with the saturated potassium carbonate solution to yield neutral potassium chloride:

$$2\ HCl + K_2CO_3 \rightarrow 2\ KCl + CO_2 + H_2O$$

Potassium chloride has much lower solubility than potassium carbonate, and will precipitate at a concentration of about 2% in saturated potassium carbonate at 100 ºC. Thus the reaction product of potassium hydroxide and hydrogen chloride can be removed from the system by cooling (and then reheating) the liquid recirculated through a series of small heat exchangers. The overall reaction is then:

$$HCl(g) + KOH(aq) \rightarrow KCl(s) + H_2O$$

The superheat vs. temperature or pressure curves for a 70% by weight solution of potassium carbonate are given in Figures 4-5 and 4-6. The values in the figures were actually measured at Thermochem Laboratories—not taken from the literature or derived from calculations. The solubility of potassium chloride in saturated potassium carbonate at 100 ºC was also directly measured in the Thermochem laboratory. It is likely that higher equilibrium superheat is possible at higher temperatures— to date, the limit for the laboratory tests by Thermochem is 300 ºC. At 20 bara, the superheat measured in the Thermochem apparatus was 63 ºC. Additional testing up to 380 ºC and with higher potassium carbonate concentrations needs to be performed to determine the maximum superheat possible for this process.

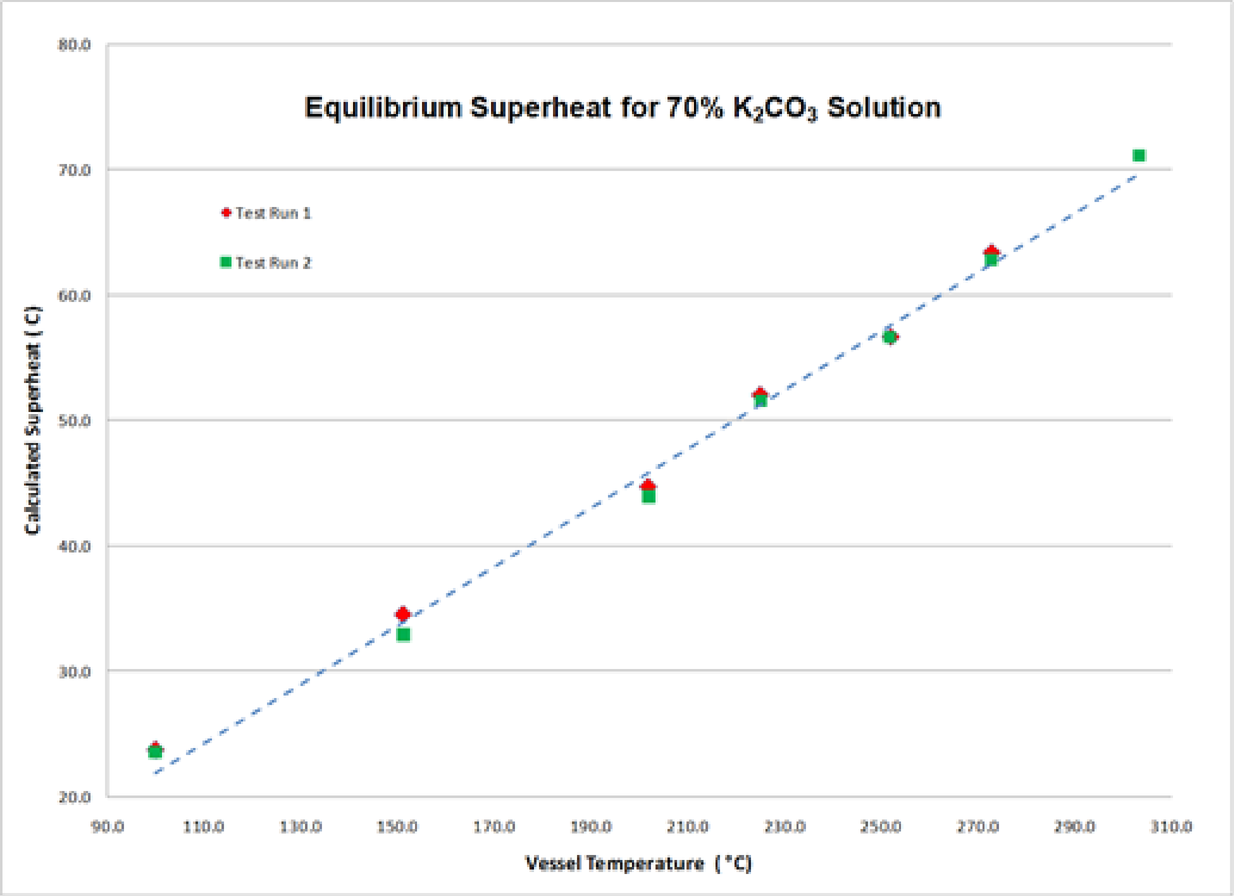


Figure 4-5
Potassium carbonate solution superheat vs. temperature

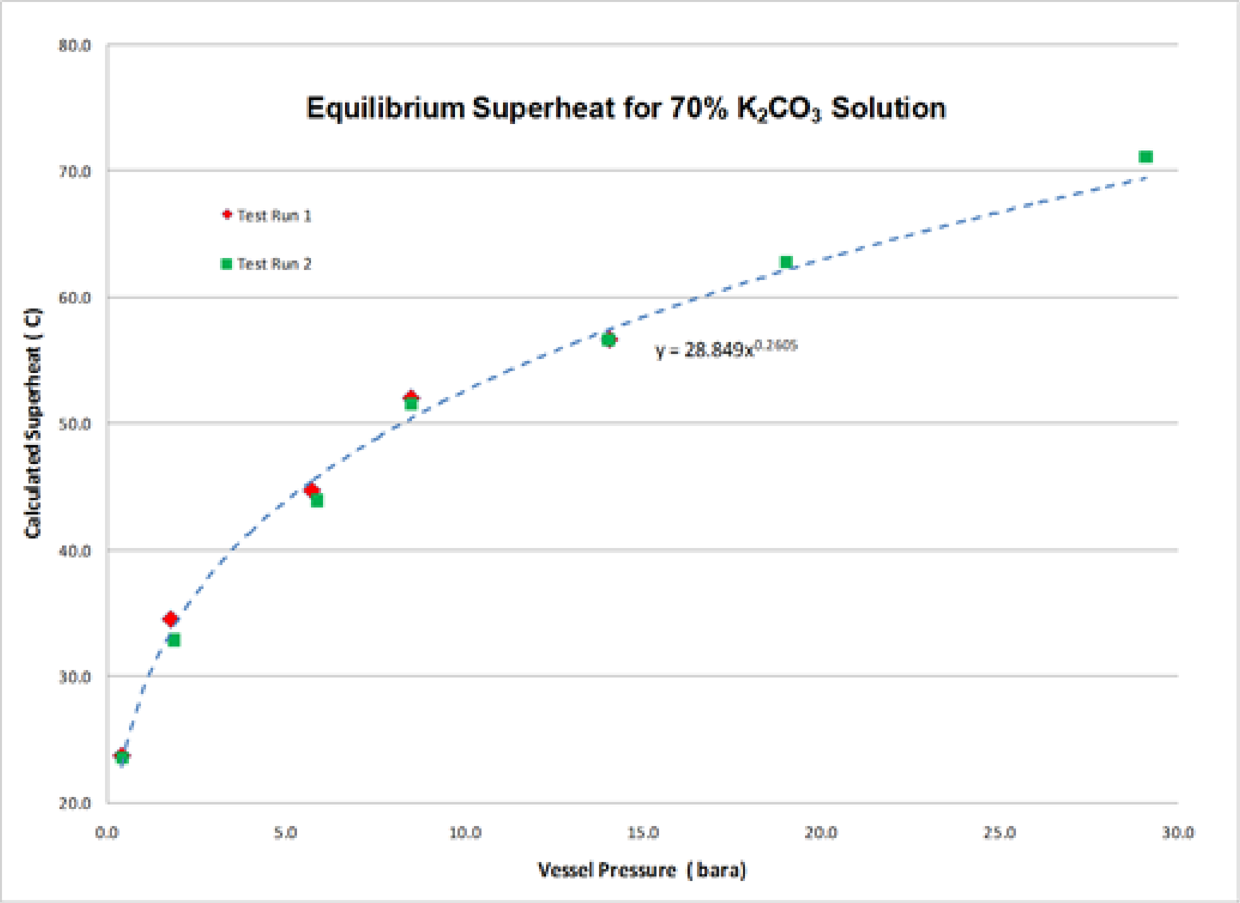


Figure 4-6
Potassium carbonate solution superheat vs. pressure

A conceptual process flow diagram for this system operating at 20 bara and 63 ºC superheat is given in Figure 4-7. The annual chemical cost would be about US$450,000, based on bulk pricing in the United States for 50% potassium hydroxide. Potassium carbonate solution could be used instead of potassium hydroxide solution, but the total annual chemical cost for this choice, per U.S. pricing, is even higher.

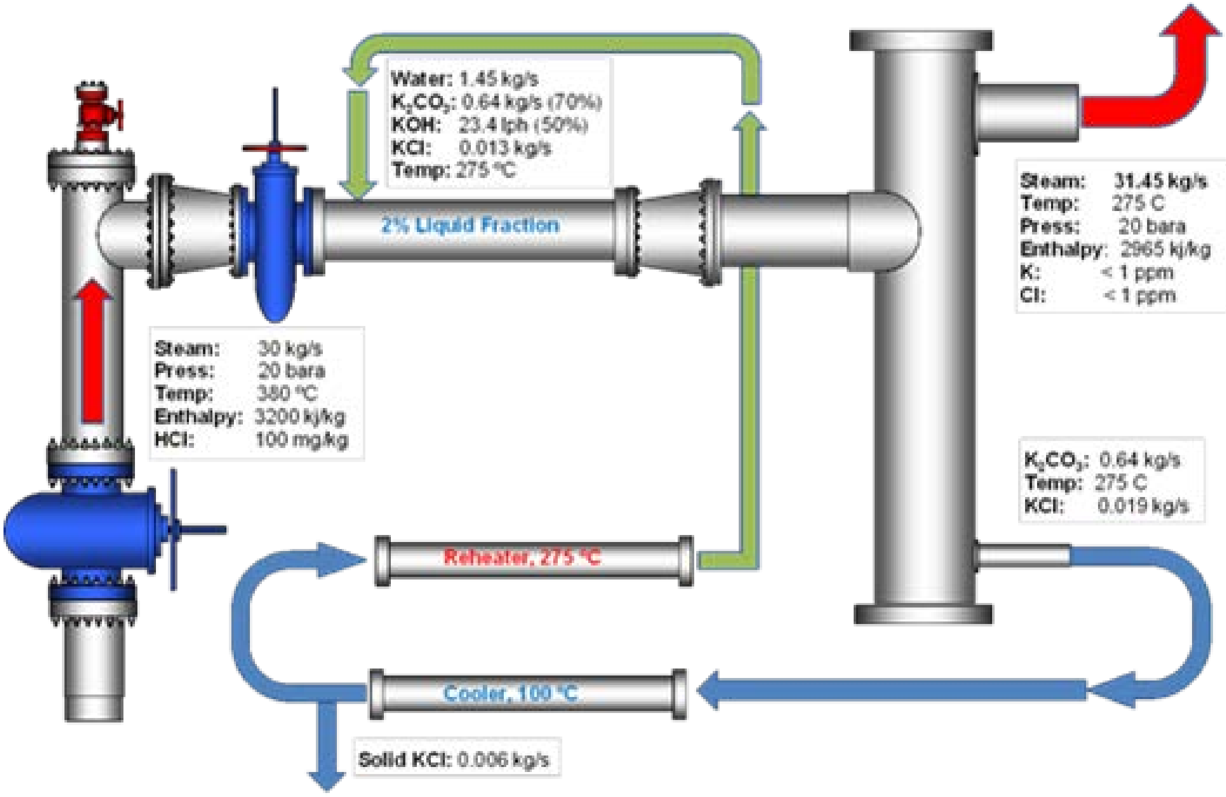


Figure 4-7
Hybrid potassium carbonate process flow diagram—20 bara

Calcium Chloride–Calcium Oxide system ($CaCl_2$–CaO)

This process recirculates a concentrated solution of calcium chloride ($CaCl_2$) as the carrier solution, with addition of lime (CaO) or hydrated lime ($Ca(OH)_2$) as the base to neutralize hydrogen chloride. The carrier solution is actually the reaction product, so only a blowdown stream is required to maintain solution volume and concentration, rather than the selective precipitation and separation required in the potassium hydroxide process. (Note that calcium chloride is much more soluble than potassium chloride.) The overall reaction chemistry is as follows:

$$2\ HCl(g) + Ca(OH)_2(s, aq) \rightarrow CaCl_2(aq) + 2\ H_2O$$

The pH of a calcium chloride solution drops with increasing temperature due to complexing of hydroxide (OH^-) with calcium (Ca^{2+}), so an excess of lime is maintained in the system. Lime reacts with water to form hydrated lime, which has low solubility but provides free hydroxide as needed to neutralize a strong acid such as hydrogen chloride. The bulk of the hydrated lime will be present as a suspension in the calcium chloride solution. Based on chemical modeling, the solution pH will be slightly alkaline at temperatures above 200 ºC (pH ~ 7.7 at 200 ºC and 7.2 at 300 ºC). At this pH, minimal carbon dioxide will be absorbed. As with the caustic and potassium hydroxide processes, any carbonate (CO_3^{2+}) that does form will also be available as a base to react with hydrogen chloride. It seems unlikely that calcite ($CaCO_3$) precipitation will be an issue, but a calcite scale inhibitor could be added if necessary. Given low blowdown rates, the inhibitor consumption would be very low.

At temperatures above 200 ºC, calcium chloride solubility reaches 80% by weight or higher, and the liquid phase can maintain a superheat of more than 100 ºC at a 300 ºC solution temperature. The superheat vs. temperature or pressure curves for an 80% by weight mixture of calcium chloride in water are given in Figures 4-8 and 4-9.

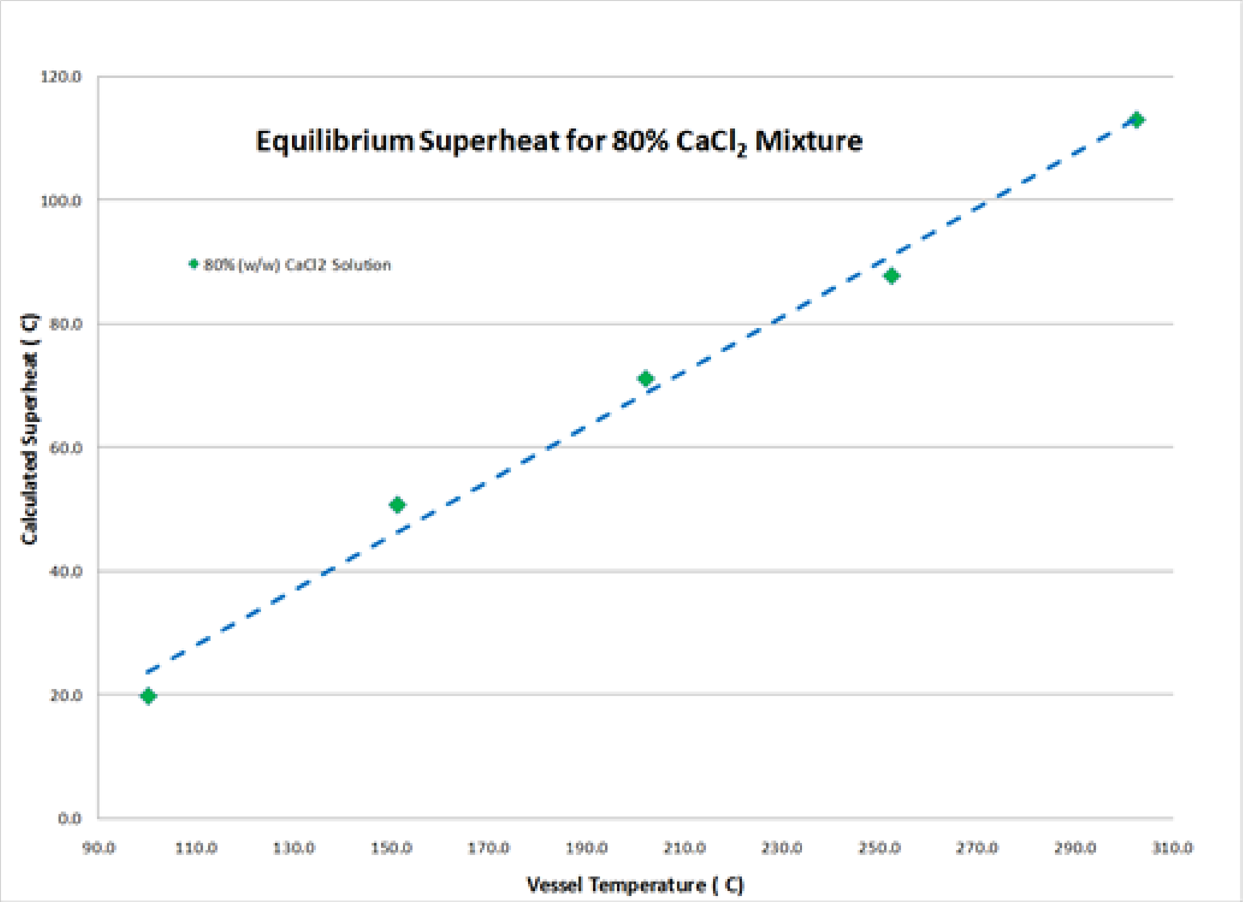


Figure 4-8
Calcium chloride solution superheat vs. temperature

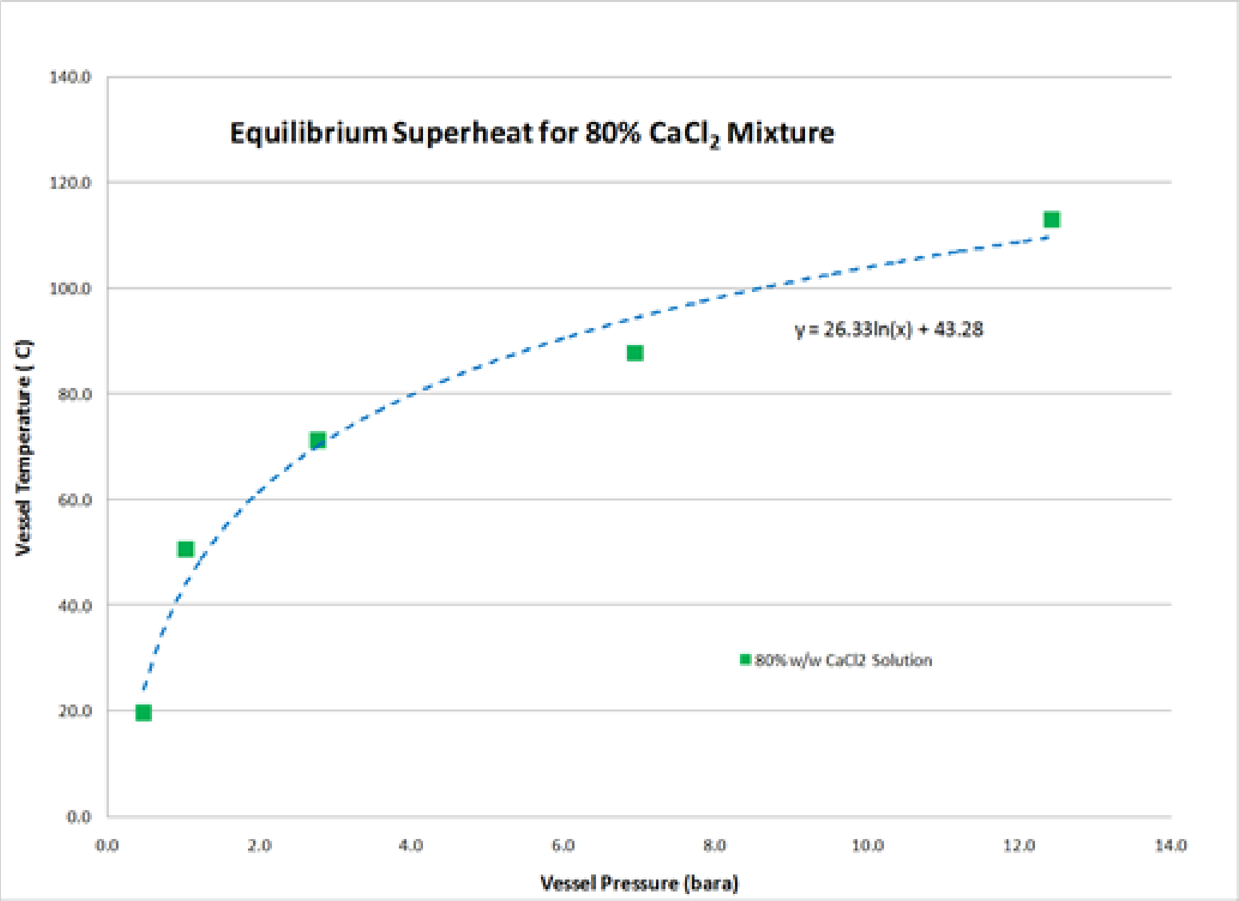


Figure 4-9
Calcium chloride solution superheat vs. pressure

A conceptual process flow diagram for the calcium chloride system operating at 20 bara and 113 ºC superheat is given in Figure 4-10. The annual chemical cost would be US$50,000, based on calcium oxide (anhydrous lime) pricing in the United States. Given the low chemical cost, high superheat retention, and simple operation, this currently appears to be the preferred process for scrubbing hydrogen chloride from high-temperature, high-superheat geothermal wells producing substantial amounts of hydrogen chloride.

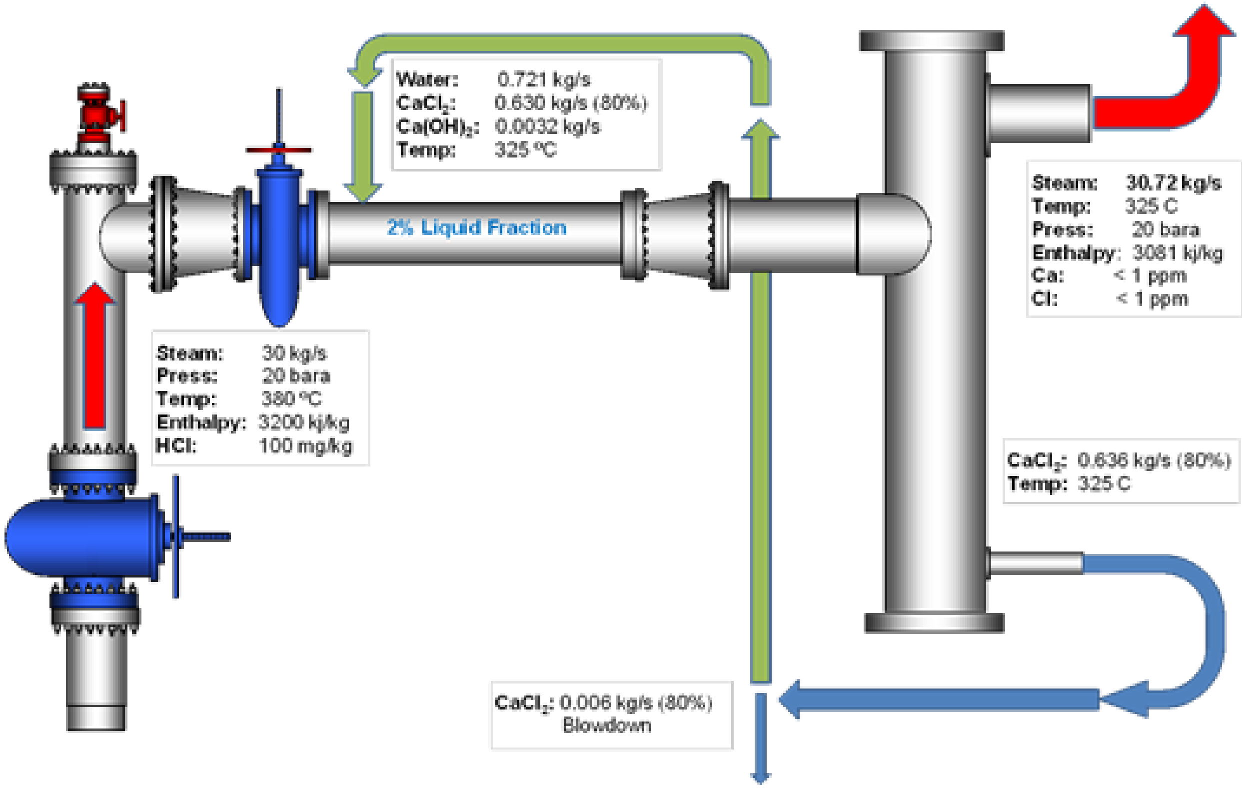


Figure 4-10
Hybrid calcium chloride process flow diagram—20 bara

Steam Polishing

Steam scrubbing processes are not 100% efficient—the wet, dry, and hybrid processes all can potentially leave 1 to 5 ppm hydrogen chloride remaining in the steam. At The Geysers, the final steam polishing before the turbine is accomplished by second-stage steam scrubbing using hotwell condensate only. Second-stage steam scrubbing removes residual hydrogen chloride from the few caustic and water wellhead systems, and any dry steam scrubbing wellhead systems in the field. It also removes low-level hydrogen chloride (1–5 ppm) from other wells without wellhead scrubbing. At Larderello, most steam scrubbing is accomplished at the power plant using hotwell condensate and caustic. Steam entering the turbines is saturated.

It is important to optimize any steam scrubbing system for maximum hydrogen chloride removal, ideally to less than 0.1 ppm at the turbine inlet. For wet scrubbing systems, this can easily be accomplished through second-stage polishing at the plant inlet. But for dry and hybrid scrubbing systems, a steam wash at the plant would defeat the purpose of maximum pressure and superheat retention for minimum exergy loss.

It might be possible to find turbine blade and rotor material that can tolerate hydrogen chloride in steam at levels of a few ppm over the long term. Because hydrogen chloride is more volatile and less acidic at high temperatures, it may not be a problem in the early stages of the machine use. A number of alloys were tested in Italy in the 1980s as possible alternatives to steam scrubbing, including X15CrNiMo13, XCrMnNiMoN2564, Ti6A14V, X12CrMo13, XCrNiMo126 [66]. Unfortunately, only the latter two were determined safe for the manufacture of turbine blades and rotors, respectively. An important research effort will be to work with turbine manufacturers to identify new materials for use in superheated steam with residual hydrogen chloride at high inlet pressures.

Hjartarson [58] performed a thermodynamic study on various options to utilize steam from the IDDP-1 well in Krafla. Some of the power cycles considered were: (a) two steam turbines in series, with the first turbine remaining superheated and wet scrubbing being employed before the second turbine, and (b) an organic Rankine cycle plant with no steam turbine, and (c) a conventional steam turbine plant with DSS upstream. It was concluded that the DSS process would be the most efficient.

A possible alternative to steam wash polishing or new turbine materials is the treatment of turbine inlet steam with filming and/or neutralizing amines. Thermochem has extensively studied amine chemistry for applications in dry steam scrubbing and corrosion control [67]. Although amines are usually not cost-effective as a primary scrubbing process, they do have application in a polishing process without loss of superheat. Hydrophobic, high-molecular-weight amines were used for primary steam scrubbing with recycling, and would also be effective in a once-through process. A water-soluble, lower-molecular-weight amine may also function well for turbine protection. The overall reaction for the amine scrubbing process from vapor to organic phase is:

$$(R)_3(R)NH_{2(org)} + HCl_{(g)} \rightarrow (R)_3(R)NH_3^+ Cl^-_{(org)}$$

There can also be significant differences in amine chemistry among amine classes. The primary amine shown in the above formula and found to be most effective was an amine with a tertiary-alkyl *(t*-alkyl) hydrocarbon chain of the general structure $(R)_3(R)NH_2$ [the straight-chain primary amine is represented as $(R)NH_2$]. In hydrocarbon solvents, tertiary-alkyl primary amines are one to two orders of magnitude more basic than primary or secondary-alkyl primary amines. The carbon-nitrogen (C-N) bonds in tertiary-alkyl primary amines are 100 to 200 kilojoules per mole (kJ/mol) more stable than their primary amine counterparts, making them less likely to decompose at high temperatures.

Another benefit of the tertiary-alkyl primary amines compared with normal-alkyl (*n*-alkyl) amines is lower melting point. A tertiary-alkyl amine may still be liquid at 0 °C, but an *n*-alkyl amine in the same weight range (C18) melts at 55 °C. A low melting point makes it easier to handle the chemical in storage and use, but is not critical to the process. A drawback in a primary scrubbing process for the *t*-alkyl structures studied is a lower boiling point—310 to 330 °C, versus 350 °C for a normal-octadecyl (*n*-octadecyl) amine. But for a polishing process, the amines would not be recovered and allowed to condense with steam through the turbine. Therefore an amine with the optimal boiling point could be selected to target specific stages of the turbine most vulnerable to attack from hydrogen chloride. For a once-through process of amine protection at the inlet for a turbine using production from the example well, the cost would be roughly US$75,000 per year. This cost is based on a 30 kg/s steam flow, 2 ppm residual hydrogen chloride in steam, 1:1 mole ratio amine to hydrogen chloride, a molecular weight of 325 grams per mole (g/mol), and a cost of about US$4.50 per kg. Amine pricing can vary dramatically, so it may be possible to find lower-cost generic amines for this purpose.

For direct use of high-pressure steam from the example well, volatile silica, volatile salts, and suspended solids carried in steam must also be considered. With brine production at separation temperatures of 240–270 °C, silica partitioning to the vapor phase will be on the order of 0.2%, resulting in several ppm silicon dioxide (SiO_2) in the steam (Figure 4-11). Silica in turbine inlet steam should be less than 0.05 ppm to prevent scaling.

Volatile silica levels may be even higher in the superheated steam at these temperatures, depending on the source of the fluid and path to the production wellbore. Wet scrubbing to saturation in the range of 200 °C or less will be capable of removing vapor-phase silica, salts, and solids. Dry and hybrid scrubbing may also be effective in removing volatile silica and entrained solids. Vapor-phase silica in steam is present as silicic acid ($SiO_2 \cdot nH_2O$) and is much less volatile in the silicate form once neutralized by a base, analogous to hydrogen chloride scrubbing from steam.

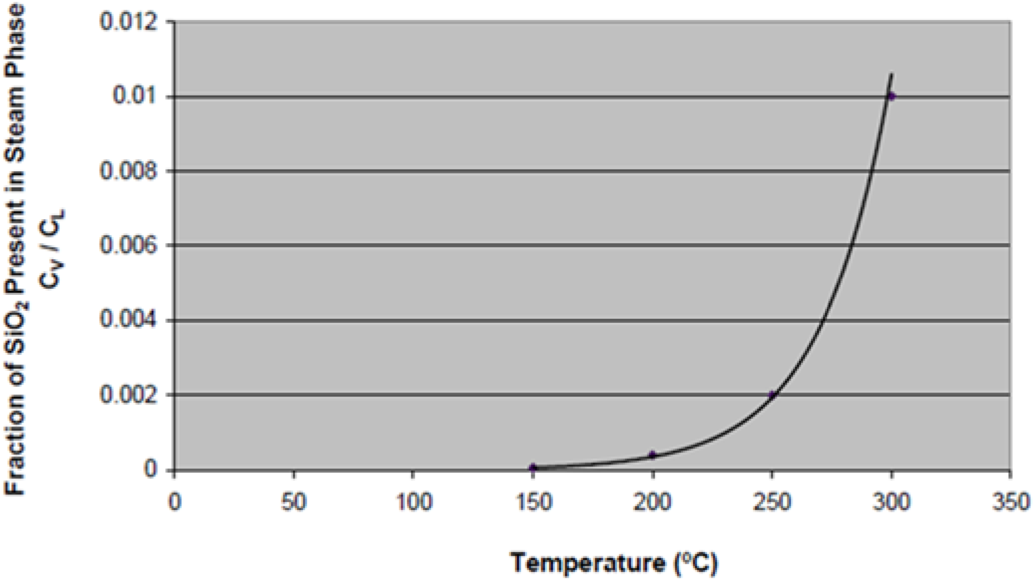


Figure 4-11
Silica partitioning between steam and water as a function of temperature [68]

Characterization of impurities in steam other than hydrogen chloride and their removal will be an important research effort for utilization of high-temperature, high-superheat steam.

Comparison of Treatment Options for Hydrogen Chloride Corrosion Control

For the steam scrubbing options considered in this report, Table 4-2 summarizes the estimated process parameters, operating costs, and potential drawbacks for each process treating the example well. At this time, the DSS process using limestone or lime, and the hybrid calcium chloride process look the most promising in terms of retained energy and chemical cost. Further pilot testing will be required to determine process efficiencies and undesirable side effects, such as scaling and residual impurities in the steam.

Table 4-2
Steam scrubbing process comparison for example well

Process	HP Steam Pressure	Temp.	Superheat	Flowrate	Enthalpy	LP steam Pressure	Flowrate	Chemical Cost US$/year	Residual HCl ppm	Other Impacts
Brine Scrubbing, Recycle	8.0 bara	170 C	0 C	34.15 kg/s	2769 kj/kg	2.2 bara	1.63 kg/s	$ -	0.1 to 1	Insufficient neutrailization of HCl, low brine pH; potential silica scaling
Brine Scrubbing, Recycle, with fresh water augmentation	8.0 bara	170 C	0 C	33.00 kg/s	2769 kj/kg	2.2 bara	1.58 kg/s	$ -	0.1 to 1	Insufficient neutrailization of HCl, low brine pH
Water / Caustic	8.0 bara	170 C	0 C	34.82 kg/s	2769 kj/kg	NA	NA	$ 209,000	0.1 to 1	Saturated steam only, chemical cost
Water / Caustic, pre-heated	8.0 bara	170 C	0 C	35.68 kg/s	2769 kj/kg	NA	NA	$ 209,000	0.1 to 1	Saturated steam only, chemical cost
Water / Caustic, pre-heated	20.0 bara	170 C	0 C	35.15 kg/s	2799 kj/kg	NA	NA	$ 209,000	0.1 to 1	Saturated steam only, chemical cost
DSS Calcite or Lime	19.5 bara	378 C	167 C	30.00 kg/s	3200 kj/kg	NA	NA	$ 65,000	1 to 5	Chemical cost, HP vessels needed, possible downstream polishing
Hybrid Potassium Carbonate	20.0 bara	275 C	63 C	31.45 kg/s	2965 kj/kg	NA	NA	$ 438,000	0.1 to 1	Chemical cost, heat exchangers, crystallizer for KCl
Hybrid Calcium Chloride	20.0 bara	325 C	113 C	30.72 kg/s	3081 kj/kg	NA	NA	$ 62,000	0.1 to 1	Chemical cost

5

SUMMARY

Research is ongoing to find cost-effective alloys for geothermal well casings. Although many metals have been proven to offer adequate protection against corrosion, they remain impractical for geothermal development because the cost of most materials is too high. 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. Although composite coatings, spray application, electrochemically deposited, and explosion cladded materials have been successful in laboratory testing, 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.

At many geothermal power stations, chemical injection to adjust fluid chemistry is the most cost-effective solution to corrosion. Sodium hydroxide injections increase pH and can improve operating conditions to reduce the immediate need for corrosion resistant alloys [69]. Chemical injection, offering a lower cost but decreased corrosion resistance, is currently the best option—until nickel and titanium costs moderate enough to justify manufacturing clad or solid piping.

Material and treatment technologies should be chosen on the basis of laboratory and/or field testing at conditions specific to a given field, or even a given well site, if practical.

6
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