Current Techniques in Acid-Chloride
Corrosion Control and Monitoring at The Geysers

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ABSTRACT

Acid chloride corrosion of geothermal well casings, production piping and power plant equipment has resulted in costly corrosion damage, frequent curtailments of power plants and the permanent shut-in of wells in certain areas of The Geysers. Techniques have been developed to mitigate these corrosion problems, allowing continued production of steam from high chloride wells with minimal impact on production and power generation facilities. The optimization of water and caustic steam scrubbing, steam/liquid separation and process fluid chemistry has led to effective and reliable corrosion mitigation systems currently in routine use at The Geysers. When properly operated, these systems can yield steam purities equal to or greater than those encountered in areas of The Geysers where chloride corrosion is not a problem. Developments in corrosion monitoring techniques, steam sampling and analytical methodologies for trace impurities, and computer modeling of the fluid chemistry has been instrumental in the success of this technology.

INTRODUCTION

The production of volatile chloride from Geysers wells was not recognized to be a problem until as late as 1986, after severe production piping corrosion/erosion damage and a wellhead failure had occurred in the Northeast Geysers. Previous corrosion damage, including turbine blade and piping failures, may have been caused by chloride, but monitoring techniques had not been established that could identify acid-chloride as the primary cause. Accurate measurements of chloride in steam produced at The Geysers were not performed before 1986, when specific sampling and analysis methods were developed. Therefore, little data is available to determine trends in produced chloride concentrations from Geysers wells, although it is generally assumed that concentrations are increasing in certain areas. The range of chloride concentrations measured in dry, superheated steam produced by wells at The Geysers is currently from <0.010 ppm_w to 200 ppm_w.

Corrosion damage due to acid-chloride at The Geysers includes extensive well casing corrosion, casing head perforation, well surface piping failures, and gathering system piping perforations or extreme wall loss. The corrosion products exfoliated from wellbores and gathering systems have had a severe impact on power plant equipment, such as the plugging of steam strainers and erosion of turbine blades. Corrosion within the power plants due to residual acid-chloride has resulted in perforations of steam piping, the freezing of stop valves and turbine damage.

The first full-scale corrosion mitigation system at The Geysers was implemented at the Aidlin project by Mission Power Engineering during start-up of the two 10 megawatt (net) units in mid-1989[1]. This system involves water and caustic (NaOH) injection at each production wellhead with subsequent liquid removal by vertical separators and a final two-stage steam washing/separator combination at the plant inlet. This project is unique to The Geysers in that all production wells produce significant levels of chloride in steam and require treatment. The corrosion mitigation system has been very successful in preventing corrosion damage to the steam gathering system and power plant, with surface piping corrosion rates typically below 10 mil/year and turbine inlet steam below 0.05 ppm_w chloride. After the first nine months of operation, a full turbine inspection was performed, including non-destructive testing and scale deposit analysis, which revealed no corrosion damage or evidence of acid-chloride or caustic deposits within the turbine. The operating results for this system encouraged the application of acid-chloride corrosion mitigation technology throughout The Geysers.

This paper outlines the design basis of acid-chloride corrosion mitigation systems currently in use at The Geysers. Details of the process chemistry are discussed, including chemical computer modeling of the vapor-liquid chemical dynamics, and mechanical equipment considerations in maintaining high mass transfer and separation efficiencies. Procedures for corrosion monitoring, fluid sampling and analytical techniques, and mass/heat balance calculations are presented. Initially, the volatile chloride phenomenon, acid-chloride corrosion and dewpoint corrosion are reviewed with analogies to corrosion problems in other industries.

BACKGROUND

The Occurrence of Volatile Chloride in Steam

Geothermal steam containing volatile chloride has been reported in steam fields throughout the world, such as Larderello, Italy; Tatun, Taiwan; Krafla, Iceland; Saint Lucia, Windward Islands, and The Geysers, USA[2,3,4]. These geothermal systems vary greatly in reservoir characteristics, including vapor-dominated, liquid-dominated and volcanic-related fields, but all have produced measurable levels of chloride in dry steam from certain wells without the associated quantities of alkali metals or alkaline earth metals (Na, K, Ca, Mg). Only a few reported cases exist for geothermal systems where it can be conclusively stated that the volatile chloride species is hydrogen chloride (HCl), although the presence of HCl has been well documented for high-temperature volcanic gases[5]. Recently, volatile chloride produced from the two vapor-dominated systems, Larderello and The Geysers, has been considered HCl, although historically chloride produced in steam from Larderello was referred to as ammonium chloride (NH_4Cl)[2,6].

In the condensate of chloride-bearing steam at The Geysers, ammonium ions (NH_4^+) are usually present in excess relative to chloride, making it unclear whether the chloride was initially HCl that reacted with NH_3 in solution, or was transported as NH_4Cl in the vapor phase. Often ferrous iron (Fe^{+2}) is present in quantities much greater than ammonium, as a result of the corrosion of carbon steel piping. This occurrence has been interpreted as proof that the original chloride species was HCl due to the apparent lack of ammonium relative to

chloride[7]. However, this argument is not convincing since ammonium chloride would also corrode carbon steel, resulting in a pH increase and the loss of ammonia to the vapor phase. The presence of dissolved ferrous iron (as a corrosion product) has frequently confounded the interpretation of chloride-enriched condensates by also drastically lowering the pH as ferrous iron oxidizes to ferric upon exposure of a sample to air. Typically, the excess of ammonia relative to chloride in most chloride-bearing steam condensates results in pH values above 5.0 units at 20°C, although systems without excess ammonia may produce condensates below 2.0 pH units at 20°C.

The presence of volatile chloride in steam is a common problem related to conventional steam turbine power plants utilizing subcritical high-pressure boilers. Chloride deposited within steam turbines can cause pitting corrosion and stress-corrosion cracking of the turbine blades. The vapor phase chloride species in this industry is frequently referred to as ammonium chloride, although extensive research has also been conducted on the volatility of NaCl at high temperatures (>300°C). Ammonia is considered a possible aid in the transport of chloride and sulfate from boilers where it is added as ammonium hydroxide for pH control. However, research on the actual transport mechanism has been inconclusive and it appears that ammonium chloride will decompose to HCl and NH_3 at temperatures of 200°C to 250°C, and possibly lower under certain conditions. Experiments performed for the Electric Power Research Institute (EPRI) showed that consistent 1:1 mole ratios, within analytical error, of NH_4^+ and Cl^- could be generated in superheated steam exposed to a saturated NH_4Cl solution at temperatures of 143°C to 190°C. But measurements of pH on the condensed steam shifted erratically between 3.2 and 8.0 units during the tests, indicating that some NH_4Cl decomposed to NH_3 and HCl, which volatilized at slightly varying ratios[8,9].

Most geothermal researchers agree that volatile chloride in geothermal steam is transported as hydrogen chloride. However, there is a considerable debate over the mechanism of HCl generation in the reservoirs. Haizlip, et al.[10], presented a model attempting to account for the chloride levels found at The Geysers and Larderello based on moderate to high saline fluids (10,000 to 100,000 ppm$_w$ NaCl) at depth within a range of temperatures and pH values expected for these reservoirs. Unfortunately, these calculations were based on extrapolated HCl vapor pressure data and HCl dissociation constants which are highly uncertain due to the wide disparities among literature values. Anderson[11] presented a more rigorous thermodynamic model of HCl volatility in high temperature saline brines and concluded that HCl would not partition to the steam phase at the higher concentrations found in The Geysers by this process (10 - 100 ppm$_w$ Cl^-).

Research on equilibrium distributions of strong electrolytes between concentrated salt solutions and dry saturated steam has been performed in the U.S.S.R., including studies of molecular NaCl, NaOH, HCl and hydrated ion solubilities in steam at temperatures of 320°C to 350°C[12,13,14,15]. Comparison of the recent modeling data to this experimental work indicates that the volatile chloride produced at The Geysers could not be the result of direct partitioning from high temperature NaCl solutions alone. Based on experimental data of Tatarinov, the total chloride (HCl + NaCl species) in equilibrium steam over water containing 24 g/Kg chloride at pH 5.5 (calculated) is only 4 ppm Cl^-, while Haizlip's calculations yield 70 ppm Cl^- (HCl only) and Anderson's calculations yield 1 ppm Cl^- (HCl only) at the same conditions. Diagram 1 compares the vapor phase Cl^- concentrations obtained from modeling to the experimentally measured values at 350°C as a function of liquid phase chloride content.

Another possible mechanism for HCl generation is through the complete evaporation of NaCl solutions at high temperature, as demonstrated by Fournier[16]. D'Amore, et al., has presented several mineral-halite reactions as possible

sources of HCl[17]. Given the wide range of geothermal reservoir conditions associated with volatile chloride production, it may be possible that more than one mechanism is responsible for its generation and transport.
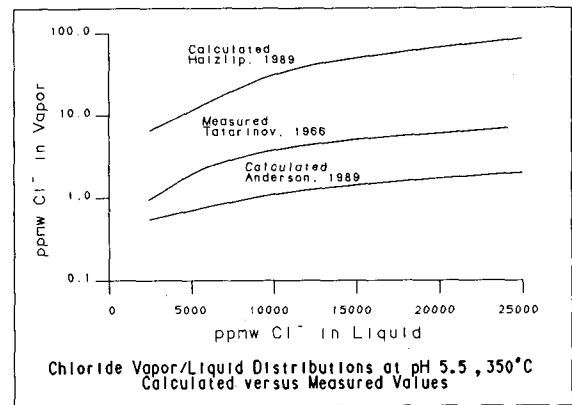

Chloride Vapor/Liquid Distributions at pH 5.5 , 350°C
Calculated versus Measured Values

Diagram 1

Chloride Induced Corrosion

Severe corrosion problems in geothermal power systems related to volatile acid-chloride species have been reported worldwide[2,3]. In Larderello, Italy, low ppm levels (1-10 ppm$_w$) of chloride in steam has resulted in etching of turbine components, mostly at the base of stationary and moving blades in the wet stages of the machines. Severe corrosion of carbon steel steam lines was caused by tens to hundreds of ppm$_w$ vapor phase chloride in contact with condensate.

In Krafla, Iceland, the Well No. 12 produced 20-100 ppm$_w$ chloride in dry superheated steam resulting in corrosion rates over 800 mils/yr for carbon steel. Excessive corrosion of 13% chromium steel turbine blade test coupons exposed to this steam was observed. Severe corrosion and erosion of the first and second stage turbine blades and damage to the main stop valves was revealed upon inspection of the unit and attributed to the steam from Well No. 12.

In conventional steam turbine power plants, chloride-induced stress corrosion cracking is considered to be one of the major problems in turbine reliability[18]. 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 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[8,9].

The turbines in use at the Cerro Prieto geothermal field (Mexico) are exposed to mechanically-entrained sodium chloride, rather than volatile chloride, and have experienced negligible corrosion[19]. The turbine blade material in use at these units is 12% chromium steel, similar to The Geysers units. The caustic scrubbing process for volatile chloride removal described in this paper generates sodium chloride, which is entrained in the turbine steam at trace levels, but would be expected to have similar turbine impacts as experienced at Cerro Prieto.

Sodium chloride is the primary component dissolved in moderate salinity geothermal brines, which are universally produced through low-carbon steel piping. Corrosion rates in

these systems are typically 1 to 12 mils/yr when the pH is greater than 6 units, the chloride concentration is under 20,000 ppm_w and no oxygen is present[20]. These fluids contain substantial quantities of dissolved silica and often other scale-forming minerals that tend to form stable, protective films on carbon steel surfaces, inhibiting corrosion. The caustic scrubbing process for volatile chloride removal generates similar water chemistry to these geothermal brines, except that scale-forming minerals are absent, requiring higher pH values to limit the corrosion of carbon steel.

Acid-chloride corrosion of carbon steel proceeds by the hydrogen ion reduction reaction:

$$Fe + 2H^+ \rightarrow Fe^{+2} + H_2$$
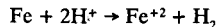
Chloride ions do not participate directly in the electrochemical reaction, but play an important role in the corrosion process[21]. Pitting corrosion, which is the primary mode of failure under these conditions, is largely the result of chloride ions which accelerate the localized dissolution of metal by electrically balancing the rapid build-up of positively charged metal ions and increase their solubility through complexation. This process is in contrast to oxygen reduction, in neutral or basic aerated solutions ($2Fe + O_2 + 2 H_2O \rightarrow 2Fe^{+2} + 4OH^-$) which generates hydroxide ions that migrate more slowly than chloride to the newly formed metal ions and precipitate metal hydroxides that tend to inhibit further attack. Chloride ions can initiate the corrosion process by breaking down protective magnetite films (Fe_3O_4) that passivate the interior surfaces of carbon steel steam piping. Localized corrosive attack is also enhanced by the migration of chloride ions beneath scale deposits and within crevices, where iron chlorides can hydrolyze, generating HCl ($FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$). Pitting corrosion is predominant under stagnant or low turbulence flow regimes, such as within the dead-legs of tees, or just inside welded valve ports. At The Geysers, damage can be just as severe in high velocity, turbulent, piping configurations due to the combined effects of corrosion/erosion when entrained particulates, such as exfoliated corrosion products, are present.

Dewpoint Corrosion Phenomenon

Volatile chloride corrosion of geothermal production piping and equipment is analogous in many ways to dewpoint corrosion in fossil fuel power plant flue gas systems. Dewpoint corrosion occurs when a gas is cooled below the saturation temperature relevant to the concentration of a condensable corrosive species contained in the gas. Power plants burning coal containing on average 0.3 wt. % Cl and 1.5 wt. % S will emit flue gas with an HCl concentration of about 200 ppm_v and total sulfur oxide concentration of about 1200 ppm_v[22]. The presence of acid gases in the flue gas stream causes acidic condensate to form at temperatures much higher than the saturation temperatures for pure water vapor. Several "dewpoint temperatures" are associated with these flue gas systems, beginning with the lowest vapor pressure component, H_2SO_4, which typically condenses in the 120 to 150°C range, then HCl condensing at 50 to 60°C and water vapor below 40°C. Upon initial condensation, liquid films contain up to 80% by wt. sulfuric acid, and as temperatures decline, the condensate will contain thousands of ppm_w hydrochloric acid. Corrosion rates of mild steel studied in simple flue gas systems correlate well with the rates of acid deposition, as shown in Diagram 2. Above the acid dewpoint temperature, the corrosion rate is nil, but increases rapidly just below the dewpoint as acid deposits and follows a decrease in the acid deposition rate about 40°C below the dewpoint temperature. This decrease is considered to be due to a lower diffusion rate of acid through the boundary layer as the acid is transformed from a supersaturated vapor to a condensed mist. Corrosion rates increase rapidly again near the water dewpoint temperature as the bulk of the acid dissolves in the condensate. When possible, the primary method of dewpoint corrosion mitigation is to maintain the flue gas temperature above the acid dewpoint temperature. Under these conditions, the corrosion rate of mild steel is negligible.
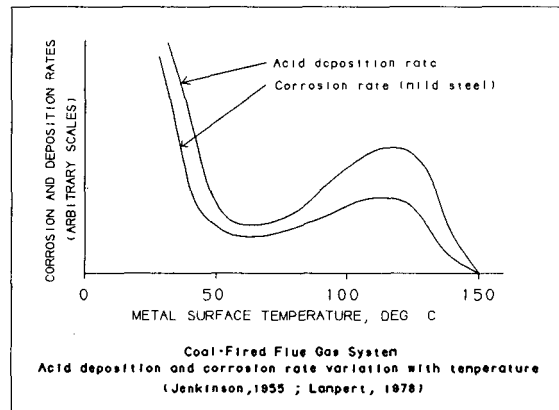

Coal-Fired Flue Gas System
Acid deposition and corrosion rate variation with temperature
(Jenkinson, 1955 ; Lanpert, 1978)

Diagram 2

Most flue gas streams require wet scrubbers for desulfurization, making it impossible to maintain temperatures above the acid-dewpoint. The prime area of corrosion within wet scrubbers is in the hot gas quench zone. At the wet/dry interface, rapid cooling occurs that can induce condensation immediately upstream of the alkaline scrubbing liquor. Solid deposits form downstream of the interface in the wet zone which can also promote localized attack. As the wet/dry interface line shifts with changing load conditions, deposits can trap concentrated acids and shield them from the high-pH scrubbing solution. Under these conditions, the most effective means to combat corrosion is to line the exposed walls with sheets of high alloy material, such as Hastelloy C-276.

Within geothermal well casings and gathering systems, the concept of acid-dewpoint temperature is important whenever volatile chloride is produced in dry steam. Corrosion rates vary dramatically with differences in volatile chloride concentrations and levels of steam superheat, and correlate qualitatively with expected acid deposition rates. Wells producing acid-chloride at The Geysers can be grouped into three general categories on the basis of dewpoint corrosion phenomenon.

1. *Wells producing steam with high levels of superheat, 30-120°F above the pure water saturation temperature.* These wells have low general corrosion rates in the well casing, wellhead and surface piping regions, but can cause substantial corrosion in the downstream gathering system as pipeline heat-loss or contact with saturated steam results in acid-dewpoint conditions. These wells are also highly subject to localized corrosion in the near wellhead region at points of conductive heat loss induced by exposed wellhead wing valves, piping tees, pipeline supports, and instrument taps. The highest volatile-chloride producing wells at The Geysers are in this category.

2. *Wells producing low-superheat (10-20°F) or saturated steam.* At the same acid-chloride concentration, these wells typically have much higher general corrosion rates than Group 1 wells, since they are normally at or below the acid dewpoint temperature. Temperature profile measurements across a pipe diameter for these wells often indicates a superheated core with near-saturation conditions at the pipe walls. Most corrosion damage is associated with the wellhead and near-wellhead piping, with some downhole problems. These can be the most difficult wells to maintain in production.

3. *Wells producing significant quantities of water (condensate), with steam qualities of 95 to 99%.* Corrosion damage for these wells is limited mostly to the well casing, with essentially all the acid-chloride in solution and often completely reacted with iron when it reaches the wellhead. Stoichiometric ratios of iron to chloride frequently approach the 2 to 1 limit, rendering the liquid relatively noncorrosive to surface piping as long as oxygen is excluded. Downhole corrosion is usually severe, resulting in casing perforation and failures. These wells have a limited lifetime if the casing is left unprotected.

It is important to note that individual wells can progress through all three groupings, depending upon production modes (wellhead pressure), changing reservoir conditions and production history (new wells). A Group 1 well can be transformed to a Group 3 well by a downhole problem such as a bridge, causing a reduction in steam flowrate and wellbore condensation. New production wells in high chloride areas can progress steadily from Group 3 to Group 1 conditions as local reservoir liquid is depleted.

In addition to steam superheat conditions, the acid-dewpoint is controlled by the concentrations of volatile electrolytes in the steam. The presence of ammonia can induce the formation of saturated ammonium chloride solutions at temperatures well above the dewpoint of pure steam or steam containing only HCl. Ammonium chloride has a much lower vapor pressure than hydrogen chloride in aqueous solutions, causing this dewpoint elevation. Diagram 3 shows the calculated dewpoint temperature of steam containing 10 ppm_w and 100 ppm_w HCl and a range of ammonia concentrations typical for The Geysers. At 130 psia, a dewpoint temperature of 376°F is possible, 28°F above the 348°F pure water saturation temperature, with original steam phase concentrations of 100 ppm_w HCl and 800 ppm_w NH_3. Just below this dewpoint, the ammonium chloride concentration in liquid films and droplets would be about 7 molal (25% by wt. Cl^-) and have a pH of 3.3 units. At 10 ppm_w HCl and 200 ppm_w NH_3, the dewpoint would

be elevated by 10°F and initial liquid pH values would be about 3.5 units (7% by wt. Cl^-). Actual dewpoints could vary depending upon nucleation factors, such as the presence of particulate matter, or localized external heat sinks. Metal ions generated in corrosion processes could cause hysteresis effects, resulting in liquids stable at temperatures above the initial dewpoint due to the formation of highly concentrated non-volatile $FeCl_2$ solutions.

Dewpoint corrosion can be minimized at the wellheads and adjacent surface piping of Group 1 and Group 2 wells by adequate thermal insulation techniques. Wellhead cellars must be free of standing water and the surface casing should be insulated to 10 or 20 feet below grade. Wellhead wing valves must be entirely insulated or eliminated completely from the wellhead configuration. At least 4" thick insulation should be provided on the wellhead tee, and all piping, vessels and blind flanges downstream. Pipeline supports should be insulated from and never welded to the pipeline. Instrument taps should be minimized and thoroughly insulated.

Production modes are also critical in minimizing dewpoint corrosion. Wells should be produced at the lowest wellhead pressure possible to maximize superheat. High chloride wells should only be produced in an on/off mode, either full flow or shut-in, but never under throttled production that might generate dewpoint conditions.

Volatile chloride corrosion at The Geysers is also similar to conventional flue gas dewpoint corrosion with respect to problems within the quench zone of scrubbing equipment. Superheated steam is rapidly brought to saturation near the water/caustic injection point as part of the corrosion mitigation process. Pipe wall temperature gradients can reach 100°F over very short intervals, inducing acid-dewpoint conditions adjacent to the alkaline wet zone. The alkaline wet region may not completely coat the pipe until several feet downstream of injection, and its coverage will vary depending upon superheat, steam velocity, water injection rate and piping/nozzle geometry. Scale deposits can trap acid-chloride beneath as the wet/dry
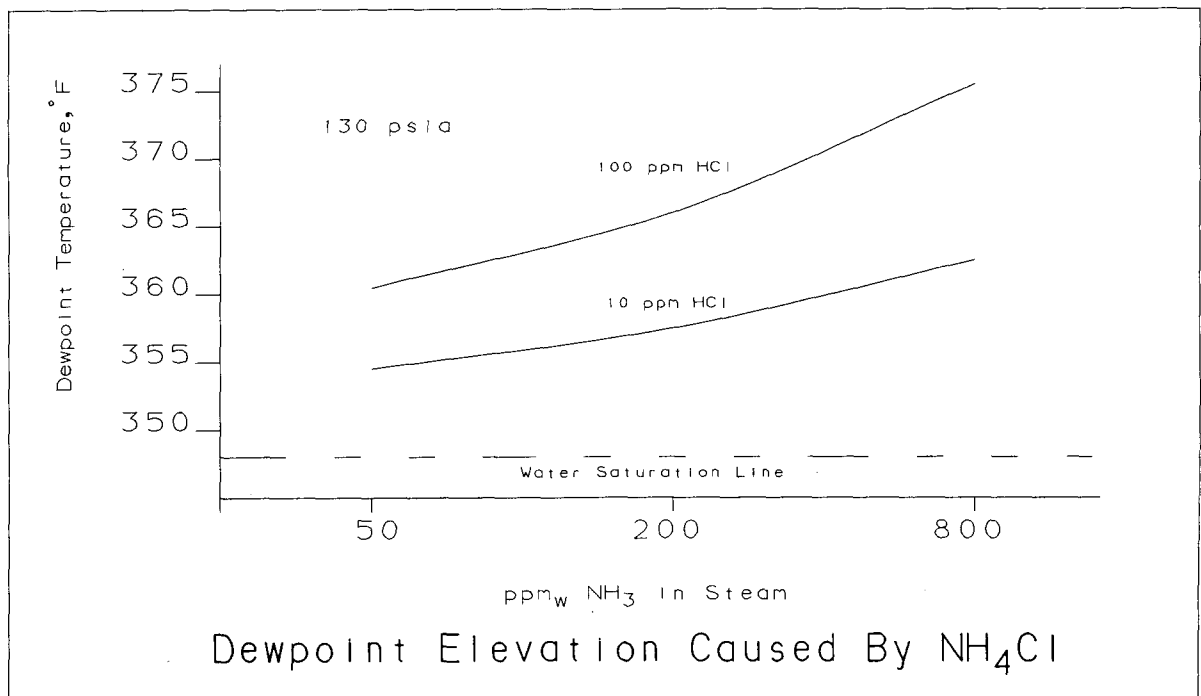

Dewpoint Elevation Caused By NH_4Cl

Diagram 3

interface shifts with changing production conditions. Corrosion in this zone is highly localized and can only be effectively eliminated through the use of high-alloy or lined mixing spools.

PROCESS CHEMISTRY

Concentrated solutions of ammonium chloride can deposit on the pipe walls of volatile chloride producing wells at the Geysers resulting in pH values of 3.0 to 3.8 units at 175 to 200°C. The excess of ammonia in Geysers steam is not effective in neutralizing HCl, since ammonia becomes a very weak base at high temperatures, and actually increases the acid dewpoint temperature and acid deposition rate. The basis of the current acid chloride corrosion mitigation process at The Geysers is steam scrubbing and neutralization through the injection of hotwell condensate and sodium hydroxide near the wellhead and subsequent water removal using steam/liquid separators.

Preliminary assessments indicated that the addition of only water to scrub and dilute the acid chloride from Geysers wells would result in unacceptably low pH values for carbon steel piping (pH 4 to 5.5 units at 175°C)[23]. It was obvious that neutralizing amines, commonly used in steam systems to control pH where trace carbonic acid is present, would be costly and ineffective due to the high acidity and relatively large quantities of chloride to neutralize. Chemical modeling has shown that sodium carbonate would be effective in neutralizing the acid chloride, but this chemical would be expensive and difficult to handle due to its availability only as a relatively dilute solution (15% by weight).

Sodium hydroxide was chosen due to its low cost, availability as a concentrated solution (25 - 50% by weight), and the fact that it reacts rapidly with CO_2 under steam line conditions, effectively forming a sodium carbonate solution[23,24], thus minimizing the possibility of free hydroxide entering the turbine and causing caustic embrittlement or cracking.

The hydration of CO_2 proceeds rapidly at Geysers steam-line pressures and temperatures in the presence of free hydroxide, according to the reactions:

$$CO_2 + OH^- \rightarrow HCO_3^-$$
(fast)

$$HCO_3^- + OH^- \rightarrow CO_3^= + H_2O$$
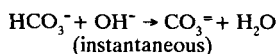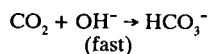(instantaneous)

Diagram 4 depicts the rate of reaction under typical conditions, indicating that excess hydroxide is rapidly converted to carbonate, while the equilibrium pH stabilizes in the alkaline region. The interaction of CO_2 in the corrosion mitigation process is critical in eliminating potential problems due to caustic corrosion and embrittlement, while CO_2 partial pressures are low enough to maintain alkaline scrubbing conditions.
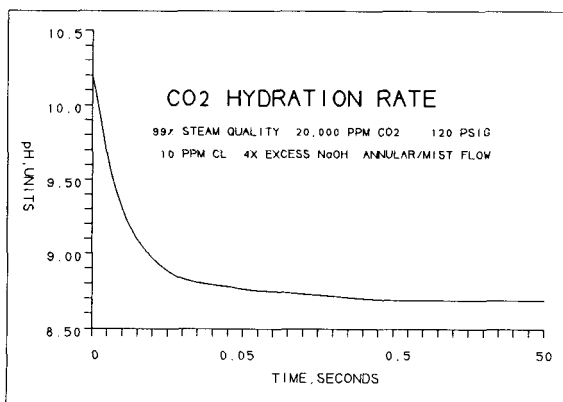

Diagram 4

Boric acid is another natural component of Geysers steam that is a significant pH buffer in the corrosion mitigation process, although unlike CO_2, boric acid does not benefit the process chemistry. The presence of boric acid requires excess caustic injection to maintain the scrub-water pH above 7.8 units due to the boric acid pka of about 9.0 at the process temperature. This effect is most obvious in lower chloride wells (<10 ppm$_w$) where boron to chloride ratios can be very high, requiring over 8 moles of NaOH per mole HCl to maintain the pH above 8.0 units.

The ideal pH range of the process water has been determined to be 8.0 to 8.5 units (at process temperature), based on extensive corrosion rate tests utilizing corrosimeter probes during system operation at varying caustic injection rates. As shown in Diagram 5, boric acid is the primary pH controlling species in this pH range under typical Geysers conditions. A NaOH/HCl mole ratio of over 8 to 1 would be required for steam containing 100 ppm boron to achieve a pH of 8.25 units under the conditions shown, and a NaOH/HCl ratio under 2 to 1 would be required if no boron was present. Hydrogen sulfide only affects the pH above 8.25 units and therefore is not a factor when maintaining the process at this pH value. Ammonia has no effect above 8.0 units, but is important in the low pH range. Under the conditions shown in Diagram 5, steam containing 50 ppm boron yields a process water pH of 6.5 units at a NaOH/HCl ratio of 1, however, this pH would drop to 4.8 units if ammonia was absent. Carbon dioxide is a major pH buffering component of Geysers steam, although in a typical concentration range of 2,000 to 20,000 ppm$_w$, the pH values shown in Diagram 5 differ by no more than 0.2 units at NaOH/HCl ratios above 2.

In order to validate the pH and electrolyte equilibria computer modeling used to study the corrosion mitigation process chemistry, direct comparisons are routinely made between model predicted chemistry and analytically measured values. The model incorporates the effects of HCl, NH_3, NaOH, H_3BO_3, H_2S and H_2CO_3 electrolyte equilibria in addition to vapor/liquid partitioning and CO_2 hydration kinetics.

Analytically determined values for the vapor and liquid phase species in the separators, including total water mass and enthalpy, are input to the model which computes high-temperature pH, electrolyte dissociations and vapor/liquid distributions. Comparison of the calculated concentrations for dissolved electrolytes such as H_2S and NH_3 to measured concentrations indicates that the model adequately describes the chemistry, since the distributions of these species are very sensitive to pH conditions. Table 1 summarizes the model validation data over a wide range of steam qualities and NaOH to chloride ratios from previously published data for the Aidlin project.

As expected, the high temperature pH values are consistently lower than the measured values at 20°C due to the increasing acidity of water and other weak electrolytes with temperature. This effect is most pronounced at pH values above 8 units, as hydrogen ions become very scarce.

The fact that the computed versus measured concentrations of volatile electrolytes in the separator water (Table 1) are in substantial agreement also demonstrates that the vapor/liquid chemistry was essentially in equilibrium for these tests. Although CO_2 absorption and hydration is the slowest of the vapor/liquid reactions, this species was also determined to be in equilibrium by varying the modeled reaction time from 2 seconds (actual) to 60 seconds. Complete CO_2 hydration occurs within about 0.5 seconds under the conditions studied. Evaluation of the vapor/liquid equilibrium for these gases provides an important tool in accessing the overall mass transfer efficiency of a corrosion mitigation scrubbing system. Scale deposition within corrosion mitigation systems can be a problem if the residual water fraction after injection is too low. Sodium borate is the least soluble product
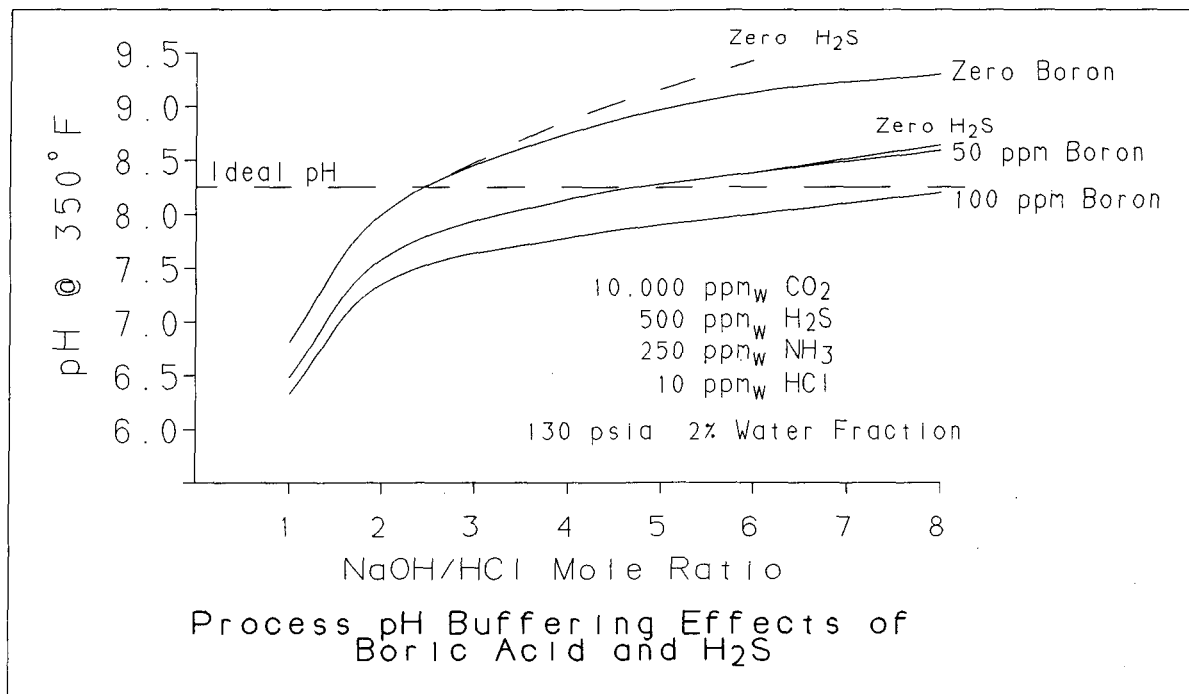
Diagram 5

Chart text:
- y-axis: pH @ 350°F — 9.5, 9.0, 8.5, 8.0, 7.5, 7.0, 6.5, 6.0
- x-axis: NaOH/HCl Mole Ratio — 1 2 3 4 5 6 7 8
- Zero H$_2$S
- Zero Boron
- Zero H$_2$S
- 50 ppm Boron
- 100 ppm Boron
- Ideal pH
- 10.000 ppm$_W$ CO$_2$
- 500 ppm$_W$ H$_2$S
- 250 ppm$_W$ NH$_3$
- 10 ppm$_W$ HCl
- 130 psia 2% Water Fraction

Process pH Buffering Effects of Boric Acid and H$_2$S

of the process, and has been known to deposit in separators and plug water drain lines when residual water fractions drop below 0.5%. Under most conditions at The Geysers, the solubility limit of sodium borate is not exceeded if water fractions are maintained in the 1-2% range. Iron sulfide is a common scale deposit for Group 3 wells that produce substantial quantities of dissolved iron which can plug rock-trap strainers and separator baffles as dissolved iron contacts the alkaline scrubbing solution. The use of untreated surface or ground water for injection results in calcium carbonate scaling of injection nozzles and mixing spools due to the calcium content of these waters, the high process temperature and high carbonate concentrations. Hotwell condensate is currently used exclusively as the source of injection water due to the low concentrations of dissolved minerals and oxygen.

MECHANICAL CONSIDERATIONS

The selection of water/caustic injection points for a Geysers well depends on the type of well (i.e., Group 1, 2, or 3) and the existing wellhead/piping configuration. For a Group 1 well that can be maintained sufficiently above the acid-dewpoint temperature at the wellhead, injection can be performed immediately downstream of the rock catcher, as shown in Diagram 6 (point A). Unless the injection spool is protected through the use of high alloy materials, corrosion induced by desuperheating near the alkaline wet region is highly possible

for Group 1 wells. For this reason, injection should not occur further upstream where repairs and well isolation may be more difficult.

Group 2 wells produced under near-saturated conditions are best protected by injection through a 3-inch wing valve (Point B) or at the wellhead tee (Point C). Increased corrosion induced upstream of injection is not a significant problem for these wells since dewpoint conditions already exist, making it important to protect as much of the wellhead as possible. Injection at these points will flood the rock catcher leg, which should be blown-down periodically to prevent build-up of excessive salt concentrations, but not automatically or continuously which would prematurely remove the scrubbing water.

Wells in the Group 3 category can be treated as Group 2 wells if the casing is protected with coated, high alloy or "sacrificial" liners. If downhole protection does not exist, these wells should be treated using downhole injection techniques. Tubing of adequate diameter for the water injection requirements can be lowered downhole through a 45° to 60° angle 3-inch wing valve and lubricator assembly, similar to downhole calcite scale inhibitor injection applications (point D)[25]. The injection depth will depend upon the amount of casing considered critical to protect and the mechanical integrity of the injection tubing string. A restrictor at the end of

Table 1. Computer Model Validation Data

Well	Steam Quality	NaOH/Cl Mole Ratio	Computed, ppm$_w$			Measured, ppm$_w$				
			pH[1]	H$_2$S	NH$_3$	pH[2]	H$_2$S	NH$_3$	Cl	B
AD40	98.2	1.2	7.29	57	105	7.30	60	116	2080	2150
AD40	98.1	1.9	8.02	205	99.3	8.10	187	103	2520	2620
AD10	98.1	5.8	8.09	92.2	41.0	8.20	103	41.0	201	1520
AD20	94.8	120	8.46	150	45.3	8.80	159	47.5	7.7	301

1. pH units at process temperature (175-200°C).
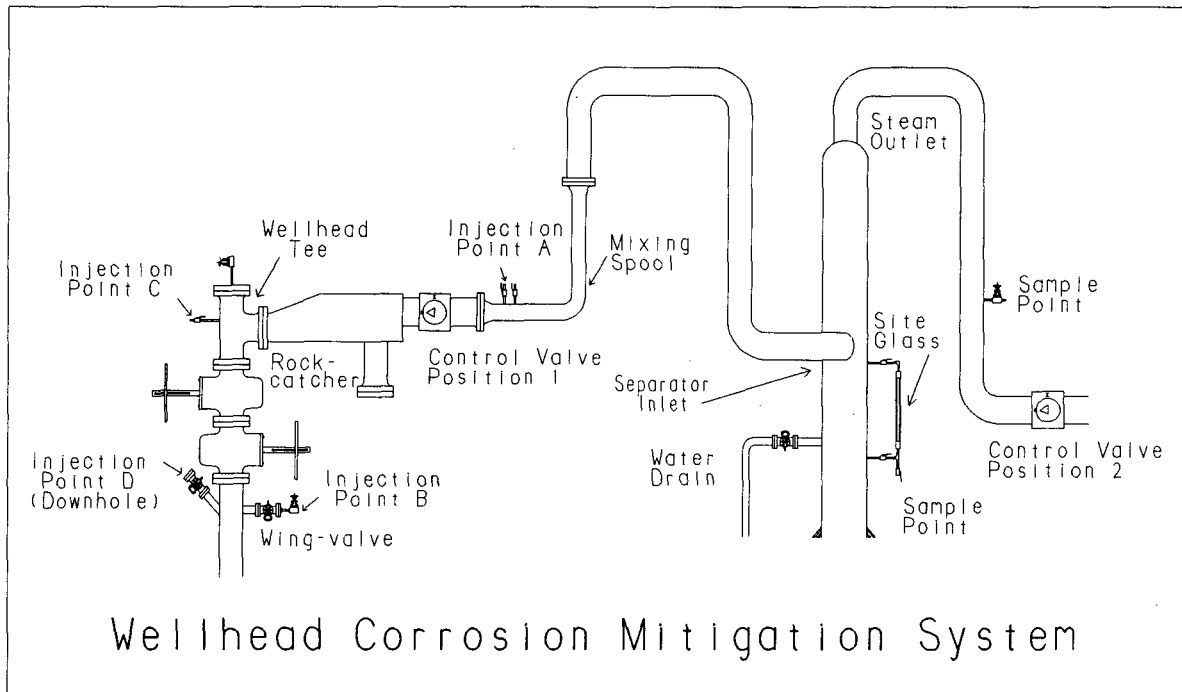2. pH units at 20°C.

Diagram 6

the tubing must be sized to maintain adequate backpressure and prevent boiling of the injection fluid given the injection water rate, wellhead pressure, and injection depth. Alloy tubing is recommended for this service due to the injection mixture composition and temperature.

At surface injection points, retractable injection probes should be utilized in conjunction with spray nozzles. This enables servicing of the nozzles during production and adjustment of the nozzle tip position in the flow stream. Nozzles should be sized for maximum pressure drop to increase the spray penetration into the steam flow. Multiple probes placed around the circumference of an injection spool and spaced 1 to 2 feet apart on the axis may also improve contacting. However, inspection of injection spools after service indicates that the spray patterns from nozzles degrade rapidly in the steam flow, leaving fan-shaped water marks expanding axially downstream from the nozzle tips.

Mixing spools located immediately downstream from the injection point provide most of the vapor/liquid contacting. These spools are simply smaller diameter piping sections without internal components. This section of pipe can be incorporated with the injection spool (point A) and/or extend up the vertical riser section of an expansion loop. Optimal mass transfer occurs under high velocity annular/mist flow regimes where the pipe behaves as a wetted-wall absorber. Extensive studies of H_2S mass transfer from steam into caustic solutions under similar conditions at The Geysers has shown that the highest efficiencies are obtained at steam velocities of 300-500 ft/sec[24]. The high velocity mixing sections can vary in length from 10 to 20 feet.

As shown in Diagram 6, steam/water separators are best located after an expansion loop to maximize vapor/liquid contacting time. The highest separation efficiencies are achieved with the vertical recycling separators common to The Geysers. Horizontal style separators are typically less efficient, but are much less costly to install into existing wellpad piping systems. Horizontal separators are more easily fouled by particulates and scale deposits which can degrade their performance dramatically. This can be a problem with Group 3

wells producing dissolved iron and particulate corrosion products which form deposits upon contact with the alkaline scrubbing solution.

The flow control valve for a well can be placed immediately after the rock catcher or downstream from the separator, as shown in Diagram 6 (Positions 1 and 2). If located in the latter position, steam scrubbing and separation pressures would be equivalent to wellhead pressure rather than line pressure. Under these conditions, less injection water is required to achieve the same steam moisture content for scrubbing. Given a 70 psig pressure drop across the control valve, about 20% less water would be required for a typical well. This factor can be important in certain areas of The Geysers where limited hotwell condensate is available for injection. Water separation upstream of the control valve also results in superheated steam entering the gathering system which can minimize condensation and corrosion rates.

The gathering system can also play an important role in steam purification. Entrained water from separators and condensate enriched in impurities can be effectively removed through multiple stages of drop-pots spaced throughout the gathering system. These drop-pots must have properly operating automatic drain valves to be of any use, however. In addition, manual dumping of the drop-pot contents periodically helps prevent the build-up of excessive salt concentrations and solids.

The final stage of steam purification before entry to the turbine occurs at the "desuperheating" system upstream of the plant inlet. Hotwell condensate is injected through multiple sets of spray nozzles into the main steam line upstream of a steam/water separator. The steam is desuperheated and brought to approximately 0.5 to 2% moisture content. Injection nozzles are often placed in the vertical riser to a separator which provides minimal contact time but reasonable chloride removal. Mass transfer efficiencies can be improved by injecting further upstream of the separator or through the use of a steam venturi mixing device[26]. A two-stage scrubbing process with two vertical separators in series was employed at the Aidlin project to maximize turbine steam purity. Vertical

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recycling separators are normally used at the plant inlets for high moisture removal efficiencies. Under optimum conditions, desuperheating systems at The Geysers can remove over 95% of the residual chloride from the main steam.

MONITORING TECHNIQUES

Chloride Survey Techniques

The identification of acid-chloride producing wells requires specialized sampling and analysis techniques. Steam field surveys to locate these wells are critical in that corrective action must be taken before costly well casing, pipeline and power plant damage or field accidents occur. Accurate wellhead temperature and pressure measurements during sampling and information regarding water production are required to initially classify a well in the Group 1, 2 or 3 category.

Most of the acid-chloride produced by Group 3 wells is in the liquid phase and significant amounts produced by Group 2 wells can be associated with concentrated liquid films and droplets, making representative sampling extremely difficult. A Group 3 well typically produces measurable quantities of liquid which can be collected from an in-line separator, if present. Measurements of chloride concentrations in the separator water and separator outlet steam in conjunction with the respective flowrates can be used to calculate total flow chloride concentrations for such wells.

Group 2 wells producing less than 100% steam quality should be sampled using isokinetic probe techniques as close to the wellhead as possible. The 3-inch wing valves below the wellhead master valves (Diagram 6) provide an ideal isokinetic probe sampling location. Through the use of an isokinetic sample nozzle that extracts steam at the same velocity as the bulk flow at several points across the pipe diameter, representative samples of vapor and liquid droplets can be collected, as depicted in Diagram 7. Major flow disturbances such as bends in piping should be limited to 8 pipe diameters upstream and 2 pipe diameters downstream of the sample point. Sample nozzles are sized for the steam velocity expected and isokinetic sample rates are based on the formula:

$R = (An/Ap) (7.57) Qs$
R = Sample rate, g/min steam condensate
An = Cross sectional area of nozzle face
Ap = Cross-sectional area of pipe
Qs = Steam flowrate, lbs/hr

Adjustments can be made for reduced velocities near pipe walls due to friction factors in turbulent flow conditions[27].

Group 1 and Group 2 wells above the acid dewpoint at the wellhead can be accurately sampled with a non-isokinetic probe technique since all the acid chloride is in the vapor phase. Sampling should be performed upstream of the rock catcher which may contain liquid, either at the wellhead tee or 3-inch wing valve, as shown in Diagram 6. Probe tip geometry and sample rate are not important when sampling gaseous species, although a probe is critical in eliminating condensation loss which occurs when sampling directly from large side-wall mounted valves. Sampling directly from the 3-inch wellhead wing valve of a superheated well can result in chloride measurements less than 50% of actual total flow concentrations. However, if a 1-inch bleed flow is maintained through the wing valve for an hour or more, chloride concentrations typically approach the total flow value for Group 1 wells.

Steam samples collected by the various methods are condensed directly in a stainless steel tubing condenser immersed in an ice bath or circulating cooling fluid. Condensate samples are often analyzed for sodium and other alkali and alkaline earth metals to verify the chloride measured is volatile chloride and not associated with water entries to the wellbore. Measurements of condensate pH are of little value at The Geysers in interpreting the chloride chemistry since the excess ammonia neutralizes HCl at ambient temperature and the pH is controlled primarily by CO_2 and H_2S partial pressures. This is demonstrated by the fact that a typical wellhead steam pH at The Geysers is 5.5 units after condensation at atmospheric pressure, and over 9.0 units when condensed under vacuum in a power plant, regardless of chloride content.

Qualitative chloride surveys can be conducted by sampling liquid accumulated in production well separators or drop-pots
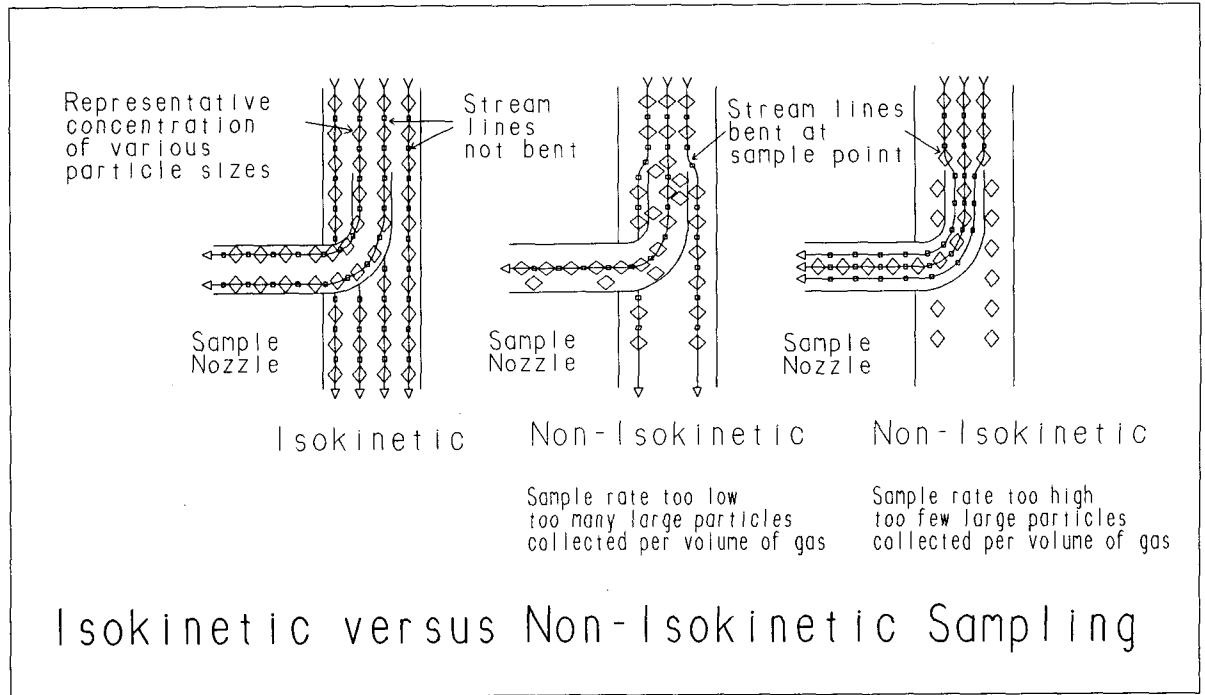

Diagram 7

that have been blown dry 6-24 hours before testing. Chloride concentrations over 10 ppm usually indicate a significant acid chloride producing well if sodium, potassium and calcium are absent. The analysis of these liquids for dissolved iron and manganese provides insight into active corrosion processes. Dissolved manganese to iron ratios are often in the same range as reported for carbon steel casing and pipe (0.5 - 1.5%). Samples for these metals must be passed through an in-line filter upstream of the condenser and collected in nitric acid to eliminate solids and prevent precipitation before analysis. Measurements of pH must be performed in the field since the oxidation of dissolved iron in samples exposed to air can drastically lower the pH. Ammonia measurements are useful in estimating the high temperature pH of these liquids due to the inverse relationship of water phase ammonia concentration and pH in vapor/liquid systems. Boron concentrations can be used to ascertain the extent of vapor/liquid equilibrium based on known boric acid distribution coefficients. The above assays are also important in characterizing Group 3 wells where corrosion processes are dominated by the water phase chemistry.

Corrosion Mitigation System Monitoring

The initial start-up of a corrosion mitigation station requires sampling and analysis of the injection water/caustic mixture, separator water and separator outlet steam in order to adjust and optimize the process chemistry. Regular, less extensive monitoring is required to maintain the chemical parameters in the proper range and to verify efficient equipment operation. Process flowrates, temperature and pressure data must be obtained concurrently during sampling to perform a complete mass and heat balance evaluation. Many of these measurements must be performed directly in the field or based on chemical mass balances due to the unreliability of distributed control system (DCS) instrumentation at The Geysers.

Injection fluid samples are collected downstream of the caustic pump, before the injection nozzles, by slowly filling a 1 liter plastic bottle using a needle valve for flow regulation. The sample should be integrated over a 5 minute interval in order to average concentration surges caused by pulse-type metering pumps. This injection mixture is analyzed for sodium to verify the water injection rate based on caustic dilution and for chloride which should be accounted for as a contaminant of the sodium hydroxide solution. The injection mixture temperature must be measured for heat balance calculations. Before or after sampling the injection fluid, precise caustic injection rates are measured using a calibrated volumetric draw-down tube on the suction of the caustic pump. The caustic feed solution is also sampled to verify the exact concentration by density or sodium measurement if not previously determined.

Separator water samples are collected from the separator drain piping or liquid-level sight glass connection. Samples for iron and manganese analysis are usually collected unfiltered and treated with nitric acid for preservation. Dissolved iron and manganese produced by a well through corrosion processes precipitates as sulfides upon contact with the alkaline scrubbing solution injected into the well, making it necessary to perform a total metals analysis to account for these species. Untreated samples are collected for Cl, Na, B and pH analysis which provides the primary chemical data needed for process evaluation and adjustment.

Samples for total inorganic carbon (CO_2) and NH_3 are collected in gas-tight glass vials and H_2S samples are collected in a cadmium chloride preservative solution. These species are important when modeling the high temperature pH and extent of gas/liquid equilibrium.

The volumetric flowrate of water into the separator is measured by timing the rate of water level rise observed at the sight glass after the separator discharge has been isolated. The separation pressure can be assumed to be equivalent to the outlet steam line pressure and used to estimate the separator temperature.

Separator outlet steam samples must be collected using an isokinetic probe, usually at the vertical down-leg of the steam piping (Diagram 6). Steam condensate samples are collected at four to five points across the pipe diameter to obtain an accurate moisture profile. In cases of substantial liquid entrainment ($>0.5\%$ outlet moisture), up to 10 points may be required. Samples are collected for sodium and chloride analysis to determine the outlet steam quality, liquid entrained chloride concentrations and residual volatile chloride concentrations for separator efficiency and mass transfer evaluations. Steam samples may also be collected for boron, silica and iron analyses to determine levels of these impurities and for gas analyses to perform pH and vapor/liquid equilibrium modeling. Temperature measurement profiles can be performed using a probe at the same sample port to evaluate thermal equilibrium conditions.

Samples for direct total flow chloride determinations can be collected at the wellhead in cases where the water/caustic is injected downstream of the rock catcher, provided the temperature is above the acid dewpoint. Wellhead superheat measurements can also be determined under these conditions as a verification of heat/mass balance calculated enthalpies. These methods would be the same as described previously for chloride survey techniques.

Gathering system drop-pots downstream from a corrosion mitigation system separator are often monitored to qualitatively evaluate liquid entrained and vaporous carry-over. Ratios of sodium to chloride provide an indication of residual vapor phase chloride if these ratios decline at increasing distances from a well separator. In some cases, the total salt concentration in drop-pots increase further from the well separator when pipeline superheat levels are high and drop-pots are not draining properly. Other sampling and interpretive techniques for drop-pot fluids would be the same as described for chloride survey testing.

Analytical Methodologies

Trace level chloride analysis of geothermal steam condensate is plagued by interferences from dissolved gases such as hydrogen sulfide, ammonia and carbon dioxide. Complete removal of H_2S is required before direct potentiometric ion-specific electrode measurements can be performed due to the positive response of sulfide ions. These measurements are usually only valid to about 1 ppm Cl⁻ unless the sample is preconcentrated. Precipitation titrations using silver or lead also require elimination of sulfide and most of the ammonia which complexes the metal ions and obscures the end-point. These titrations are accurate to about 10 ppm Cl⁻ if the samples are pretreated properly. Conventional water-analysis ion-chromatography methods are overwhelmed by high concentrations of sulfide, ammonium and bicarbonate ions. These species overload separation columns and conductivity detectors and make it impossible to concentrate samples by ion-exchange methods. The current method used to achieve high accuracy, low-level detection of chloride in this matrix is by high resolution gradient ion chromatography in conjunction with conventional chemical suppression and detection by digital conductivity measurement (Dionex 4500i system). This method provides detection limits to 0.010 ppm_w with minimal interference problems.

Trace level sodium analyses in steam condensate are performed by flame atomic absorption spectroscopy with detection limits down to 0.002 ppm_w. The main difficulty in this procedure is preventing sodium contamination. Iron concentrations in steam condensate are determined by graphite furnace atomic absorption to detection limits of 0.005 ppm_w. Boron analyses are performed by inductively coupled emission spectroscopy (ICP) or azomethine colorimetry. Ammonia is

routinely determined by a flow injection analysis procedure involving gas diffusion across a Teflon membrane with conductivity detection, allowing direct analysis without pretreatment to remove sulfide. Determinations of pH are performed in the field using a Ross pH electrode to minimize sulfide interferences and a temperature compensation probe.

Mass and Heat Balance Calculations

Values for wellhead enthalpy, steam and water fractions in the scrubbing process, caustic and chloride mass flow rates and residual separator steam impurities are necessary for the optimization and routine operation of the corrosion mitigation process. Many of these parameters cannot be measured directly, and due to problems in instrumentation and variations in system designs, few are consistently available. Table 2 summarizes the process parameters that are measured or calculated and the relevant mass and heat balance equations used by a computer program configured for this application. Since many parameters can be obtained through more than one type of measurement or calculation, this computer mathematical modeling program is used with iterative and back-solving capabilities to achieve complete mass and heat balances with various types of input data. Table 2 includes typical input data and calculated results for a corrosion mitigation system mass and heat balance.

Water injection rates are often calculated or at least verified based on the caustic pump rate and sodium concentration in the injection water. The water mass flowrate after injection (residual water) is normally based on the change in sodium concentration due to the flashing of injection water or condensation of steam. Wellhead enthalpy can then be calculated through heat and mass balance equations using the injection water temperature, mass flowrate of water before and after injection, the separator pressure and steam outlet flowrate. This information is necessary to determine the separator inlet moisture fraction and to calculate the required injection water rate when adjusting this moisture fraction.

The residual water flowrate is also used to calculate the total mass flow of chloride in conjunction with the separator water chloride concentration. The separator fill rate is measured when possible and compared with the residual water flowrate based on the sodium balance calculations. The difference between these two rates can be used to estimate liquid entrainment in the separator outlet steam in cases of excessive separator water carryover. Total flow chloride mass flowrates based on the residual water flowrate and chloride concentration are unaffected by separator efficiency, but are normally adjusted for mass transfer efficiency.

Isokinetic sampling of the separator outlet steam is performed to obtain concentrations of sodium and chloride used to determine entrained liquid and residual volatile chloride levels, which are the basis of separator efficiency and mass transfer efficiency calculations. Sodium measured in the separator steam is assumed to be present entirely in entrained droplets of separator water, which has a directly measurable sodium concentration. Based on the simple mass balance calculation (Table 2), the moisture content of the separator steam can be determined. The ratio of sodium to chloride concentration in these droplets is assumed to be equivalent to the sodium/chloride ratio in the separator water. Liquid entrained chloride concentrations in the separator steam are then based on the steam phase sodium concentration and sodium to chloride ratio. The difference between the total measured chloride concentration in the separator steam and the calculated liquid-entrained chloride concentration is the result of residual volatile chloride not absorbed in the scrubbing process. A typical separator outlet steam sodium and chloride concentration profile is shown in Diagram 8. Moisture concentrations are normally higher near the pipe walls as indicated by the sodium levels, and decline toward the pipe center where much of the chloride may still be in the volatile form.

A primary use of the completed heat and mass balance for a corrosion mitigation system is to simultaneously optimize the separator efficiency and mass transfer efficiency. The steam quality, in terms of moisture content, at a separator outlet improves non-linearly as inlet water fractions are reduced. However, reducing the inlet water fraction raises the dissolved sodium and chloride concentrations in direct proportion which can result in greater mass flowrates of liquid entrained impurities even though outlet moisture levels are lower. Mass
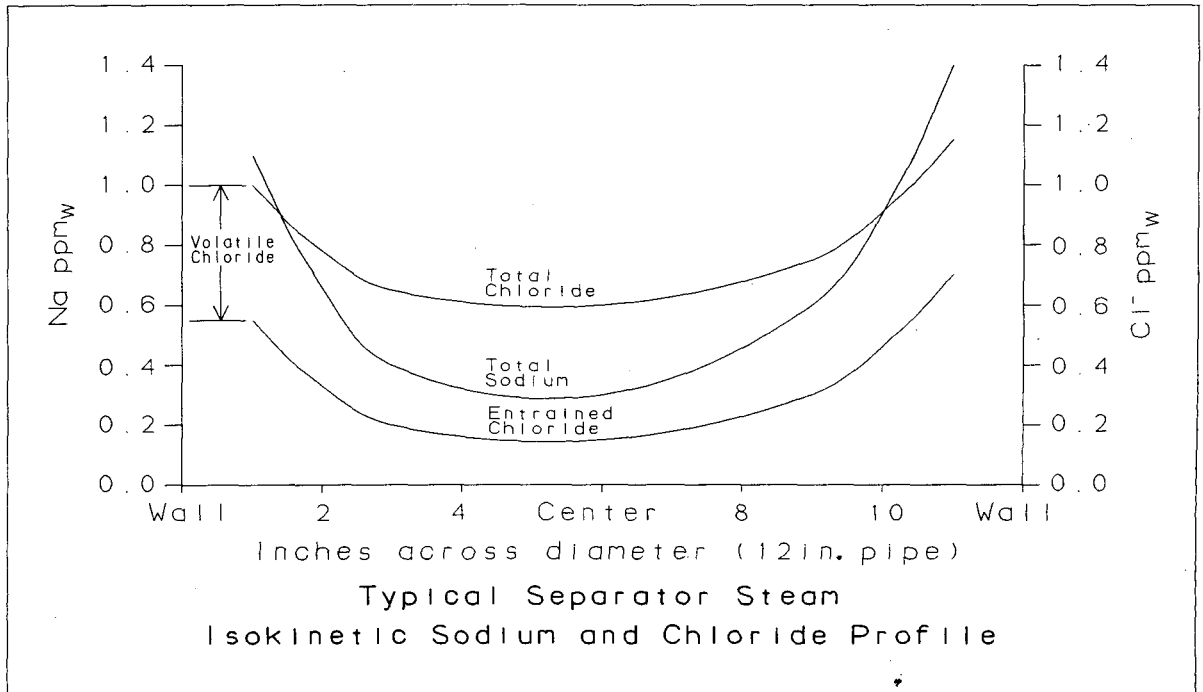

Typical Separator Steam
Isokinetic Sodium and Chloride Profile

Diagram 8

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Table 2
Variables

Input	Name	Output	Unit	Comments
146	P		psig	Separation pressure
	T	363.34859	F	Separation temperature
	HF	335.89539	BTU/lb	Water enthalpy
	HG	1195.95	BTU/lb	Sat. steam enthalpy
85	TW		F	Injection water temperature
	FW	3419.0599	lb/hr	Injection water mass rate
	FGI	71406.182	lb/hr	Steam mass rate initial
	HGI	1227.4841	BTU/lb	Steam enthalpy initial
72900	FGF		lb/hr	Steam mass rate final
	FFF	1925.2414	lb/hr	Water mass rate final
13.5	BARO		psia	Barometric pressure
	GFRAC	97.427016		Steam fraction
	FFRAC	2.5729839		Water fraction
2.91	DR		in/min	NaOH drawdown rate
	NGPH	1.5008587	gph	NaOH injection volumetric rate
	NMR	4.9888543	lb/hr	NaOH mass rate
	NACONC	1489.9904	ppmw	Na conc. separator water
839	NAW		ppmw	Na conc. injection water
	CLR	1.2379302	lb/hr	Chloride mass rate
643	CLCONC		ppmw	Cl conc. separator water
	NACL	3.5262468		Na/Cl mole ratio
	CLTOT	17.336458	ppmw	Cl conc. in total flow
.35	NASS		ppmw	NA conc. in separator steam
.29	CLSS		ppmw	Cl conc. in separator steam
	ENTCL	.01101091	lb/hr	Entrained Cl in separator steam
	VOLCL	.01013009	lb/hr	Volatile Cl in separator steam
	SQUAL	99.97651	%	Separator steam quality
	MTE	99.181691	%	Mass transfer efficiency
	TRE	98.29223	%	Total Cl removal efficiency

Equations

Equation	Comments
PA=TVP(T)	Steam saturation pressure function
T=PVT(PA)	Steam saturation temperature function
HF=PVH_F(PA)	Water enthalpy function
HG=PVH_FG(PA)	Steam enthalpy function
HFG=PVH_G(PA)	Latent heat function
VF=PVV_F(PA)	Steam volume function
PA+P+BARO	Absolute pressure
PW=TVP(TW)	Injection water saturation pressure
TW=PVT(PW)	Injection water saturation temperature
VFW=PVV_F(PW)	Injection water volume function
HFW=PVH_F(PW)	Injection water enthalpy function
FGF=((HGI*FHI)+(HFW*FW)-(FGI+FW)*HF)/(HG-HF)	Enthalpy/mass balance
FFF=(FGI+FW)-FGF	Mass balance
GFRAC=FGF/(FGF+FFF)*100	Steam fraction
FFRAC=(100-GFRAC)	Water fraction
GPMSEP=FFF*VF*7.48/60	Separator water volumetric flow
NAOHR=DR*32.54	NaOH volumetric rate
NGPH=NAOHR*.01585	NaOH volumetric rate
NMR=NGPH*3.324	NaOH mass rate
NACONC=(NMR/FFF)*10^6*23/40	Na mass balance separator water
NAW=(NMR/FW)*10^6*23/40	Na mass balance injection water
CLR=(CLCONC*FFF)/10^6	Total mass flow Cl
NACL+(NMR/CLR)*35/40	Na/Cl mole ratio
CLTOT=(CLR/FGI)*10^6	Total flow Cl concentration
ENTCL=(NASS/NACL)*35/23*FGF/10^6	Entrained Cl separator steam
VOLCL=(CLSS*FGF/10^6)-ENTCL	Volatile Cl separator steam
SQUAL=(1-NASS/NACONC)*100	Separator steam quality
MTE=(1-VOLCL/CLR)*100	Mass transfer efficiency
TRE=(1-(ENTCL+VOLCL)/CLR)*100	Total removal efficiency

transfer of volatile chloride to the liquid phase also degrades with decreasing inlet water fractions, generating higher concentrations of vapor phase chloride in the separator steam. By properly evaluating this process and adjusting the water injection rate, both liquid and vapor-phase impurities exiting the separator can be minimized. Diagram 9 displays these process relationships as a function of separator inlet water fraction for a typical corrosion mitigation system. As shown, both entrained sodium chloride and residual volatile chloride can usually be minimized at separator inlet moisture levels of about 2%. These curves will shift depending upon the specific separator configuration used and inlet flowrates, making it necessary to test each system for precise optimization.

Corrosion Rate Measurements

The process chemistry of the corrosion mitigation system has been largely optimized through the use of electrical resistance corrosion probes. These instruments provide a measurement of corrosion rate as the cross-sectional area of an exposed steel surface is reduced by corrosion, resulting in an electrical resistivity change across the element relative to a shielded reference element at the same temperature. Incremental changes in electrical resistivity are directly proportional to the rate of metal loss, allowing corrosion rate measurements over fairly short intervals (hours to days). Continuous data collection via transmission directly to computers can be used to provide nearly real-time trends in corrosion rates. Corrosion probes placed in the two-phase region of a corrosion mitigation system have enabled the optimization of process water pH and salt content by monitoring relative changes in corrosion rates as water and caustic injection rates are adjusted. Corrosion probes are also placed downstream of separators to monitor the effects of residual volatile and entrained chloride on the gathering system and upstream of injection when possible to evaluate acid dewpoint corrosion.

Both cylindrical "finger" probes and flat flush mount probes have been used successfully at The Geysers. The cylindrical probes are extremely durable due to their welded construction, but flush-mount probes probably generate more realistic corrosion data for pipewalls under dewpoint and two-phase flow conditions. High temperature probes must be specified, and in the case of the flush mount probes, special high temperature epoxy is required in construction. The primary limitation in these devices is that general and pitting corrosion cannot be differentiated, rendering the results generated in terms of mils/year metal loss only qualitative under most conditions at The Geysers.

Ultrasonic thickness testing is routinely performed as a direct measurement of corrosion damage to piping systems. Ultrasonic thickness instruments measure the elapsed time required for sound waves to pass through and reflect back from a pipe wall. Calibration is performed using specimens of the material to be tested in a range of known thicknesses. Corrections for changes in sound velocity through the material as a function of temperature are made. Also, high-temperature probes must be used for steam piping measurements. This testing is critical to determine if piping can be safely kept in service and to locate spots of localized corrosion damage requiring repair. Measurements are made over a grid pattern across areas suspected to be damaged or known to be prone to localized corrosion. Regular monitoring of the same locations can provide a direct indication of corrosion rates. The limitation in this method is also the fact that most corrosion due to acid chloride is highly localized, making it difficult to pinpoint damage over large areas of pipe.

CONCLUSIONS

Volatile chloride produced in superheated steam from certain areas at The Geysers can deposit in piping at temperatures well above the steam saturation temperature through the formation of concentrated ammonium chloride solutions, a process known as acid dewpoint corrosion. Wells producing acid-chloride at The Geysers can be classified into three general groups based on acid dewpoint phenomenon: high superheat, low superheat or saturated and low steam quality wells. These categories represent distinctly different corrosion processes and require specialized treatment to effectively control corrosion. The pH of acid-chloride liquids in steam lines can be as low as 3.0 units, even with excess ammonia present, which causes rapid localized corrosion of carbon steel through the destabilization of protective magnetite films and
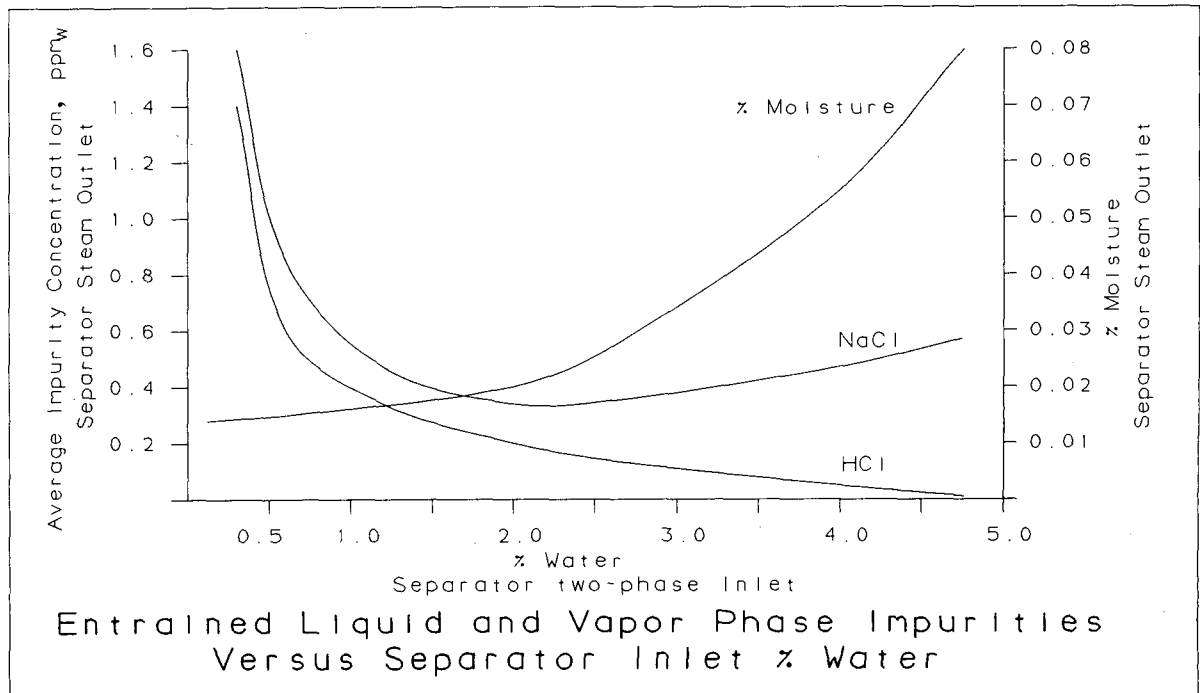

Entrained Liquid and Vapor Phase Impurities Versus Separator Inlet % Water

Diagram 9

hydrogen ion reduction. This corrosion process has caused extensive damage to well casing, pipelines and possibly steam turbines at The Geysers. However, corrosion can be mitigated by the injection of water and caustic near the wellhead of acid-chloride-producing wells, or downhole, with subsequent liquid removal using steam/water separators.

Process parameters have been defined to minimize corrosion rates and residual steam-phase impurities, resulting in corrosion rates of less than 10 mil/yr and turbine steam purities well below 50 ppb chloride. Carbon dioxide in Geysers steam benefits the process by neutralizing excess hydroxide and buffering the pH in an optimum range, while boric acid hinders the process by increasing caustic requirements and forming sodium borate deposits. Precise scrubbing process water fractions, properly designed injection hardware and state-of-the-art vapor/liquid separation equipment are critical to the overall efficiency. The development of steam sampling and analysis methodologies for trace impurities, refinement of corrosimeter and ultrasonic corrosion testing, and use of chemical modeling programs has enabled the optimization of the corrosion mitigation process. At least 1.5 million lbs/hr of produced steam at The Geysers is currently treated by this process with minimal operational costs.

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