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OPERATIONAL RESULTS OF A DRY-STEAM RESOURCE CHLORIDE CORROSION MITIGATION SYSTEM

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ABSTRACT

The Aidlin geothermal power plant, located in the West Geysers steam field, began commercial operation in June of 1989. Unique to this plant is a comprehensive corrosion mitigation/steam scrubbing system that has been in service since inception. This system was designed by Mission Power Engineering Company for Geothermal Energy Partners, Ltd., to prevent acidic chloride-induced corrosion of the gathering system and to protect the turbine from pitting corrosion, stress corrosion cracking and erosion related to the presence of chloride in the steam. To date, no failures of steam piping have occurred and ultrasonic testing (UT) has shown no significant pipe wall losses downstream of the injection points, in spite of the relatively high initial chloride concentrations in the steam. A range of chemical process conditions have been defined to effectively remove chloride from the steam, while maintaining the liquid pH and salinity at levels necessary to minimize corrosion rates and to prevent the deposition of scales. In addition, a two-stage steam scrubbing system at the plant inlet was optimized to maintain the steam purity at least 5 to 20 times higher than specified by the turbine manufacturer. In March of 1990, both units were brought off-line for inspection and non-destructive testing of the turbines and ancillary equipment. This inspection revealed only minor scale deposits and no apparent corrosion damage in the turbines. This system, effectively operated, is projected to extend turbine and piping life to expectancies equal to or greater than those encountered in geothermal areas producing little or no volatile chloride.

INTRODUCTION

The Aidlin Geothermal Project, owned by Geothermal Energy Partners, Ltd., consists of two 10 megawatt (net) turbine/generator units and four production wells, located in the West Geysers steam field approximately 10 miles east of Cloverdale, California. Mission Power Engineering Company of Irvine, California, developed the project, provided construction financing, engineered and constructed the plant, retaining 50% ownership of the project through its wholly owned subsidiary, Western Geothermal Company. Both the plant and steam field are operated and maintained by Calpine Corporation of San Jose, California, under contract to the owners. Met Life Capital Corporation, and Calpine, purchased the remaining 50% of the project from Mission Power Engineering Company.

The two units began operation in June of 1989, and to date have operated with a capacity factor of better than 92%. The turbines at the Aidlin Project are single-flow non-extracting, condensing units with 13 stages. The turbine inlet pressure is typically 100 psia at 335°F with a turbine steam rate of approximately 15.75 lbs. steam per gross KW. Each turbine/generator set has a separate surface condenser and 2-stage steam jet gas removal system. The two units share a common counterflow, film fill, cooling tower and circulating water system. The plant was designed to be flexible, capable of handling a wide range of resource conditions such as steam pressures, noncondensible gas levels and chloride levels.

Steam is supplied from two well pads through a total of 1.5 miles of gathering system piping. Production rates from each well range from 60 KPH to 180 KPH with up to 80°F of superheat at the wellheads.

Volatile chloride-bearing steam was expected from the Aidlin wells due to their location with respect to other steam fields with chloride corrosion problems (Northwest and Southwest Geysers), their high noncondensible gas content and superheat which typically correlates with the presence of chloride[1], and preliminary chemical analyses of the produced fluids during drilling and flow testing. However, the concentration ranges of chloride in the steam under production conditions was unknown prior to construction of the power plant and gathering system.

Acidic chloride condensate formed in the well casings and steam lines of certain fields in The Geysers has caused corrosion-induced failures of these components, resulting in frequent outages and curtailments of power plants and the permanent shut-in of some wells. The corrosion products exfoliated from the wellbores and gathering systems in these fields 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 has resulted in perforations of steam piping, the freezing of stop valves and turbine damage.

Rather than follow a "wait and see" approach to the potential acid chloride problem at the Aidlin project and risk facing the severe impacts encountered by others, Mission Power Engineering decided to install a complete steam treatment system at the outset, utilizing caustic/water injection and steam washing as part of an overall corrosion mitigation system.

This paper presents the results of the first nine months of operation of the Aidlin corrosion mitigation system.

Chemical process parameters have been defined that will be of use at other geothermal projects requiring mitigation of acid chloride corrosion. Data on the effectiveness of related hardware and the impacts of the process on the gathering system and turbines are discussed. Initially, a review of the volatile chloride phenomenon, acid chloride corrosion and the design basis of the corrosion mitigation system is presented.

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, 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 (semi-solid) 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 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 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 318°C to 347°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.

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 Induced Corrosion

Severe corrosion problems in geothermal power systems related to volatile acid-chloride species have been reported[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 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 (including Aidlin). 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.

## Corrosion Mitigation System Design Basis

The Aidlin corrosion mitigation system design was based primarily on contacting the steam with water (hotwell condensate) and sodium hydroxide to absorb the vapor phase chloride while maintaining a slightly alkaline liquid phase. Separators and steam washing stages downstream of chemical injection were included in the design for removal of the process water and purification of the steam. Chemical modeling of a range of conditions possible for the Aidlin gathering system had shown that condensate films on pipe walls could generate chloride concentrations well over 10,000 ppm_w and pH values under 3.0 units at 175°C[21]. These conditions would be extremely corrosive to carbon steel by destabilizing protective magnetite scales, resulting in the oxidation of iron by

hydrogen ions, a process enhanced by chloride and ammonia complexation of the corrosion products. The presence of excess ammonia prevents the pH of these condensate films from dropping to less than 1.0 unit, but is unable to effectively neutralize the acidity at the steam line temperatures (175 - 200°C), since ammonia becomes a very weak base at high temperatures. In fact, there is some evidence to suggest that ammonia will increase corrosion rates under superheated conditions by depositing saturated ammonium chloride on pipe walls, if ammonium chloride solubilities in steam are exceeded[8].

Addition of only water to scrub and dilute the chloride would still result in unacceptably low pH values for carbon steel piping (pH 4 to 5.5 units at 175°C)[21]. 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 had 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[21,22], thus minimizing the possibility of free hydroxide entering the turbine and causing caustic embrittlement/cracking.

The chemical injection and mixing spools used at the Aidlin Project were designed to provide effective mass transfer of vapor phase species from steam to liquid at high velocities with minimal contact time. The configuration of vertical separators and gathering system liquid drop-out pots was designed to maximize the removal of steam impurities. The engineering and construction details of the Aidlin corrosion mitigation system was previously discussed by Bell[23]. A diagram showing the basic layout of the corrosion mitigation system in relation to the wells and plant is given in Figure 1.
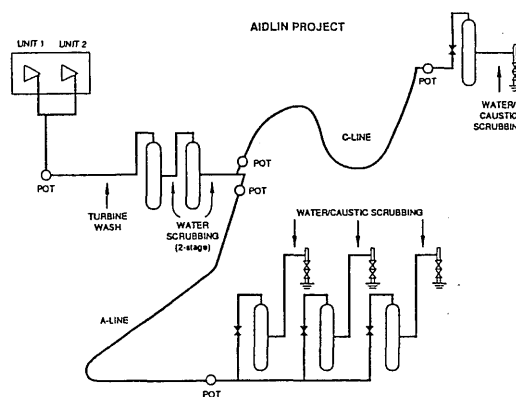
NOTE: Steam is saturated from wellhead injection point to control valve downstream of separator, then superheated 10-15°F to first scrubbing stage at plant, saturated again from first scrubbing stage to turbines. Only drop-pots routinely sampled are shown.

FIGURE 1

Aidlin Corrosion Mitigation System

CHEMICAL PROCESS ANALYSIS

Initial Start-up

The wells produced water initially under throttled conditions while providing steam to the first 10 MW unit, making it unnecessary to inject water since the chloride was already effectively scrubbed from the vapor phase. During the initial start-up of the plant, therefore, no water or caustic injection was performed. All vertical separators and steam-line drop-pots were fully operational, however, to remove water from the steam. Wells AD10 and AD20 were produced initially during start-up of the first unit; wells AD30 and AD40 were brought into service for full load operation of both units. Fictitious well names have been used to maintain the proprietary nature of the resource data.

While under high wellhead pressure and saturated conditions, the concentration of chloride in the separator water of well AD10 was 90 ppm_w with an excess of ammonium and no significant quantity of dissolved metals. Within 5 days of production, the separator water contained 800 ppm_w chloride with excess ammonium and 8 ppm_w dissolved iron. The increase in chloride concentration was largely due to decreasing water production rates which apparently also resulted in significant levels of vapor phase chloride. During this period, the concentration of chloride in the drop-pot downstream of the separator increased from 25 to 87 ppm_w, while the concentration in the last drop-pot before the turbine increased from 1.1 ppm_w to 100 ppm_w chloride. Levels of chloride in the plant main steam were initially undetected, but reached a maximum of 2.1 ppm_w.

With the initiation of water scrubbing at each well, the chloride in the main steam dropped below 1.0 ppm_w and chloride in the last drop-pot before the turbine was reduced to 22 ppm_w. Corrosion rates for AD10 measured with electrical resistance (ER) corrosimeter probes during the period of water injection were 31 mils/yr upstream of injection, 18.1 mils/yr downstream of the injection (before water removal) and 18.6 mils/yr downstream of the separator. The corrosion rate initially measured at the plant inlet was 4.9 mils/yr. The maximum concentration of chloride in the total flow from AD10 during this period was less than 5 ppm_w, with approximately 20°F superheat at the wellhead. The total flow chloride concentrations gradually increased for each well with increasing wellhead enthalpy.

Optimization of Fluid Chemistry

Caustic injection was initiated after the preliminary water injection period during plant start-up. The caustic was fed into the suction of the water pumps, delivering the same dilute caustic solution to each well for operational simplicity. The water injection rates were individually adjusted to maintain steam qualities between 96 and 99.6%, while the caustic feed rate was set to achieve a separator water pH range of 7.5 to 8.5 units (20°C). Given the wide range of chloride production rates among the wells, this resulted in NaOH to chloride mole ratios between 2 to 1 and 50 to 1. The amount of overfeed to low-chloride wells was insignificant in cost, with less than $35.00/day expended on total caustic usage. Also, the excess NaOH had no significant chemical impacts since it

was immediately neutralized by CO_2 which prevented the pH from rising above 8.8 units (20°C). Care was taken to insure that sufficient water was present to prevent salt deposition as the wellhead enthalpies increased. The total dissolved solids of the separator water did not exceed 20,000 ppm_w (including borate) for any well under normal operating conditions.

Corrosimeter testing was focused on well AD10 during initial caustic injection since it produced 10 to 20 times more chloride than the other wells in service. Corrosion rates were measured upstream of injection, downstream of injection (before water removal) downstream of the separator, and at the plant inlet. The acid chloride scrubbing and neutralization process was optimized by correlating the corrosion rate measurements with the separator water pH and steam quality after injection. Caustic and water injection rates were adjusted step-wise to minimize the corrosion rates measured over steady-state operation intervals of 5 to 10 days. Efforts were made to reduce caustic usage while maintaining the steam quality in a safe range that would not exceed the separator capacity or result in complete flashing and salt deposition. Gross separator capacities were determined by monitoring relative concentration changes of sodium and chloride in drop-pot liquids downstream of the separators. Table 1 summarizes the results of this optimization procedure.

As shown in Table 1, separator water pH values of 8.1 to 8.5 units were required to reduce corrosion rates to approximately 1 mil/yr or less throughout the system. Steam qualities of 98.2 to 98.4% proved satisfactory in maintaining low corrosion rates without overloading the separator or risking complete dry-out of the caustic solutions. Separator capacities were exceeded at 96% steam quality as determined by drop-pot impurity monitoring. Injection rates of water and caustic were adjusted to maintain the separator water pH and steam quality in the desired range as the wellhead superheat increased to 50°F and the total flow chloride approached 10 ppm_w. These changes in well conditions had no measurable impact on the corrosion rates downstream of chemical injection.

The other two lower chloride producing wells were treated in a similar manner to well AD10, although caustic was usually fed in excess of the minimum required to mitigate corrosion. Corrosion rates for these wells downstream of scrubbing and downstream of the separators were maintained at approximately 1 mil/yr or less. The maximum corrosion rates upstream of injection ranged from 5.9 to 13 mils/yr. The chloride concentrations in the total flow from these two wells reached maximums of 2 to 3 ppm_w with superheat at the wellheads of 20 to 25°F.

Well AD40 was brought into service with intermittent water/caustic scrubbing followed by stable injection conditions. Process conditions defined by initial testing on well AD10 were directly applied to the corrosion mitigation for well AD40. During the intermittent scrubbing period, the corrosion rate was 17 mils/yr downstream of injection and 25 mils/yr downstream of the separator. With steady injection conditions producing 98.1% steam quality and 8.1 pH units (20°C) in the separator water, corrosion rates downstream of injection were reduced to 1.0 mil/yr and corrosion rates downstream of the separator stabilized at approximately 2

Table 1. Optimization of Injection Rates, Well AD10

Date	Separator Water pH, 20°C	NaOH/Cl Mole Ratio	% Steam Quality	Corrosion Rate, mils/yr			
------	--------------------------	--------------------	-----------------	Upstream of Injection	Downstream of Injection	Downstream of Separator	Plant Inlet
06-16-89	6.7	0	98.2	31	18	19	4.9
06-26-89	7.8	4.6	98.7	33	3.7	1.1	1.2
07-03-89	7.6	6.5	99.6	81	-	4.1	1.3
07-08-89	6.7	3.6	99.6	-	6.3	16	1.4
07-12-89	8.1	17	96.5	-	<1.0	<1.0	<1.0
08-01-89	8.2	12	96.1	53	<1.0	<1.0	-
08-21-89	8.5	6.4	98.4	27	<1.0	<1.0	-
10-31-89	8.1	4.9	98.4	26	-	<1.0	1.1
12-28-89	8.4	6.4	98.2	37	1.2	<1.0	<1.0

mils/yr. The corrosion rate measured upstream of injection ranged from 7.6 to 15 mils/yr, which was lower than measured for AD10 at the same location, in spite of much higher chloride in the total flow of AD40. This difference is attributed to the higher wellhead superheat of AD40 (80°F), which minimizes the possibility of condensation in the bulk steam flow. However, if condensation is externally induced, corrosion rates are much higher, as discussed later.

The mole ratio of NaOH to chloride required to achieve 8.1 pH units (20°C) in the separator water for AD40 was approximately 2 to 1, as compared to the requirements for AD10 of at least 5 to 1. This difference is due primarily to the buffering effect of boric acid, which is present in large excess to chloride in both wells. A minimum quantity of NaOH must be present, regardless of the amount of acid-chloride, to raise the pH above 8.0 units (20°C), as discussed later in this paper.

Boric acid can cause other process difficulties, since sodium borate is the least soluble product of the chloride scrubbing and neutralization process. This was demonstrated when the ratio of injection water to caustic was inadvertently reduced for well AD30 which resulted in sodium borate (borax) scaling of the separator drain lines. The solubility limit for this compound was exceeded with approximately 17,000 ppm_w borate and 8400 ppm_w sodium in solution (steam quality >99.5%). By maintaining steam qualities at 99% or less, this problem has been eliminated.

In order to continue effective monitoring of the chemical process conditions, pressure, temperature, flowrate, and corrosion rate data is routinely obtained at various points in the systems in addition to fluid samples for chemical analysis. Mass and heat balance calculations are performed by a mathematical modeling program with iterative and back-solving capabilities. This makes it possible to obtain complete data sets for chemical mass flowrates, concentrations, water and steam fractions, and enthalpies, even when certain critical data points are missing due to instrument failures. The wellhead enthalpies (superheat) are typically back-solved based on water injection rates, separator water rates and steam rates, as it is difficult to obtain direct readings given the wellhead injection configuration. Mass and heat balances can also be calculated or verified based on the differences in injection water and separator water sodium concentrations due to flashing or condensation.

The net production enthalpy loss from each well resulting from the chloride scrubbing process is less than 0.5% under average conditions. With the flow control valves for each well located downstream of the separators, water consumption is minimized since the desuperheating and scrubbing process occurs at throttled wellhead pressures rather than gathering system pressures. Over 20% more injection water would be required to generate the same effective steam quality at a pressure of 100 psig versus 170 psig for a typical well. This factor is important during the summer months when excess hotwell condensate availability may be limited. Water separation upstream of the control valves also results in superheated steam conditions throughout the gathering system which minimizes condensation and corrosion rates.

Steam Quality and Mass Transfer

In conjunction with the chemical process and corrosion rate monitoring for each well, separator efficiencies were evaluated to determine the extent of mechanical liquid entrainment in the steam. Preliminary testing of separator outlet steam qualities based on heat balance calculations utilizing superheat measurements downstream of the separators and flow control valves indicated that the qualities were greater than 99.90% (<0.10% moisture). Isokinetic steam sampling was later performed at the outlets of AD10 and AD40 separators using a traversing probe with a knife-edged sample nozzle. Steam condensate samples were analyzed for sodium and chloride to determine entrainment ratios relative to the separator water concentrations in order to calculate the final percentage of moisture in the steam flow. This testing also made it possible to evaluate the mass transfer of chloride from the vapor to liquid phase.

The separator outlet steam quality measured for AD10 was 99.990% (0.010% moisture) based on the sodium analyses. A steam quality calculation based on chloride was not possible since most points were below detection (0.05 ppm_w), although total chloride removal was calculated as greater than 95%. This test was conducted at 98.4% separator inlet steam quality with a separator inlet velocity of 145 ft/sec.

The separator outlet steam quality determined for AD40 was 99.980% (0.020% moisture) based on sodium analysis and 99.950% based on chloride. Higher chloride to sodium ratios in the steam versus the separator water

indicated incomplete mass transfer of the volatile chloride. Correcting for mechanical entrainment based on sodium, the mass transfer of chloride from vapor to liquid was determined to be 98.3% complete. This test was performed at 98.1% inlet steam quality with an inlet velocity of 110 ft/sec.

A second test for AD40 was performed at the same inlet velocity, but 99.2% inlet steam quality. Under these conditions, the outlet steam quality increased to 99.984% (0.016% moisture), based on sodium. However, the chloride to sodium ratios were even higher, and the mass transfer of chloride from vapor to liquid phases was only 94.8% complete. The higher inlet steam quality reduced the mass transfer of chloride and increased the separator water sodium chloride concentration by more than a factor of 2. This also resulted in higher mass flow rates of entrained sodium chloride, even though the percent moisture entrainment was lower. These results, summarized in Table 2, validated the 98% steam quality process parameter determined previously by corrosimeter testing and drop-pot monitoring during start-up.

Steam purity at the plant inlet was monitored by isokinetic steam sampling downstream of the dual separator/steam washing system. Liquid in the final drop-pot before the turbine was also tested to qualitatively determine the concentrations of impurities that may be present in condensate films on the pipe walls. As shown in Table 3, single stage washing of the steam reduced the residual steam and drop-pot chloride concentrations by over 90%. With well AD40 on line, a significant portion of the chloride in the plant inlet steam was volatile, rather than mechanically-entrained sodium chloride, as evidenced by the ratios of chloride to sodium. Two-stage steam washing was required to reduce the drop-pot chloride and sodium levels below 10 ppm_w, the target value for normal operation. Under these conditions, the chloride in the drop-pot was present primarily as sodium chloride, even though vapor phase chloride was still evident in the steam. With well AD40 off-line, only single-stage steam washing was required, and the primary form of chloride in both vapor and liquid phases was sodium chloride. Even with well AD40 in service and only single stage steam-washing, the steam purity was well below the turbine manufacturer specified limits of 1 ppm_w chloride and 1 ppm_w sodium.

Chemical Process Modeling

In order to determine the pH and electrolyte equilibria of the process water exposed to the carbon steel piping and separators at steam temperatures (175 - 200°C), a chemical modeling program was utilized. This model incorporated 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[24]. It was also desired to determine the pH-controlling species since the mole ratios of $NaOH$ to chloride required to maintain separator water pH values were not consistent between wells.

Analytically determined values for the vapor and liquid phase species in the separators, including total water mass and enthalpy, were input to the model which computed 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 4 summarizes the model validation data over a wide range of steam qualities and NaOH to chloride ratios.

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 are in substantial agreement also demonstrates that the vapor/liquid chemistry was essentially in equilibrium, as previously indicated by the volatile chloride mass transfer results. Although CO_2 absorption and hydration ($CO_2 \rightarrow H_2CO_3$) 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, as shown in Figure 2.

Table 2. Steam Quality and Mass Transfer Efficiency

Well	Inlet Steam Quality	Outlet Moisture Content	Mass Transfer Efficiency	Entrained NaCl	Residual Volatile Cl	NaCl in Separator Water
AD10	98.4%	0.010%	>95.0%	0.01 lbs/hr	<0.07 lbs/hr	635 ppm_w
AD40	98.1%	0.020%	98.3%	0.10 lbs/hr	0.10 lbs/hr	4180 ppm_w
AD40	99.2%	0.016%	94.8%	0.18 lbs/hr	0.32 lbs/hr	9380 ppm_w

Table 3. Steam Purity at Plant Inlet

Status of AD40	Plant Inlet Steam Wash 1st Stage	2nd Stage	Main Steam, ppm_w Chloride	Sodium	Final Drop-Pot, ppm_w Chloride	Sodium
On-line	0 gpm	0 gpm	1.7	0.39	1220	18.0
On-line	10 gpm	0 gpm	0.15	0.055	109	62
On-line	9.5 gpm	3.7 gpm	0.15	0.030	8.2	8.0
Off-line	6.3 gpm	0 gpm	<0.05	0.043	5.6	4.8

Table 4. Chemical Modeling Results Versus Measured Values

Well	Steam Quality	NaOH/Cl Mole Ratio	Separator Water Concentrations, ppm_w Computed			Measured		
			pH^1	H_2S	NH_3	pH^2	H_2S	NH_3
AD40	98.2	1.2	7.29	57	105	7.30	60	116
AD40	98.1	1.9	8.02	205	99.3	8.10	187	103
AD10	98.1	5.8	8.09	92.2	41.0	8.20	103	41.0
AD20	94.8	120	8.46	150	45.3	8.80	159	47.5

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

FIGURE 2

CO2 HYDRATION RATE

99% STEAM QUALITY   20,000 PPM CO2   120 PSIG

10 PPM CL   4X EXCESS NaOH   ANNULAR/MIST FLOW
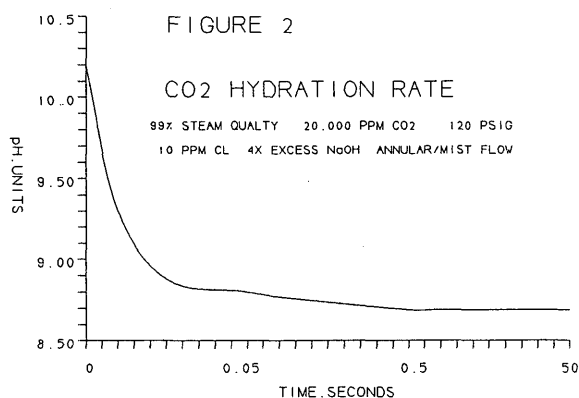
It was determined by chemical modeling of the process chemistry that boric acid was primarily responsible for buffering the pH in the range of 7.8 to 8.8 units. This is not surprising given the boric acid pKa of approximately 9.0 at the process temperature. Even though well AD40 produces over four times the CO_2 of AD10, the mole ratio of NaOH to chloride required to achieve 8.0 pH units is only 2 to 1 versus over 5 to 1 for AD10. Modeling of the same process chemistry for AD10 as given in Table 4, but without boric acid, results in a separator water pH of 8.63 units (190°C), versus the 8.09 units (190°C) calculated with boric acid present.

Caustic feed rates for the Aidlin wells can now be estimated by calculating the stoichiometric amount of NaOH to neutralize acid-chloride, plus an additional 20 to 30 mole % of the boric acid present in the separator water, in order to achieve pH values of at least 8.0 units. Boric acid concentrations in the separator water can be determined based on vapor/liquid distribution coefficients, accounting for the extent of boric acid dissociation at the desired pH.

GATHERING SYSTEM CORROSION TESTS

Ultrasonic Results

Comprehensive ultrasonic thickness testing (UT) of the chemical injection spools and steam gathering system piping has been performed since the units came on-line. A grid system was mapped out and baseline data collected for each monitoring location. Carbon steel pipe surfaces both upstream, downstream, and on the caustic injection spool have been regularly monitored to determine corrosion rates and establish the effectiveness of the

chloride removal system. The testing procedures have been designed to identify points of localized corrosion by utilizing high-density grid patterns in known trouble-spots (heat loss points), since acid chloride corrosion is not usually manifested as uniform corrosion.

From the data collected to date, the steam gathering system piping downstream of the caustic injection spool has shown no appreciable wall loss (<10 mils) over the first nine months of operation. Data capture shows no significant trend or indication that localized corrosion is occurring in the steam pipeline. Some UT points actually show an increase in wall thickness, probably due to magnetite formation on the pipe walls.

A corrosion problem has developed immediately upstream of injection on the well AD40 chemical injection spool. Condensation and subsequent acid-chloride attack resulted from the desuperheating process that generates internal temperature gradients of up to 80°F near the injection point. Within four months of service, severe pitting upstream of the injection nozzles resulted in several small leaks. A new injection spool was fabricated and modified to minimize heat loss near the welded fittings. Additional insulation was also installed as a countermeasure to limit condensation and subsequent corrosive attack in the superheated zone. The other three existing production well injection spools are still in service and have not experienced similar failures, probably due to much lower chloride levels. These, along with the new AD40 spool, are closely monitored and inspected to determine the useful life of carbon steel for this application. High alloys resistant to chloride and caustic, such as Inconel, were originally considered in the design of the mixing spools for all wells. Due to uncertainties in the levels of chloride expected from the wells and the high cost of alloy spools, carbon steel was chosen as the initial material. An economic evaluation can now be made to determine if the injection spools for specific wells should be fabricated from an alloy material to prevent corrosion and eliminate regular replacement.

A similar, but transient, phenomenon occurred upstream of injection on well AD10. Under high wellhead pressure (490 psig), throttled production, the saturated steam conditions at the wellhead resulted in measured corrosion rates of 378 mils/yr. The well was immediately opened up to full production and the corrosion rate dropped to 34 mils/yr under the normal superheated conditions. Current production practice is to not throttle the two high chloride wells, maintaining at least 20°F superheat at the wellheads.

TURBINE INSPECTION RESULTS

Non-Destructive Tests

In March of 1990, after nine months of operation, both turbine/generator units were brought off-line to perform visual and non-destructive test (NDT) inspections. Based on experience from other operating plants with similar steam chloride concentrations, the nine month run period was considered sufficient time for corrosion damage (pitting, cracking, crevice corrosion) to appear. The NDT techniques performed during the inspection were dye penetrant tests (PT), magnetic particle tests (MT) and ultrasonic tests (UT).

The turbines are single-flow, non-extracting, condensing units with 13 stages. The turbine stationary and moving blades are 13% chromium, low carbon stainless steel, typical of Geysers units. The casing and blade holders are fabricated from carbon steel. A 1% chromium, 1% molybdenum, 0.75% nickel and 0.25% vanadium low carbon alloy was utilized for the rotors.

Visual inspection revealed minor iron sulfide scaling (<5 mils) at the base of the first five stages of moving blades on both machines. Scaling progressively diminished in magnitude (<1 mil) from the third to fifth stage and disappeared altogether from the sixth stage on. The last two stages showed minor water erosion on the face of the blades. The first two stages of moving blades also showed very slight erosion at the leading edge. The most important finding of the visual inspection was that no pitting or any other form of corrosion had occurred on the turbines or ancillary equipment (main stop valve, control valve, steam strainers, and belly drains). The only visual sign of corrosion was slight scaling inside the carbon steel turbine exhaust duct.

Non-destructive testing was performed on the rotor, selected stationary and moving blades, steam strainers, bearings, and the upper casing. The PT work showed no signs of surface cracking and the MT and UT work revealed that no subsurface cracks or damage had occurred. At this juncture, there is no evidence of caustic or chloride-induced stress corrosion cracking.

Scale Deposit Analyses

Table 5 lists the analytical results for turbine scale deposits collected during the turbine inspection. All deposits were collected immediately upon exposure of the turbine and placed in air-tight containers to minimize the effects of air contact. The presence of sodium hydroxide, sodium carbonate, ammonium chloride or hydrogen chloride was not detected in any of the deposits. Sodium chloride, boric acid, ammonium borates and iron chloride borates were present in turbine casing samples. The pH values at 20°C for saturated solutions of the halite-containing deposits were 7.6 to 8.1 units.

Magnetite and iron sulfides were the primary components found within the turbine. These compounds, which are common corrosion products of the steam gathering system, were also found on the turbine inlet steam strainers and probably entered the turbine as particulates.

CONCLUSIONS

The Aidlin Geothermal Project volatile-chloride corrosion mitigation system, designed by Mission Power Engineering Company, has successfully prevented corrosion damage to the steam gathering system and steam turbines. This has been determined based on comprehensive electrical resistance corrosimeter testing, ultrasonic thickness testing and thorough turbine inspections after nine months of operation. Experience at other steam fields producing similar levels of volatile-chloride indicates that numerous steam piping failures and measurable turbine damage would have occurred in this time period without such a corrosion mitigation system in service. It is anticipated that the life expectancy of the Aidlin turbines and steamfield piping will be at least equal to that of other geothermal projects with negligible levels of volatile chloride.

By optimization of the process chemistry, injection of water and caustic at rates to yield a 98% steam quality and water pH of 8.0 - 8.5 units (175 - 200°C), will minimize corrosion rates, residual vapor-phase chloride and salt entrainment from the separators. This water pH range required to minimize corrosion is somewhat higher than the pH of most flashed geothermal brines at the same temperatures, suggesting that the absence of silica and other minerals in the process water is responsible for the increased need for hydroxide.

Chemical process modeling and chemical analyses show that CO_2 effectively converts excess sodium hydroxide to sodium carbonates, which is further supported by the fact that free hydroxide has not been detected in the turbine. It has also been concluded that

Table 5.0   Scale Deposit Compositions, Weight %

| | Elemental Composition[1] | | | | |
Location	Na	Fe	SiO_2	B	X-ray Diffraction Mineralogy
1st Stage Diaphragm	0.83	48	2.1	1.4	12% Fe_3O_4, 34% FeS, 6% FeS_2, 1% NaCl
1st Stage Rotor	0.69	51	-	-	1% Fe_3O_4, 30% FeS, 9% FeS_2
Casing Belly Drain	0.33	0.46	0.29	19	50-100% $NH_4B_5O_8$, $(NH_4)_2B_{10}O_{16}$
Casing Bottom	8.5	2.8	0.32	14	23% NaCl, 1-15% $Fe_3B_7O_{13}Cl$, 15-50% H_3BO_3
Upper Casing	8.7	8.6	0.29	14	22% NaCl, 11% FeS_2, 1-15% $Fe_3B_7O_{13}Cl$
Steam Inlet Strainer	0.04	53	2.1	0.07	50-95% FeS, 1% Fe_2O_3, 4% Fe_3O_4

1.   Only major elements detected are listed.

the process water pH is buffered by boric acid, which must be accounted for when estimating NaOH feed rates.

The chloride scrubbing and steam washing process is also expected to remove silica and particulates, although not originally intended to do so, which have caused problems at other power plants at The Geysers. Under the prescribed conditions, the vertical separator outlet steam qualities are at least 99.98%, and the steam purity at the plant inlet can be maintained at 5 to 20 times higher than specified by the turbine manufacturer.

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