Geothermal Resources Council, Monograph on The Geysers Geothermal Field, Special Report No. 17, 1991

NONCONDENSIBLE GAS AND CHLORIDE ARE CORRELATED IN STEAM AT THE GEYSERS

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ABSTRACT

Noncondensible gas and hydrogen chloride (HCl) concentrations correlate positively in steam from two areas of The Geysers, Unit 15 and Coldwater Creek, which produce corrosive HCl-bearing steam. Although Unit 15 has been producing for over 10 years, the production of HCl-bearing steam is relatively recent. Coldwater Creek, which has just begun production, produced HCl-bearing steam from initial flow tests. According to basic chemistry and models of the reservoir, there are common reservoir characteristics which generate HCl and relatively high concentrations of noncondensable gases in steam from vapor-dominated systems such as The Geysers. These are: (a) a relatively hot (≥ 300°C) saline source such as a deep brine, adsorbed ("irreducible") water, or connate power water; (b) a relatively dry or poorly connected shallow (although originally condensate-saturated), 240 to 250°C, "typical" reservoir zone. As in the case of Unit 15, this zone may be dried out by production, removing its ability to scrub HCl and to dilute gases.

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INTRODUCTION

Wells producing chloride (Cl) in superheated steam at The Geysers are of interest to steam field and power plant operators because the steam is highly corrosive. Chloride is transported in the steam as HCl that becomes corrosive to steel in the presence of liquid water. The characteristics of a reservoir producing superheated HCl-bearing steam are: high (>300°C) temperatures of boiling (much higher than that of the typical (240°C) Geysers reservoir), and brine of at least moderate salinity (>10,000 ppm NcCl) at the expected almost neutral pH. In other words, HCl-bearing steam can be generated at high temperatures from a hot brine (Haizlip and Truesdell, 1988; Truesdell and others, 1989) or generated from reaction of solid NaCl with silicates (Fournier, 1983; D'Amore, Truesdell and Haizlip, 1990). Subsequent transport of HCl in vapor requires the absence along the flow path of lower temperature (<275°C) neutral liquid in which it would rapidly dissolve. The conduits leading to an HCl-producing well must be dry and/or hot. At The Geysers HCl-bearing steam is incompatible with condensate at normal reservoir temperatures (240 to 250°C).

Noncondensible gas is present in widely varying concentrations at The Geysers (Truesdell and others, 1987), ranging from<500 parts per million by weight (ppmw) in the southeast to over 75,000 ppmw in the northwest. Models of The Geysers suggest that the reservoir is two-phase and that steam is derived from reservoir vapor and vaporized reservoir liquid (e.g. Truesdell and White, 1973; Pruess, 1985). Models of gas chemistry in two-phase geothermal systems (Giggenback, 1980; D'Amore and Celati, 1983; McCartney and Lanyon, 1989; McCartney and Haizlip, 1989) indicate that there is a strong positive correlation between the fraction of steam derived from reservoir vapor and the total noncondensible gas content of the steam. In this paper, data are presented on the positive correlation between the concentrations of HCl and total noncondensible

sible gases in steam from two areas of The Geysers, and the implications for the reservoir are discussed. A better understanding of the processes that generate corrosive steam may help promote a long-term, economically feasible solution to corrosion problems at The Geysers.

DATA

Analyses of HCl and total noncondensible gases in steam from production wells in the northwest Geysers Coldwater Creek and Unit 15 in the southwest Geysers are presented in Table 1. Coldwater Creek is a newly exploited area that has produced HCl-bearing steam from the start. The Unit 15 steam field, which has been producing for over 10 years, has shown signs of increased amounts of HCl-bearing steam in the last few years.

Samples were collected by GEO Operator Corporation as part of routine geochemical monitoring of production wells. Analyses of noncondensible gas and Cl were performed by Thermochem (noncondensible gases) and by the University of Utah Research Institute (Cl). The data presented in Table 1 are the best currently available but are not necessarily from the most recent collection. All data were collected from wells producing to the plant at least 2 months after start-up.

Chloride concentrations listed in Table 1 are from analyses of samples collected from both the steam outlet and liquid outlet of a Weber separator installed on the side wall of a steam line, just downstream of the wellhead. A Weber separator centrifugally separates lower density steam from a higher density fluid, usually liquid. When used as described here on a flow of steam without obvious liquid, it separates steam into samples that may be identical or may contain different concentrations of suspended liquid droplets or particulates. Steam with higher particulates has a higher density and is collected from the "liquid" outlet.

Because Cl comes from the reservoir as HCl gas, which partitions readily into any moderate- or low-temperature liquid present, it is very difficult to assess Cl concentrations from steam samples alone. Even in dry or superheated steam, the "liquid" outlet sample from a Weber separator appears to concentrate liquid droplets. Chloride and other constituents that partition preferentially into the liquid phase are more concentrated in samples from the liquid outlet than in those from the steam outlet. Because the amount of liquid cannot be measured and is extremely variable, concentration data for samples from the liquid outlet are qualitative. This method of sampling is very useful for detecting the presence of Cl when the total steam samples contain insignificant (<1 ppm) quantities. The absence of Cl in samples from the steam outlet is not necessarily diagnostic of non-HCl-bearing steam. Observed concentrations range from <1 to 30 mg/l in samples from the steam outlet and 1 to 800 mg/l in samples from the liquid outlet.

The total noncondensible gas data (Table 1) are from the most recent laboratory analyses of total gas in steam, confirmed by field data when available. Gas concentrations range from 4,000 to 80,000 ppmw. The indication of corrosive character of steam is a qualitative assessment that is based on observed metal loss and steam chemistry.

Table 1. Gas and chloride concentrations in steam from some Unit 15 and Coldwater Creek wells, in ppmw, collected from a miniseparator steam outlet (so) or water outlet (wo).

Well	Gas	Cl (so)	Cl (wo)	Corrosion*
U15- 1	16,500	2	10-56	#
U15- 2	13,000	2-5	16-180	#
U15- 3	12,000	4	12	#
U15- 4	12,000	2.5	3.5	.
U15- 5	11,000	1	2	.
U15- 6	10,500	2-3	3-17	o
U15- 7	10,500	<1	2-4	--
U15- 8	8,000	<1-5	4-9	--
U15- 9	7,000	<1	1	--
U15-10	6,500	<1-2	2-4	--
U15-11	6,000	<1	1-2	--
U15-12	4,500	<1	2	--
U15-13	4,000	1	2-5	--
CWC- 1	80,000	5	20-50	#
CWC- 2	38,000	25	400-800	#
CWC- 3	36,000	3	15-50	#
CWC- 4	20,000	30	50-250	#
CWC- 5	20,000	3	300	#
CWC- 6	20,000	1-3	15-30	#
CWC- 7	19,000	8-17	25-50	#
CWC- 8	19,000	6-10	11-27	#
CWC- 9	17,000	8.5	20-30	#
CWC-11	8,500	<1	4.5	--
CWC-10	8,100	1	3	--
CWC-12	6500	<1	4.5	--
CWC-13	6000	1	4	--

**Corrosion: #, definite; 0, moderate; ., slight; --, none.*

RESULTS

In general, there is a positive correlation between noncondensible gas and HCl in steam (Table 1; Figures 1 and 2). This correlation is stronger in steam from the Coldwater Creek area (Figure 1), than from Unit 15 (Figure 2). At Coldwater Creek, corrosive steam contains Cl in concentrations >3 mg/l from the steam outlet and >25 mg/l from the liquid outlet. This steam contains ≥17,000 ppmw noncondensible gases. There is a clear distinction between these samples and samples of noncorrosive

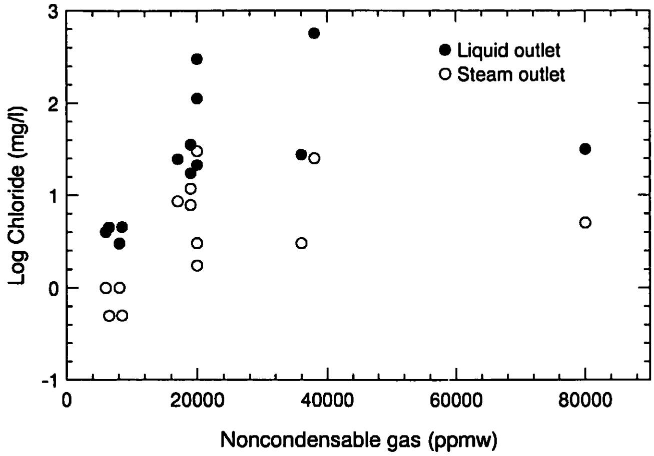

Figure 1. Noncondensable gas vs. chloride - Coldwater Creek.

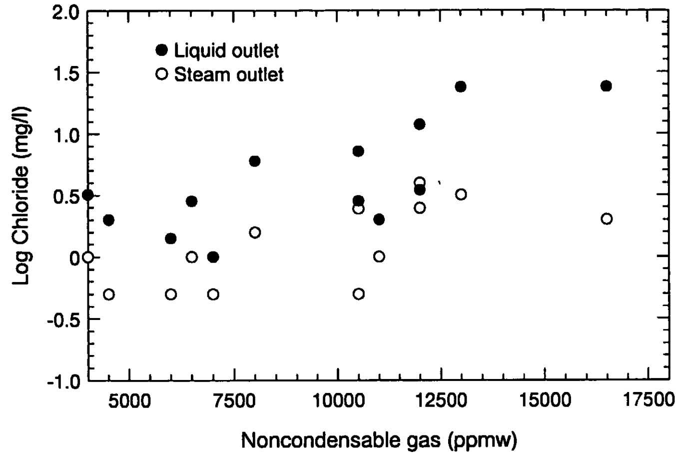

Figure 2. Noncondensable gas vs. chloride - Unit 15.

steam from Coldwater Creek wells. The noncorrosive steam contains negligible Cl and 8,500 ppmw noncondensible gases. The relation betweeen measured HCl and noncondensible gases is more gradational at Unit 15. Most Unit 15 samples of corrosive steam with significant Cl (>2 mg/l from the steam outlet and >10 mg/l from the liquid outlet) have >10,500 ppmw noncondensable gas. Noncorrosive steam with insignificant HCl contains ≤10,500 ppmw noncondensible gas.

From the time of initial production flow testing, Coldwater Creek wells have produced steam with high Cl concentrations and noncondensible gases relative to the rest of The Geysers (Truesdell and others, 1987, and unpublished data). Steam produced from Unit 15 wells, however, has changed during the course of exploitation. Gas concentrations have increased since initial production, though most of the increase occurred in the first 5 years. Chloride was first discovered in steam from Unit 15 wells after 7 or 8 years of production. The clear distinction between noncondensable gas and Cl concentrations of corrosive and nncorrosive steam in the Coldwater Creek area versus the gradational one at Unit 15 is probably related to differences in development and the mechanism of producing HCl-bearing steam.

DISCUSSION

The correlation between concentrations of HCl and noncondensible gas at The Geysers suggests that the physical and chemical conditions in steam are similar and that there may be a common source for these constituents. Alternatively, the transport of gas and HCL to the wells may be controlled by the same factors.

HCL Transport Related to Gas Dilution

At The Geysers, HCl and gas concentrations may be related to near-wellbore liquid saturation. If HCl in steam reaches the surface, it cannot have contacted significant quantities of liquid water at temperatures below 275°C. Therefore, the area surrounding the wellbore must be dry and/or hot. In HCl-producing wells with typical Geysers temperatures (240°C), such as those in the Unit 15 area, the near-wellbore area must be dry, and the steam must be coming from a hotter, more distant zone. Earlier models of The Geysers (e.g. Truesdell and White, 1973; Pruess, 1985) have postulated that the vapor-dominated reservoir contains descending condensate, which fills pore spaces and small fractures. Steam production from boiling this liquid is relatively low in gas. As pressures near the wellbore and in major steam conduits decrease, this liquid evaporates completely and those zones dry out. They no longer scrub HCl from steam passing through to the well and no longer contribute low-gas vaporized liquid to the steam flow. Thus, drying along steam conduits and near wells enables HCl-bearing steam to reach the wellbore and eliminates dilution of gas-rich steam by the low-gas condensate. Evidence from long-term (>1 month) shut-in periods at Unit 15 supports this model. After long-term shut-ins, many wells unload water when opened up. Initial gas concentrations are often relatively low and flow rates relatively high for a period of few days to a few months, depending on the well and the length of the shut-in. This is presumably because steam condensed and filled the area around the wellbore during the shut-in period, while the gas was probably bled off at the wellhead. However, in recent years at Unit 15, this phenomenon has not been observed. This may be the result of near-wellbore drying to the extent that saturation is not recovered when production ceases.

For many wells in the Coldwater Creek area, high measured downhole temperaures in the deeper parts indicate that a high-temperature (>300°C) reservoir exists overlain by a typical Geysers (240°C) reservoir (Walters and others, 1988). This high-temperature reservoir produces steam with gas concentrations that are 2 or 3 times higher than average lower-temperature steam. The presence of HCl in steam from these wells suggests that either steam from the high-temperature reservoir does not pass through typical reservoir conditions before it enters the wellbore, or that the typical reservoir in that area has insignificant liquid saturation. The fact that the typical reservoir contributes significant amounts of steam to the total production from these wells (Walters and others, 1988) suggests the former. Once in the wellbore, superheating of the steam from both reservoirs due to depressurization prevents removal of HCl. HCl in steam suggests the presence of a component from the high-temperature reservoir, and dryness or lack of connectivity with the overlying typical reservoir. However, the correlation of high noncondensible gas and HCl concentrations in steam from the high-temperature reservoir could be related to both temperature and the different evolutionary history of that reservoir.

Temperature, Salinity and Reservoir Source

Both HCl and noncondensible gas concentrations are related to reservoir temperaure. HCl is volatilized at temperatures >300°C under reservoir conditions typical of The Geysers (Haizlip and Truesdell, 1988). If gas pressures are buffered by mineral reactions then gas production may also depend on temperature. Mineral buffering of CO_2 has been suggested for Larderello (Pruess and others, 1985) and Giggenback (1981), and Arnorsson (1985) found that gas partial pressures, particularly carbon dioxide, increased with temperature.

Salinity—whether in a deep brine, irreducible saline water, or halite—is a major factor in producing HCl. Saline water and gas-rich steam represent the original fluids of The Geysers reservoir. Saline water or halite was produced by boildown of connate water or older hydrothermal brine (e.g. Sternfeld, 1981) and gas was produced by reaction of hot fluid with minerals, such as CO_2 from calcite (now almost completely removed in the reservoir but abundant in overlying graywacke). Saline water and gas may also be removed together by flushing with meteoric water, which has been suggested for the southeast Geysers (Truesdell and others, 1989).

At Larderello, correlations between temporal changes in flow rate decline and concentrations of gas and HCl were viewed in terms of a vertically layered model consisting of a condensate zone, a two-phase vapor-dominated reservoir, and a deep brine (D'Amore and Truesdell, 1979; D'Amore and Pruess, 1985). In The Geysers, the correlation between HCl and noncondensible gas may also be related to multiple steam sources. Parts of the reservoir that contain original gas-rich, saline fluids (e.g. deep brine or saline irreducible water) may be capable of producing steam with high concentrations of noncondensible gas and HCl under the proper reservoir conditions. The high-gas, high-HCl steam source at The Geysers doe not appear to be equivalent to the deep brine at Larderello, which was low in gas. This difference may be due to the greater gas-buffering capacity of the carbonate, vapor-dominated reservoir at Larderello.

CONCLUSIONS

In a vapor-dominated system such as The Geysers, high-gas and high-HCl in steam are related through mechanisms of production and transport. Generation of high HCl concentrations requires high temperatures (>300°C) and high salinity fluids or the presence of halite (and other chloride minerals). High salinity fluids at The Geysers are remnants after boildown of original connate waters, and halite results from further boiling in a dry reservoir. Gases (largely CO_2) are also produced by high-temperature water-rock reactions. During steam production, vaporization of condensate under normal conditions (240°C) produces low-gas steam with no HCl and the presence of condensate removes HCL from deeper steam. To contain HCl, steam must originate at high-temperature and follow a dry path to the well, and be undiluted by vaporized low-gas condensate.

In the case of Unit 15, the dry zone could have been created by production. Increases in noncondensible gas, the presence of HCl, and changes in flow rates and temperatures during production are consistent with drying near the wellbore. At Coldwater Creek, a combination of variations in the evolution of the reservoir (affecting the temperaure, saturation, and thickness of the condensate-filled, vapor-dominated zone), relatively low permeability in the shallow zone, and close vertical proximity to the high-temperaure reservoir may have created a near-wellbore zone that does not scrub HCl or produce low-gas steam.

In both cases, steam related to high-temperature brine (or halite) and rock-fluid reactions is the source of both HCl and noncondensible gases. High-temperatures and long heating times tend to increase both gas and salinity in reservoir fluids. Both gas and Cl (as brine and halite) would be removed by flushing, and therefore, there may be parts of The Geysers where corrosive, gas-rich steam does not exist. At Unit 15, HCl-bearing gas-rich steam may have always been present, but until recently liquid saturation in the shallow zone diluted the gas and removed the HCl. The continued productivity of these wells, and of the Coldwater Creek wells (Drenick, 1986; Walters and others, 1988(indicated that there is a hotter, more saline, probably deeper source of steam in The Geysers.

In order to use this hotter, HCl-bearing steam, its corrosivity must be mitigated. Large-scale reinjection, replenishing liquid in the shallow 250°C zone, could theoretically scrub HCl before it enters the wellbore, reduce noncondensible gas concentrations, and increase flow rates. Such reinjection may also be effective in high-temperature zones of the reservoir originally poor in liquid. Injection has successfully reduced HCl production in Larderello (Truesdell and others, 1989).

ACKNOWLEDGMENTS

We appreciate the release of data by GEO Operator Corporation, a wholly owned subsidiary of Geothermal Resources International, Inc. We thank Jim Combs (GEO), and Cathy Janik and Lynne Fahlquist (USGS) for reviewing the manuscript.

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