

PRELIMINARY EXPERIMENTAL INVESTIGATION OF WATER INJECTION TO REDUCE NON-CONDENSIBLE AND CORROSIVE GASES IN STEAM PRODUCED FROM VAPOR- DOMINATED RESERVOIRS

Timothy J. Kneafsey, Karsten Pruess, and Nicolas Spycher

E.O. Lawrence Berkeley National Laboratory
1 Cyclotron Road
Berkeley, California 94720 USA
e-mail: TJKneafsey@lbl.gov

ABSTRACT

Water injection at The Geysers, California, has acted to sustain reservoir pressures and production rates, as well as to improve steam composition by reducing the content of non-condensable gases (NCGs). Improved steam composition is thought to result from producing steam formed from boiling the relatively clean injection water, and from increased pressurization that decreases the production of deeper native steam having large NCG concentrations. A possible additional effect that could lower NCG concentrations in produced steam is dissolution in a condensed aqueous phase that would form due to reservoir repressurization from injection-derived steam (IDS).

We are performing laboratory experiments to evaluate the dissolution of hydrogen chloride (HCl) gas in the injection-derived condensation. In the experiments, we form a condensed water phase by water vapor sorption and capillary condensation in a porous medium, and then introduce hydrogen chloride gas. The pressure decline caused by dissolution of the HCl into the condensed water phase, and possible interaction with solid surfaces are used to provide kinetic information on the sorption process, and endpoint HCl vapor concentrations are verified analytically. Preliminary results show strong HCl sorption to silica surfaces, rock wettability changes due to HCl interaction at very low water contents, and HCl scrubbing from the vapor phase. Our experiments suggest an additional effect that promotes vapor condensation and HCl scrubbing, namely, vapor pressure lowering due to HCl dissolution, and subsequent increase in ionic strength of the condensed phase.

INTRODUCTION

Water injection into vapor-dominated geothermal systems such as The Geysers (USA) is recognized as a powerful technique for enhancing energy recovery. In addition to increasing sustainability of the

reservoir by maintaining reservoir pressures and production flow rates, injection has been shown to decrease the concentration of non-condensable gases (NCG) in the produced steam. Three mechanisms may be responsible for lowering the NCG concentration: 1) boiling clean injectate produces clean steam with low NCG concentration, 2) the steam from the injectate pressurizes the upper regions of the reservoir, reducing upflow of "native" NCG-containing steam from deeper in the reservoir, and 3) injection-derived steam increases pressures throughout the surrounding region, causing vapor adsorption and capillary condensation in previously drier regions, and allowing partitioning of the NCGs into the condensate (scrubbing). The third mechanism, NCG scrubbing into condensate, is the subject of this investigation.

The presence of some NCGs, particularly hydrogen chloride (HCl), strongly affects corrosion of metal components in the steam production, transport, and electrical generating systems. Hirtz et al., 1991 examined the chemistry of the produced steam at The Geysers and described the impacts on corrosion. Based on their understanding, these authors also suggested monitoring and corrosion management strategies for equipment at The Geysers. They concluded that chloride can be deposited well above the steam saturation temperature (at the acid dewpoint), and suggested the injection of water and caustic in or near the wellheads of acid-producing wells to control corrosion.

Understanding the occurrence of the HCl vapor has been the objective of many studies [e.g. *Haizlip and Truesdell*, 1988; *Truesdell et al.*, 1989a; *Truesdell et al.*, 1989b]. Using the chemistry of waters and steam condensates from The Geysers and extending published HCl vapor-liquid equilibrium data, Haizlip and Truesdell (1988) reasoned that corrosion-causing chloride was most likely transported by HCl gas. At temperatures less than 250°C, apparent HCl solubility is high because of the nearly complete dissociation of the HCl to H⁺ and Cl⁻. At temperatures above 300°C,

HCl becomes a weak acid, with undissociated HCl present in the liquid phase that partitions into the gas phase. In The Geysers system, these authors hypothesized that the HCl is transported in superheated steam that does not equilibrate with dilute water at more moderate temperatures, and that reactions with mineral surfaces tend to moderate HCl production.

In the Larderello (Italy) reservoir, Truesdell et al, (1989a) examined historical chloride data in produced steam. The concentration of chloride decreased around the time that water injection into the reservoir was implemented to increase the reservoir pressure. Based on this observation, these authors suggested that water injection into The Geysers could be used to lower chloride produced in the steam.

In an examination of four reservoirs, Tatun (Taiwan), Krafla (Iceland), Larderello, and The Geysers, Truesdell et al. (1989b) noted that chloride can be volatilized from geothermal brines over a wide range of temperature, pH, and chloride concentrations with a lower chloride concentration needed at lower pH values. The authors also noted that the HCl can be easily scrubbed by liquids at lower temperatures or higher pHs.

Pruess et al (2007) examined the scrubbing of NCGs from reservoir steam using a numerical model of an idealized five-spot pattern. The modeled region was subjected to reasonable reservoir conditions and both mineral mediated and non-mineral mediated conditions were modeled. The resulting liquid saturation profiles from water injection show moderate to large increases (2 to 25-fold) over time periods of up to about 2.5 years over a large fraction of the reservoir. For quite soluble NCGs such as HCl and CO₂, the relative concentrations in the produced steam decline significantly due to gas dissolution into the condensed phase. Less soluble NCGs that may be present in trace concentrations show intermittent increase in relative concentration in the produced steam for a short time, after which their relative concentration falls drastically.

In this work, we examine HCl scrubbing by condensate water in a mineral porous medium, and focus on laboratory observations of the mineral/capillary-held water/vapor-gas system.

THEORETICAL CONSIDERATIONS

Several factors must be considered when experimentally investigating the HCl/mineral/water system: 1) safety, 2) mineral properties such as specific surface area, reactivity, water retention capacity with water potential, 3) properties of the

physical system (vessel, lines, etc), 4) HCl/water phase behavior.

Safety

HCl is a very reactive and toxic gas and its use is typically restricted and carefully managed in industrial and research facilities. While most safety requirements are advantageous to both health and science, some restrict the flexibility in performing an investigation. In this set of tests the requirements stipulate that all connections must be vented to a safe location, all vessels and tubing in contact with the HCl must be resistant to strong hydrochloric acid, and all components must be pressure rated with a factor of safety at the highest foreseen pressure at the highest expected temperature.

Mineral Properties

Mineral properties will strongly affect the behavior of HCl in a number of ways. First, the condensation of water on the mineral surfaces is dependent both on the mineral shape (roughness and pore dimensions) and chemistry. Water condensation in pores and indentations in the mineral surface is described by the Kelvin equation [Pruess and O'Sullivan, 1992], which expresses vapor pressure as a function of temperature and liquid saturation,

$$P_{\text{vap}}(T, S_{\text{liq}}) = f_{\text{VPL}}(T, S_{\text{liq}}) P_{\text{sat}}(T) \quad (1)$$

where

$$f_{\text{VPL}} = \exp \left[\frac{M_w P_{\text{suc}}(S_{\text{liq}})}{\rho_{\text{liq}} R (T + 273.15)} \right] \quad (2)$$

is the vapor pressure lowering (VPL) factor. P_{sat} is the saturated vapor pressure of bulk aqueous phase at the temperature T (in °C) of interest, S_{liq} is the saturation of liquid (condensed) phase, the "suction pressure" $P_{\text{suc}} < 0$ is the difference between aqueous and gas phase pressures, ρ_{liq} is liquid density, M_w is the molecular weight of water, and R is the universal gas constant. "Suction pressure" P_{suc} is a phenomenological concept that includes conventional capillary pressures, as well as pressures generated by adsorption of liquid water on hydrophilic mineral surfaces. When $f_{\text{VPL}} = P_{\text{vap}}/P_{\text{sat}}$ increases because of pressurization from injection-derived steam (IDS), then P_{suc} in Eq. (2) tends towards a value of 0, corresponding to an increasing saturation S_{liq} of condensed phase.

Measurements of water vapor sorption to a variety of minerals and mineral assemblages including rock from The Geysers at temperatures and pressures relevant to geothermal conditions have been performed previously [Gruszkiewicz et al., 2001]. No direct proportionality between the measured nitrogen

sorption indicating the available surface area and the capacity for the rocks to adsorb water at high temperature was found. The analysis showed that multilayer sorption rather than capillary condensation was the storage mechanism for water in the reservoir rocks. Changes in BET surface area and average pore diameter were observed for the samples measured before and after exposure to reservoir conditions. The order of magnitude for water sorption for this set of tests ranged from milligrams water/gram solid (mg/g) to tens of mg/g at $P_{\text{vap}}/P_{\text{sat}}$ values of 0.98 depending on the mineralogy of the samples.

The mineralogy of the rock also affects HCl behavior by reaction with the hydrochloric acid formed by the dissolution of HCl gas in water. Some minerals such as carbonates would be expected to react rapidly with the acid, allowing continued HCl consumption from the vapor phase. Other minerals such as silica would be expected not to react to the acid, thus continued scrubbing would be limited by vapor liquid equilibrium, and not enhanced by reaction.

Physical system properties

The experimental system we are using is composed of materials varying in inertness, some of which are prescribed by safety and economic considerations. These affect experimental outcome.

HCl/H₂O Phase Behavior

Measurements of HCl/H₂O phase behavior have been made over a wide range of temperatures and HCl concentrations applicable to both industrial and geothermal applications [Brandes, 2005; Simonson and Palmer, 1993]. Crystalline hydrated forms of HCl have also been found in nature. The addition of HCl gas to the water vapor system alters the thermodynamic saturation point (acid dew point) of the mixture [Hirtz *et al.*, 1991; Kiang, 1981], typically lowering the point at which condensation will occur for the conditions of interest. This adds a chemical vapor pressure lowering effect to the physical vapor pressure lowering already discussed. The HCl/H₂O system also forms a negative azeotrope at concentrations varying with temperature.

EXPERIMENTAL INVESTIGATION

Laboratory experiments were performed to investigate the ability of capillary-condensed water to scrub HCl gas from the vapor phase, and a series of preliminary tests have been performed in which HCl has been introduced into mineral samples containing various amounts of sorbed water.

Experimental Setup

An experimental system has been constructed to flash and subsequently condense injected water onto a

porous mineral medium (Figure 1). Oven temperatures can be set as high as 250 °C; the experiments reported here were performed at 90 °C. HCl gas can be introduced in the system, and the resulting headspace can be sampled.

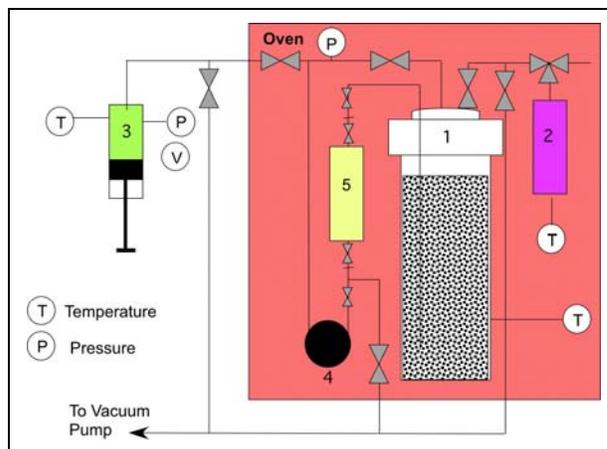


Figure 1. Experimental setup: 1 - 600 ml Hastelloy vessel with glass liner containing media; 2 - water introduction chamber; 3 - HCl gas introduction chamber (stainless steel syringe); 4 - gas circulation pump; 5 - sample collection vessel

In this system, the vessel is a 600 ml Hastelloy-C pressure vessel with a pressure rating of 2000 psi at 350 °C containing a glass liner. The tubing in contact with the HCl is treated using the Silcosteel®-CR Surface Treatment (Restek) enhancing corrosion resistance of the stainless steel by an order of magnitude. The valves are stainless steel, and connections are Monel where possible, or stainless steel. Pressure is measured with a Sensotek® Model TJE transducer without buffer tube or remote seal with output amplified externally and recorded using a Keithley 2750 multimeter/switch system. Temperatures are measured using type T or K thermocouples (Omega Engineering, Stamford CT). A modified Eldex HPLC pump having stainless steel, PEEK, gold, and sapphire components is used for gas circulation. HCl is injected using a stainless steel syringe on a Harvard Apparatus 33 syringe pump.

Tests performed

Three types of tests have been performed to gain a preliminary understanding of system behavior: 1) interaction of dry HCl and “dry” silica sand, 2) interaction of dry HCl and moist silica sand, and 3) interaction of moist HCl and moist silica sand.

Dry HCl/dry silica sand test

A sample of dry silica sand [F110, US Silica, Berkeley Springs, VA, (99.8% silica), and Lone Mountain 30 mesh silica sand] was placed in the glass sleeve in the Hastelloy vessel. Preliminary tests

were performed such as incrementally adding nitrogen using the syringe pump, heating the sample to 90°C, and then condensing aliquots of water in the sample until the system reached saturation (Figure 2). The heated sample was then dried at 90°C and a total pressure of less than 0.1 psi for approximately 2 weeks. After drying, aliquots of dry HCl were added periodically using the syringe pump, and the system pressure was recorded.

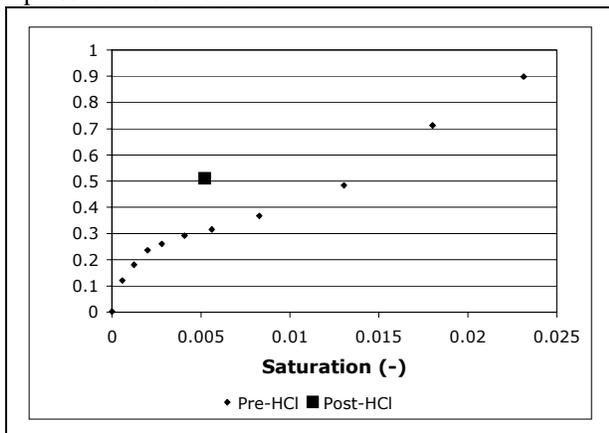


Figure 2. f_{VPL} for one of the samples used.

We had expected that the introduction of HCl into the system after two weeks of drying would not induce chemical interactions. Instead we observed an exponential decline in pressure from the initial pressure following each introduction of HCl with the rate of the decline slowing with increased HCl addition. Following the addition of the HCl, the system was evacuated and an aliquot of water was condensed on the sample. The resulting pressure was much higher than the pressure observed prior to the HCl addition. This indicates a dramatic chemical change in the surface of the sand and an apparent change in wettability. The system was disassembled, and the previously white, water-wetting sand had become yellowish and strongly non-wetting to the point that a subsample of sand sank in a beaker of water causing the formation of an air bubble surrounding the sand.

Dry HCl/moist sand

These isothermal tests were similar to the tests described above, except that we condensed water onto the silica sand sample prior to the introduction of the HCl. At the initiation of these tests, P_{vap}/P_{sat} was 0.6 to 0.7, with only a few hundred milligrams of water required to establish this condition for ~600 g of dry sand. When introduced, the HCl pressure was typically in excess of 1.5 P_{sat} , however upon each HCl addition, the total system pressure dropped significantly (Figure 3). The pressure partially recovered over time, but remained well below the starting pressure. Following the final HCl addition, a gas sample was collected by opening the vessel to the sampling bulb and circulating the gas. Ten grams of

water was introduced into the sampling bulb, and the bulb was cooled and the water collected. Chloride analysis on the water samples has yet to be performed.

After the tests were terminated, the samples were cooled and the systems disassembled. The top 5 cm or so of the sand had developed a greenish tint, and dark spots were present in the sand, presumably where more reactive materials were present. The top layer of the sand was weakly cemented, and the normally free-flowing sand contained many small clumps that were easily broken.

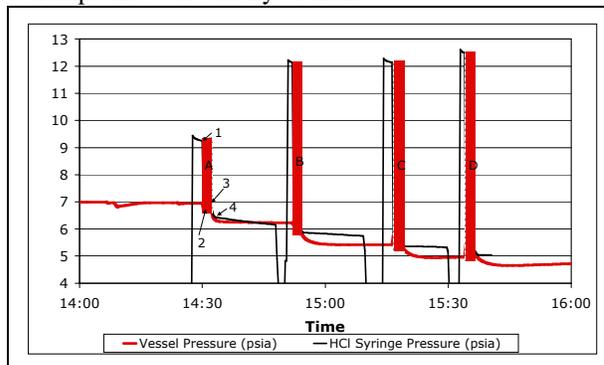


Figure 3. Pressure behavior on four sequential HCl additions (shaded areas labeled A–D). In each, the initial HCl pressure (1) is well above the system pressure in the vessel. Upon opening the syringe to the vessel the pressure in both falls (2), increases slightly on injecting (3), and the pressure in the system continues to fall after shutting the vessel in. ($T=90^{\circ}\text{C}$)

Moist HCl/moist sand

In these tests, water was introduced such that the sampling bulb was open to the vessel and formed part of the headspace over the sand. Upon water vapor equilibrium, the sampling bulb is shut in from the sample and a quantity of HCl gas is mixed with the water vapor in the sampling bulb. This resulting gas is then circulated through the sand containing adsorbed water, and a gas sample is collected upon equilibrium.

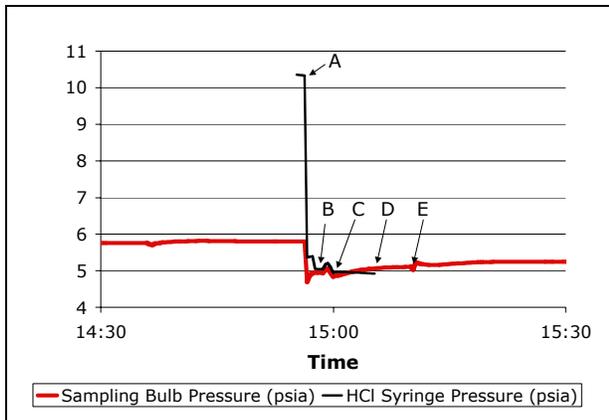


Figure 4. Pressure behavior in the moist HCl/moist sand test. (A) open HCl syringe to sampling bulb containing water vapor, (B) HCl injection, (C) shut in HCl syringe, (D) equilibrate HCl/H₂O, (E) open sampling bulb to vessel and circulate. (T=90 °C)

The sampling bulb was pre-equilibrated with sample and then isolated from it. Upon opening the HCl syringe (P~10.3 psia) to the sampling bulb (P~5.8 psia), the pressure in the sampling bulb immediately dropped to about 4.7 psia (Figure 4) and then began to slowly increase. Upon reconnection to the vessel containing the sample, the pressure in the vessel containing the sand decreased to about 5.2 psia, well below the original pressure. A gas sample was collected as discussed previously, and analysis for chloride is yet to be performed.

INTERPRETATIONS

Dry HCl/dry silica sand test

Introduction of dry HCl into “dry” silica sand produced an obvious reaction and consumption of HCl. Changes in the surface chemistry dramatically affecting the wettability occurred. Based on these observations, we hypothesize that OH groups extending from Si on the silica surface have been replaced by Cl. This is analogous to the chlorination of carbon, with water wettability decreasing with chlorination. The situation in which dry pure HCl contacts mineral surfaces is not likely to occur in geothermal reservoirs; however, in zones containing dry steam and HCl, similar reactions may occur to an extent.

Dry HCl/moist sand

In the dry HCl/moist sand tests, the HCl concentration in the vapor phase was significantly lowered when introduced into the vessel containing the moist sand. If the HCl were an inert gas, its addition to the system would have increased system pressure, rather than reduce it. As it occurred, the

addition of the HCl gas to the system caused water vapor to condense from the gas phase. If we consider the relations proposed by Brandes (2005) for our conditions (Figure 5), the system pressure decreases with increased HCl concentration until the aqueous mole fraction is about 0.13, after which it increases rapidly as more HCl remains in the gas phase. Our mass balances indicate high HCl concentrations (>12 M, mole fraction ~0.23), indicating that the gas phase should be rich in HCl. From Brandes (2005) relations, our pressure for these conditions should be orders of magnitude higher. Reaction of HCl dissolved in the water in our system increases the water mole fraction and consequently lowers the gas-phase HCl concentration.

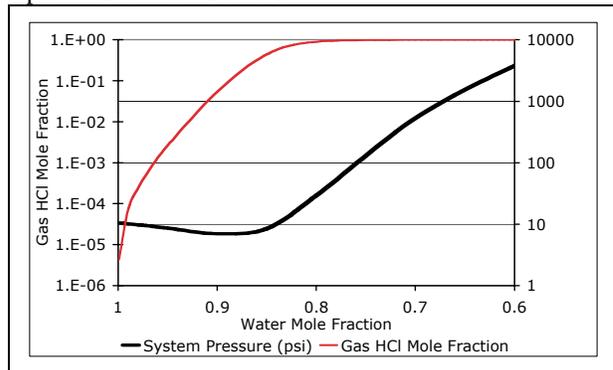


Figure 5. HCl/H₂O behavior based on Brandes (2005) for 90 °C. These relationships do not consider porous medium effects.

Moist HCl/moist sand

Introduction of HCl into a vessel containing water vapor also induced an unexpected pressure drop. The initial pressure drop upon introducing HCl into water vapor may be due to some capillary condensation in scratches in the stainless steel vessel. Introduction of this mixture into our moist silica sample resulted in an expected pressure drop in the sample, indicating condensation of water and HCl in the sand as in the case of the previous experiment.

CONCLUSIONS AND PATH FORWARD

In each of our tests, HCl was removed from the gas phase by interaction with the porous medium and/or condensed water. This is indicated by the pressure drops upon each addition of the HCl. The behavior of the system is very complicated, with vapor pressure lowering effects from physical sorption of the water on mineral surfaces, and additional vapor pressure lowering from the subsequent increase in ionic strength of the aqueous phase, as the dissolved HCl attacks and dissolves rock minerals. This additional mechanism affecting NCG response to injection is suggested by the outcome of the experiments.

It is not likely that rocks under natural conditions of interest would be “dry” to HCl gas. It is also unlikely that geothermal systems would experience HCl concentrations as large as imposed in our initial experiments. We are currently refining our experimental system and technique to add smaller concentrations of HCl to the system more akin to geothermal systems. We are also looking at different experimental techniques to improve our measurements. We intend to expand this investigation to higher temperatures, more reactive minerals, and less reactive NCGs.

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