UTILIZATION OF CHLORIDE BEARING, SUPERHEATED STEAM

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ABSTRACT

Volatile chloride (HCl) is found in geothermal fluids all over the world. When dry steam containing HCl cools to its acid dew point, the compound dissolves in the condensate and forms hydrochloric acid. This can have tremendous consequences for piping and equipment as hydrochloric acid aggressively attacks steel and other metals. Severe pitting corrosion can occur and, if this happens in the turbine, cracks can form at the bottom of the pits, which will grow larger with fatigue corrosion and lead to stress corrosion cracking. The Icelandic Deep Drilling Project (IDDP) is dealing with extreme circumstances with high enthalpy, superheated geothermal steam containing HCl. Successful corrosion mitigation is essential for the feasibility of the development of this promising resource. There are several possible methods for removing HCl from geothermal steam. The goal of this work is to map the applicability of various steam scrubbing technologies, taking into account exergy conservation.

INTRODUCTION

Corrosion is one of the main operational problems in geothermal power plants working with high enthalpy fluids. The cause and severity of the potential corrosion varies between boreholes. Hydrogen chloride is an especially problematic compound that can cause severe pitting corrosion when it dissolves in water. If this happens in a turbine, cracks can form at the bottom of the pits, which will grow larger due to corrosion fatigue and lead to a final breakdown. There are methods to remove the harmful substances, or deal with this problem in other ways, to prevent such damage. This study will analyze how the different methods perform as the enthalpy of the geofluid increases.

Chloride Induced Corrosion

Geothermal steam containing volatile chloride is found in steam fields throughout the world, such as Krafla in Iceland, Larderello in Italy, Saint Lucia in the Windward Islands, Tatun in Taiwan, and the Geysers in the USA (Hirtz et al. 1990). Most geothermal researchers agree that volatile chloride is transported as hydrogen chloride, HCl, although this has only been reported in the literature a few times (Hirtz et al. 1990).

When HCl comes in contact with liquid, the compound goes into solution as hydrogen and chloride ions. HCl does not cause any considerable damage when the steam temperature is above the dew point, however when it cools below the acid dew point, droplets start to form in the gathering system piping and equipment. The HCl readily dissolves in the droplets, forming strong hydrochloric acid, and rapid pitting corrosion can take place. Stress corrosion cracking can also happen in the turbine, where cracks form at the bottom of a pit and propagate by corrosion fatigue leading to a final mechanical break (Viviani et al., 1995). HCl is usually only threatening when small amounts of liquid are present, since its concentration can be very high which accelerates the process of corrosion. If large amounts of liquid are present, such as in two-phase gathering system pipelines, then the hydrochloric acid becomes more dilute and not necessarily of any particular concern.

It is the simultaneous attack of hydrogen and chloride ions that is especially damaging (Meeker et al., 1990). First, the chloride ion breaks the magnetite film on the steel surface, Fe_3O_4, which protects the metal against damage from many other chemicals (Hirtz et al. 1991). This is shown in the following chemical reaction.

$$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O \quad (3)$$
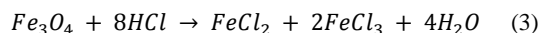
After the breaking of the film, the hydrogen ion has direct access to the metal and the actual corrosion occurs by the following electrochemical reaction (Hirtz et al. 1991).

$$Fe + 2H^+ \rightarrow Fe^{+2} + H_2 \quad (4)$$
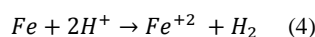
The chloride ion does not participate directly in the corrosion; it rather accelerates the process. This happens both by electrically balancing the rapid build-up of positively charged metal ions as well as enhancement by migration of the ions beneath scale deposits, where the ions can hydrolyze, generating HCl (Hirtz et al. 1991). This happens through the following chemical reaction, where the chlorine ions that initially parted from the hydrogen react with iron(II), the product of reaction shown above.

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl \quad (5)$$
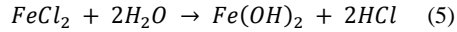
The breaking of the magnetite film inside the gathering equipment, the neutralization of the build-up of iron(II) (which, in other cases, hinders additional hydrogen ions from accessing the corrosion) and the production of more HCl is what makes the compound especially problematic. It is therefore essential to both neutralize the acid and remove the chloride ions simultaneously (Meeker et al. 1990).

It should be noted that these chemical reactions may vary, depending on other chemicals present in the steam, such as oxygen, ammonia and boron for they may affect how the corrosion takes place.

An example of such corrosion is in Krafla, Iceland. A well produced $20 - 100ppm_w$ chloride in superheated steam that resulted in corrosion rates of over 20mm/year of carbon steel. This is far above normal expectations of corrosion rates in gathering system pipelines, which may be around 0.1 mm/year. Excessive corrosion of 13% chromium steel turbine blade test coupons that were exposed to this steam was also observed (Hirtz et al. 1991).

Wet Scrubbing

Wet scrubbing is a commonly used method to remove harmful substances from industrial flue gases or other gas streams. It is the traditional method to remove volatile chloride from superheated geothermal steam, commonly using NaOH (Hirtz, 2002). This technique can be applied to neutralise the chloride in the steam, as it will dissolve and react with chemicals in the wet scrubbing fluid. The basic technique is to inject liquid water with dissolved NaOH into a stream of superheated steam. The liquid cools the steam down to saturation, forming a liquid phase. After the HCl has dissolved in the liquid phase the following reaction takes place.

$$NaOH + HCl \rightarrow NaCl + H_2O \quad (1)$$
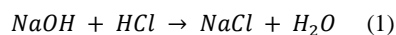
After the reaction, the flow enters a separator, separating the clean steam and liquid which bears the chlorides off to be injected. The steam scrubbing water cools the steam down, resulting in a loss of superheat. The scrubbing liquid that enters the system increases the total mass flow, and enthalpy is conserved in the process, but the loss of the superheat causes loss of exergy; which again leads to less recoverable energy.

Dry Steam Scrubbing

Another method which is under development and gaining attention is dry steam scrubbing, or simply dry scrubbing. This method does not require any cooling of the superheated steam. Solid or liquid material is either injected into the stream in a length of a pipe or in a reactor vessel built into the pipeline (Fisher et al., 1996). When the chemicals have mixed with the flow, it is driven through some sort of a separator, such as an electrostatic precipitator or a bag house filter, where the injected material is filtered out, along with the adsorbed or absorbed contaminants (Fisher et al., 1996). The waste material can often be cleaned and reinjected and thereby recycled to lower operational costs and reduce waste.

There are two similar ways to implement a solid-phase dry scrubbing: absorption and adsorption. Absorption is a chemical reaction between the contaminants and the injected material (absorbent), while in the case of adsorption, the chemical attaches to the surface of the adsorbate without a direct chemical reaction. It is easier to recycle the adsorbent than the absorbent, which lowers operational costs and reduces cost of disposal (Fisher et al., 1996).

Salt dissolved in water has strong electric fields that keep the solution in liquid phase at conditions where water would normally evaporate. The solubility of a salt is proportional to the strength of the electric field, that is, liquid salt solution can coexist with more superheated steam as the solubility of the salt increases (Weres et al. 2010).

As an example, potassium carbonate (K_2CO_3) can be used with dry steam scrubbing to fight the effects of hydrochloric acid. K_2CO_3 is a salt with high solubility and can therefore coexist with superheated steam to some degree (Weres et al. 2010) (Moore et al. 1997). The reaction between K_2CO_3 and HCl is the following

$$K_2CO_3 + 2HCl \rightarrow 2KCl + CO_2 + H_2O \quad (2)$$

Binary Cycle

Binary cycles could also be considered to handle steam with high chlorides. The heat exchanger in the power cycle that condenses a superheated geothermal steam containing HCl may suffer severe corrosion; however it could be outfitted with more exotic materials to resist corrosion. The corrosion potential has not been eliminated, but rather shifted from the turbine over to the heat exchanger.

Heat exchangers are more easily constructed with special metallurgy and, with no moving parts, are less sensitive to corrosion fatigue which can accelerate the process.

For the dry boreholes from the IDDP it would be difficult to keep the wellhead pressure of the geofluid such that it does not flash and superheat. The reason is that it seems that the steam in IDDP-1 is dry out to the fractures in the rock outside the borehole. For that reason, it is assumed that the heat exchanger will have superheated steam at the inlet and the corresponding condensate at the outlet.

This study will examine the utilization efficiency of each corrosion mitigation method, and determine their relative merits.

IDDP

The Icelandic Deep Drilling Project (IDDP) has the main goal of finding out if it is technically and economically feasible to extract supercritical fluids from hydrothermal systems. The intention is to access fluid at supercritical conditions and bring it to the surface as superheated steam (600 – 800°C) at subcritical pressure (< 220bar). One attempt has been made to drill such a borehole, which ended in a magma intrusion at 2104m depth, which is not sufficient to obtain downhole conditions with supercritical pressures. The shallow depth entails downhole pressure of around 120bar, with enthalpy of around 3150kJ/kg. This borehole, IDDP-1, contains volatile chloride and other contaminants that require the geofluid to undergo special treatment before utilization.

METHOD

For this study, we evaluated the relative performance merits of the variety of corrosion mitigation techniques proposed.

Six different software models for different equipment configurations were constructed, each with its own implementation of the corrosion mitigation methods mentioned above. All processes in the models are assumed to be adiabatic unless otherwise specified. Power cycle and gathering system piping and equipment (except turbines and pumps) are considered frictionless and elevation effects are neglected; this excludes kinetic and potential energy effects. Condensation in heat exchangers is assumed to be isobaric. These assumptions do not affect the relative performance of the various options. Some assumptions, such as anticipated mass flow rate from IDDP-1, are not conclusive, for the borehole has not yet been studied at steady state. This study will give an order of magnitude for the performance of each mitigation method, and assign them relative ranks.

Energy Conversion

Turbine Expansion

Expansion of steam inside a turbine is modeled as dry expansion for superheated steam and wet expansion for saturated steam, depending on the nature of the power cycle. The dry turbine isentropic efficiency is assumed to be constant at 85% and the Baumann rule is used in order to account for degradation in turbine performance due to moisture present in wet expansion (DiPippo, 2008). Wet turbine isentropic efficiency is given by

$$\eta_{tw} = \eta_{td} \ (1 + x_{outlet})/2 \quad (6)$$

The relation between the enthalpy of the geofluid and the isentropic turbine efficiency of the turbine is given by

$$\eta_t = (h_{in} - h_{out})/(h_{in} - h_{s,out}) \quad (7)$$

The following equation is used to determine the enthalpy of the fluid at the turbine outlet (DiPippo, 2008).

$$h_{out} = \frac{\left(h_{in} - 0.425(h_{in} - h_{out})\left(1 - h_{f,out}/(h_{g,out} - h_{f,out})\right)\right)}{1 + \left(0.425(h_{in} - h_{s,out})/(h_{g,out} - h_{f,out})\right)} \quad (8)$$

When the fluid entering the turbine is superheated steam, the modeling of the expansion is split in two. The pressure where the steam crosses the saturation curve is found by trial-and-error. The specific power output of the turbine is given by

$$\dot{W}_t/\dot{m} = h_{in} - h_{out} \quad (9)$$

Condenser

Condensing the liquid and vapor mixture to saturated liquid is carried out in the surface condenser. At steady state, mass and energy balances for a control volume enclosing the condensing side of the heat exchanger and a control volume enclosing the cooling medium side, respectively, give

$$\dot{Q}_{out}/\dot{m}_{gf} = h_{gf,in} - h_{gf,out} \quad (10)$$
$$\dot{Q}_{in}/\dot{m}_{cm} = h_{cm,out} - h_{cm,in} \quad (11)$$

Energy balance across the condenser gives

$$\dot{m}_{gf}(h_{gf,in} - h_{gf,out}) = \dot{m}_{cm}(h_{cm,out} - h_{cm,in}) \quad (12)$$

Cooling Tower

A wet cooling tower with an induced-draft counter flow is used to cool the medium (water) in the condenser. The waste heat is rejected to the atmosphere with cooling water recirculating and serving as a transport medium for the heat transfer

between the source (geofluid) and the sink (atmosphere) (Cengel, et al. 2006).

Applying the first law of thermodynamics to the cooling tower gives the following relations, assuming steady flow and overall adiabatic conditions, with reference to Figure 1.

$$\dot{m}_b h_b + \dot{m}_x h_x = \dot{m}_c h_c + \dot{m}_y h_y \quad (13)$$
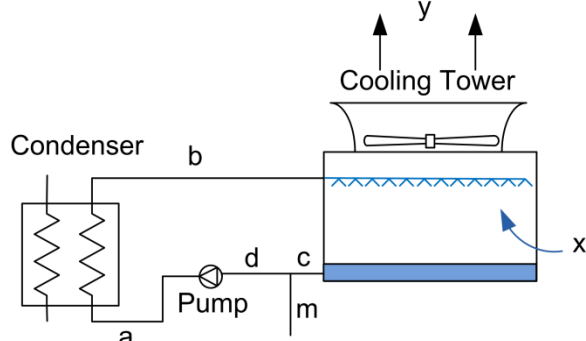

Figure 1 - Process diagram of cooling tower

In order to account for evaporation of the cooling water and the corresponding water uptake of the air, the mass conservation of water and air are evaluated given, respectively, by

$$\dot{m}_b + \dot{m}_{wx} = \dot{m}_c + \dot{m}_{wy} \quad (14)$$
$$\dot{m}_{ax} = \dot{m}_{ay} \quad (15)$$

The surrounding air is assumed to be constant at 2.5°C with 76% relative humidity, which was the average temperature at a weather station situated at Bjarnarflag, near IDDP-1, over the last 4 years.

Heat Exchanger in a Binary Cycle

The analysis of the heat exchanger in a binary cycle is a straightforward application of the principles of thermodynamics and mass conservation. The governing energy balance for the equipment, with reference to Figure 7, is

$$\dot{m}_{gf}(h_1 - h_4) = \dot{m}_{wf}(h_b - h_e) \quad (16)$$

The heat exchanger is divided in three parts during modeling, to ensure that temperatures of the geofluid are greater than the ones of the working fluid at all stages: through the preheater, evaporator, and superheater (named after the thermodynamic process that the working fluid is undergoing through each stage). The temperatures of the geofluid between each stage are found using the known properties of the working fluid at all stages along with the two following energy balances across the preheater and evaporator, respectively.

$$\dot{m}_{gf}(h_3 - h_4) = \dot{m}_{wf}(h_c - h_b) \quad (17)$$

$$\dot{m}_{gf}(h_2 - h_3) = \dot{m}_{wf}(h_d - h_c) \quad (18)$$

Feed Pump in a Binary Cycle

The specific work required to raise the pressure of the working fluid, with reference to Figure 7, is given by

$$\dot{W}_p/\dot{m} = h_b - h_a \quad (19)$$

Using an isentropic efficiency of 80%, the enthalpy at state b is found with the following relation.

$$\eta_p = (h_b - h_a)/(h_{s,b} - h_a) \quad (20)$$

Injection of Alkali Liquid in Wet Scrubbing

In order to apply wet scrubbing, the superheated steam has to be cooled down until its quality is 98% (Hirtz et al. 1990). The following energy balance for the node 1-2-7, with reference to Figure 3, is used to determine how much water at T_7 is required to be injected to get the desired quality at state 2.

$$\dot{m}_1 h_1 = \dot{m}_2 h_2 + \dot{m}_7 h_7 \quad (21)$$

Utilization Efficiency

Using the second law of thermodynamics, the efficiency of the power cycle can be measured with respect to the maximum, theoretically attainable power output; *second law efficiency*. The utilization efficiency (often referred to as the second law efficiency) is given by the following equation, where *e* is the specific exergy of the geofluid at the wellhead with respect to the surroundings.

$$\eta_u = \dot{W}_{t,net}/(\dot{m}_{gf}e) \quad (22)$$

Description of Individual Power Cycles (Models)

Dry Steam Cycle without Corrosion Mitigation

Figure 2 shows a process diagram of the power cycle. The superheated steam is led into a turbine which expands the fluid through both the superheated and saturated regimes. After that the fluid enters the condenser where it is condensed and subcooled.
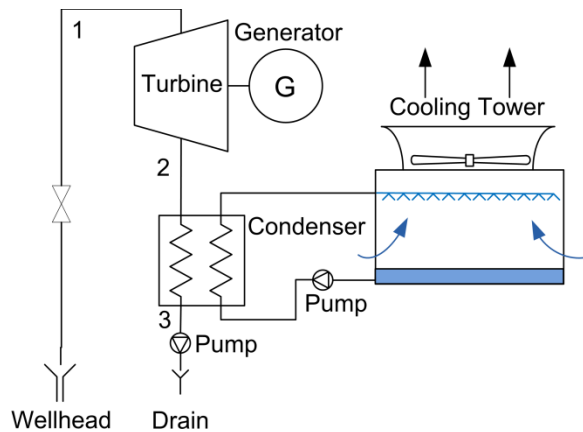
Figure 2 - Process diagram of a dry steam cycle without corrosion mitigation

Single-Flash Cycle with Wet Scrubbing

Figure 3 shows a process diagram of the power cycle. Before the superheated geofluid enters the separator, enough liquid water is injected into the steam to cool it down to a point where its quality is 98%, according to equation 21. As stated earlier, the injected water contains dissolved NaOH to neutralize the pH of the liquid water produced. Since the fluid at state 3 contains no significant superheat, the turbine expansion is assumed to be solely in the saturated regime. The turbine exhaust stream is cooled by the condenser.
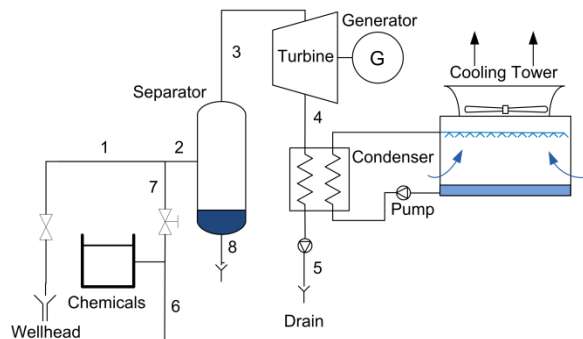

Figure 3 - Process diagram of a single-flash power cycle with wet scurbbing

Single-Flash Cycle with Wet Scrubbing and Heat Recovery (Reboiler)

Figure 4 shows a process diagram of the power cycle. Before the superheated geothermal steam undergoes traditional wet scrubbing, it enters a heat exchanger where it cools down. At the outlet of the heat exchanger, the fluid has 20°C of superheat, which should be enough to ensure that no condensation takes place. Next, enough liquid water is injected into the steam to cool it down to saturation and remove the chlorides via a liquid stream. When the stream has undergone separation the steam enters the heat exchanger and, using the recuperated energy of the incoming steam, gains superheat again. The

following energy balance is used to calculate the enthalpy of the stream at state 5.

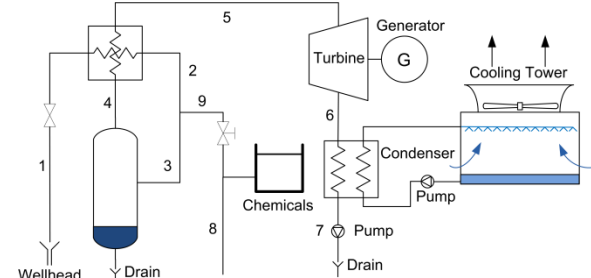$$\dot{m}_1(h_1 - h_2) = \dot{m}_4(h_5 - h_4) \quad (23)$$

Figure 4 - Process diagram of a single-flash power cycle with wet scrubbing with heat recovery

Expansion of the superheated steam in the turbine is both dry and wet.

Single-Flash Cycle with Wet Scrubbing and an Additional Turbine

Figure 5 shows a process diagram of the power cycle. Before the superheated steam enters the traditional setup of wet scrubbing, it expands through a backpressure turbine without condensing. At the turbine outlet, the fluid has 20°C of superheat, which should be enough to ensure that no condensation takes place. The turbine expansion is similar to the one described earlier. The difference is that this is solely a dry expansion, and the backpressure is adjusted to maintain the required superheat at the exit. After the steam has expanded through the backpressure turbine it undergoes wet scrubbing, enters the separator and expands through a condensing turbine.
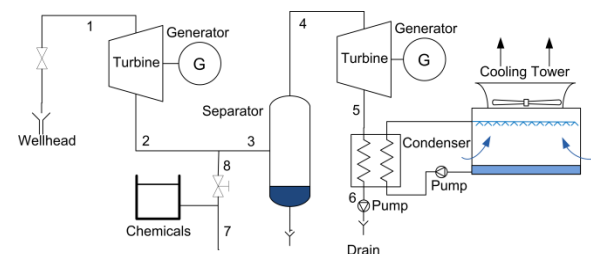

Figure 5 - Process diagram of a single-flash power cycle with wet scrubbing and an additional turbine

Dry Steam Cycle with Dry Scrubbing

Figure 6 shows a process diagram of the power cycle. The superheated steam at state 1 enters a reaction vessel. In the reaction vessel, chemicals are injected into the stream and react with or consume (via absorption or adsorption) the HCl. The mixed flow is then passed through a particulate separator such as a bag house filter or electrostatic precipitator. The

spent reactant is then recycled after being separated from the steam (Fisher et al. 1996).
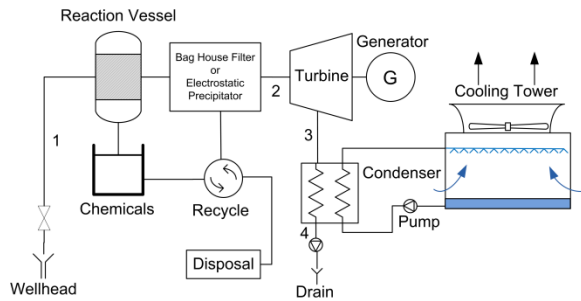

Figure 6 - Schematic diagram of a dry steam power cycle with dry steam scrubbing

Since it is a challenge to estimate the losses in this configuration, it is assumed that they are similar to the ones in the laboratory bench tests that were conducted at Thermochem Laboratories in California, USA. The total heat loss for the processes ranged from 0−0.5%; for this study they will be assumed constant at 0.5%. The total pressure drop was 0.14bar; this will also be assumed constant. There was no measurable reduction in mass flow via losses in the system. (Hirtz et al. 2002)
After this, the clean superheated steam expands through the condensing turbine.

Binary Cycle with Condensation of Geofluid in Heat Exchanger

Figure 7 shows a process diagram of the power cycle. After the working fluid has received heat from the geofluid and vaporizes in a heat exchanger, it expands through a condensing turbine and then pumped up to a higher pressure. Although binary plants harnessing low temperature resources commonly use more volatile working fluids (hydrocarbons or refrigerants), for this high-temperature application, water is used as a working fluid. Models using ammonia, isobutane and isopentane as working fluids were also constructed but showed lower power outputs by a factor of 2, and were therefore not further investigated in the study.
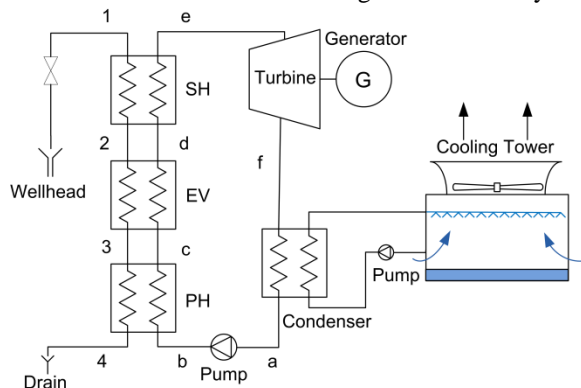

Figure 7 - Schematic diagram of a binary cycle

Execution of Computer Models

In order to determine how the power cycles may differ as a function of increasing enthalpy, the models are executed for two cases. Cases with a geofluid with an enthalpy at the wellhead of 2900kJ/kg and 3600kJ/kg, and a wellhead pressure of 10-150bar were evaluated. Since these are hypothetical wells, no productivity curve is available, hence, the power production is given in terms of specific power (MW produced, per unit mass flow rate at wellhead).

RESULTS

Figure 8 shows the specific power output for all the mitigation methods handling a geofluid with an enthalpy of 2900kJ/kg. It can be seen that dry scrubbing gives the highest power output at all pressures, while wet scrubbing with an additional turbine gives the lowest one for most pressures. Wet scrubbing and wet scrubbing with heat recovery have very similar power output for all pressures. The binary cycle gives the lowest power output at pressures up to 30bar, and the second highest at pressures above 70bar.
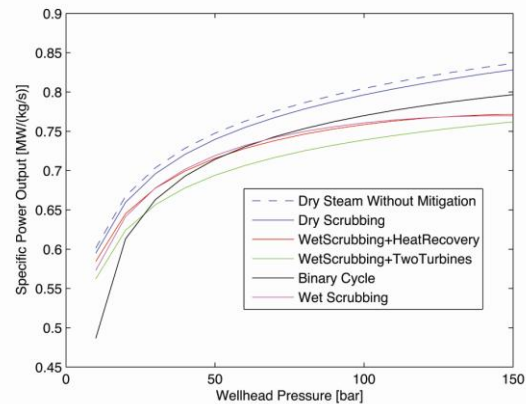

Figure 8 - Specific power production of the models, for a geofluid with enthalpy of 2900kJ/kg

Figure 9 shows the specific power output for all the mitigation methods handling a geofluid with enthalpy of 3600kJ/kg. It can be seen that dry steam scrubbing gives the highest power output at all pressures, while wet scrubbing gives the lowest one for most pressures. Wet scrubbing with heat recovery and wet scrubbing with an additional turbine have similar power outputs for all pressures, although the setup with the extra turbine produces relatively more power with increasing pressure. The binary cycle gives the second lowest power output at all pressures, but still significantly more than wet scrubbing.

The high exergy of the geofluid at the wellhead makes for a second law efficiency between 46-73%

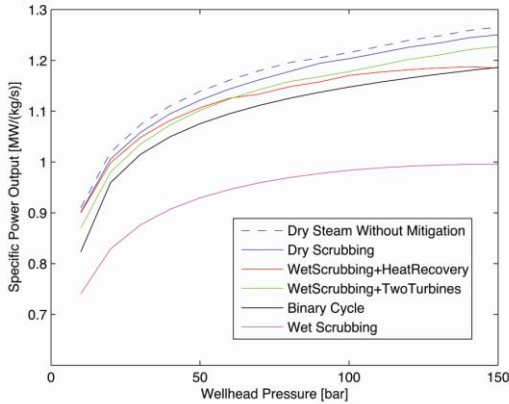for the power cycles. The first law efficiency is between 20-35%.

Figure 9 - Specific power production of the models, for a geofluid with enthalpy of 3600kJ/kg

CONCLUSIONS

It is obvious that dry scrubbing possesses great potential for increasing power output of individual wells, compared to the other corrosion mitigation techniques. As the enthalpy of the geofluid increases, the utilization efficiency of the traditional setup of wet scrubbing gets lower. Two strategies for wet scrubbing, heat recovery and an additional turbine, mitigate these losses and keep the power production slightly less than for dry scrubbing, and slightly higher than the binary cycle.

Exergy analysis shows that the exergy loss that takes place in wet scrubbing when the steam is cooled below the saturated vapor curve is compensated by the increase in mass flow rate as the scrubbing liquid is injected into the stream. The reason for the lack in performance of the traditional setup of wet scrubbing at higher enthalpies, compared to the other mitigation methods, is the decrease in turbine efficiency. The decrease in efficiency is because the turbine expansion is completely wet, while the in the other power cycles, the expansion is dry expansion and only partly wet expansion.

As the IDDP will get closer to its goals of finding even higher temperatures and enthalpy, the potential advantages of other corrosion mitigation methods than wet scrubbing will become more important. It has been shown that the destruction of superheat, caused by wet scrubbing at high enthalpies, may result in loss of considerate power, on the scale of several MW per well. It is clear that the IDDP may possesses potential for development in the geothermal industry. It has been shown that the first well, IDDP-1, is expected to produce around 8 times more power than a traditional borehole.

NOMENCLATURE

e	specific exergy (kJ/kg)
η_p	pump efficiency
η_{tw}	turbine efficiency working with wet steam
η_{td}	turbine efficiency working with dry steam
η_u	utilization efficiency
h	enthalpy (kJ kg^{-1})
h_f	enthalpy of saturated liquid (kJ kg^{-1})
h_g	enthalpy of saturated vapor (kJ kg^{-1})
h_{gf}	enthalpy of geofluid (kJ kg^{-1})
h_{cm}	enthalpy of cooling medium (kJ kg^{-1})
$\dot{m}$	mass flow rate (kg s^{-1})
$\dot{m}_{gf}$	mass flow rate of geofluid (kg s^{-1})
$\dot{m}_{cm}$	mass flow rate of cooling medium (kg s^{-1})
$\dot{m}_{wf}$	mass flow rate of working fluid (kg s^{-1})
$\dot{Q}$	heat rate (kJ s^{-1})
T	temperature (°C)
$\dot{W}_t$	turbine work rate (kJ s^{-1})
$\dot{W}_p$	pump work rate (kJ s^{-1})
x	quality of steam

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