PROCEEDINGS, 23rd Annual PNOC-EDC Geothermal Conference
Hotel Inter-Continental, Makati City, Philippines, March 13-14, 2002

COMPUTER MODELING OF MINDANAO I GEOTHERMAL POWER STATION FLUID CHEMISTRY AT MINDANAO GEOTHERMAL PRODUCTION FIELD, KIDAPAWAN CITY, PHILIPPINES

Gabriel M. Aragon

PNOC Energy Development Corporation, Merritt Road, Fort Bonifacio, Metro Manila 1201, Philippines

ABSTRACT

Investigation on the behavior of non-condensible gases in the cooling water circuit of Mindanao-1 power station was done using computer modeling. The power station utilizes the direct contact condenser in condensing the steam. The program used in the simulation work is CNOSR.

Different scenarios were modeled to determine the effects of (7) steam compositions on the pH and the concentration of dissolved H_2S on the condensate at the turbine outlet and (2) H_2S oxidation on the pH of circulating water and the amount of NaOH required to neutralize the acid generated. The predicted chemistries of the cooling water circuit were also compared with measured values.

The results showed that the pH of the liquid at the turbine outlet is primarily controlled by the amount of H_2S and NH_3 in the steam. Both NH_3 and H_2S gases in the steam show a linear ***relationship*** *with the concentration of dissolved H_2S in the condensate, though the change in the concentration of dissolved H_2S is more sensitive to the amount of NH_3 than the amount of H_2S gas.*

Oxidation of more than 10% of the dissolved H_2S in the cooling water ***circuit*** *gave unacceptable pH value of < 4.50 in the hotwell* ***fluid.*** *In this case, remedial action like NaOH dosing or biocide treatment is necessary. The calculated dosing rates of NaOH are 14, 29 and 72 g/kg steam-hour needed to neutralize the acid generated from 5, 10 and 30% oxidation of dissolved H_2S in the cooling water, respectively. The concentrations of dissolved H_2S in the condensates at various parts of the cooling circuit remained the same at all levels of H_2S oxidation due to large supply of H_2S coming from the vaporphase. The level of H_2S oxidation in the actual cooling water circuit of the power station is close to 30% based on the similarity of the analyzed concentrations of SO_4 to the* ***calculated*** *values.*

1.0 INTRODUCTION

Understanding the physical and chemical processes in the cooling water circuit is important in controlling the amount of absorption and emission of gases from the power station. By numerical modeling, the gas behavior in the cooling water circuit can be predicted. This paper examines the Mindanao-1 power station fluid chemistry by computer modeling.

There are few known softwares used for modeling the behavior of gases in contact with the circulating cooling water. CNDSR is the most widely used and has, the greatest flexibility. *Weres* developed CNDSR in the early 1980s using FORTRAN as the programming language. The accuracy with regards to predicting the partitioning of gases along the circuit was proven through the numerous modeling done by *Weres* (1983 and 1984), *Glover* and *Mroczek (1993* and 1995). Nowadays, modeling with CNDSR is almost a routine activity for checking the design flaws in cooling water circuit and estimating the gas emission to the environment by the power plant for environmental permit application prior to construction.

Numerical modeling of Mindanao-1 power plant cooling water circuit utilizing direct contact condenser is done using the CNDSR to correlate the impact of the steam composition to the chemistry of the cooling water circuit. Emphasis is given to the pH and the amount of dissolved H_2S in the liquid because these are the key parameters that **affect** the quality of the fluid along the cooling circuit. **Outputs** of numerical modeling are also evaluated to explain the partitioning of gases in liquid and vapor in different parts of the power plant. The following levels of H_2S oxidation: 5%, 10% and

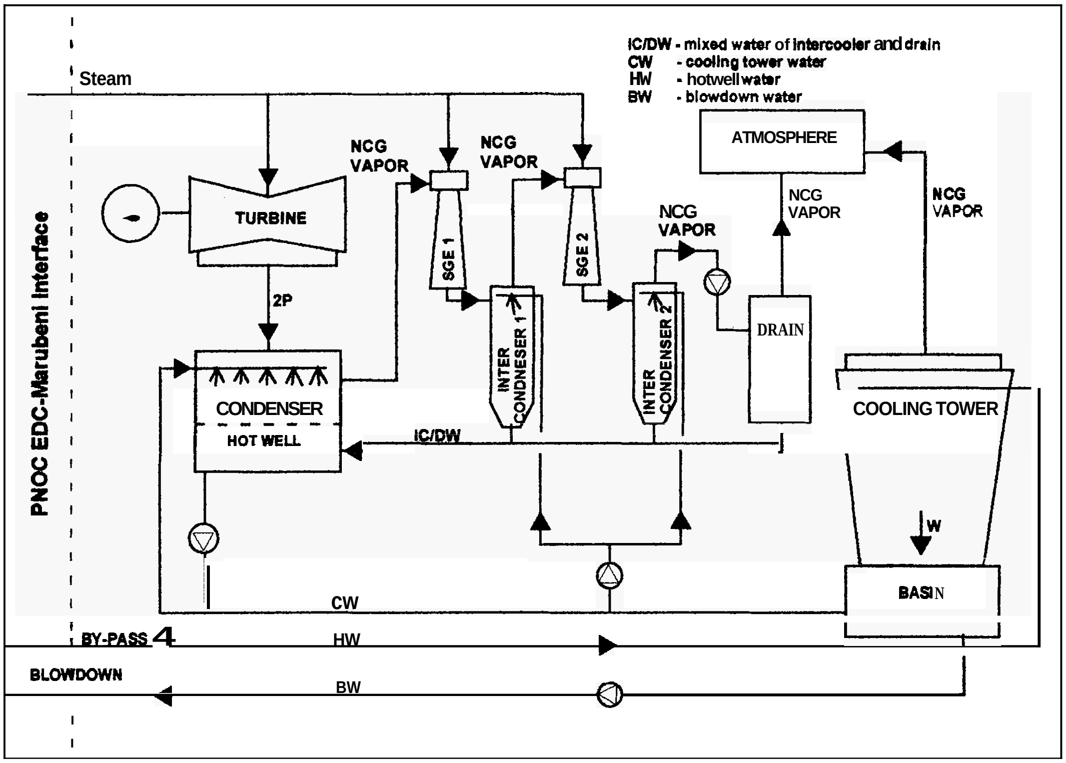

Figure 1. Simplified process flow of 52 MWe Mindanao-1 power plant

30% are simulated to determine the resulting acidity of the circulating liquid as shown in the pH drop and level of sulfuric acid produced. The 5% level of H_2S oxidation was the established value by Glover (1979) considering no bacterial activity present in the cooling circuit. *Weres* (1983) from his experience has given the range of 10 to 30% as the level of H_2S oxidation in cooling circuit without biocide treatment. The first part of the study deals with the sensitivity analysis of input steam chemistry to pH and dissolution of H_2S in the condensate at the outlet of the turbine using one box model. The second part deals with the detailed chemistry simulation of cooling water using the actual power plant design with and without oxidation of H_2S.

2.0 MINDANAO-1 POWER STATION PROCESS FLOW

The Mindanao-1 power station is located in the southern part of the Philippines inside the 701 hectares geothermal reservation at the western flank of Mount Apo. The power plant was built under BOT partnership with Oxbow-Marubeni and commissioned in year 1996. PNOC-EDC as the steam field operator delivers 370 tons of steam per hour to the plant to generate the 52 MWe base load capacity. Marubeni operates the power plant for a ten-year contract terms which upon completion the ownership will be transferred to PNOC-EDC.

Figure 1 below shows the simplified process flow diagram. The steam enters the condensing turbine at an inlet pressure of 6.89 bar abs and exits at 0.1 bar abs into direct contact condenser. Inside the condenser, the steam is partially condensed by a counter-current flow of re-circulating water coming from the cooling tower basin. The condensates accumulate in the catchment basin inside the condenser called the hotwell. The residual steam and bulk of the non-condensible gases are taken up by the two-stage steam gas ejector (SGE) system. There are intercondensers attached to the steam gas ejectors that cool and condense further the residual steam and gas, plus the additional steam used in the ejector. The liquids formed in the gas ejector system including from the drain are directed back to the hotwell. Almost dry NCG are vented to the atmosphere from the drain separator.

The mixed fluids from the hotwell are cooled to temperature slightly higher than ambient temperature in a mechanical-draft cooling tower using a large volume of air. The cooled water collected to the coding tower basin where the water level is maintained by pumping excess water into thermal pond and then reinjected to RI well.

In the six years of operation, different problems are encountered related to the fouling of the cooling water circuit. These are corrosion of the alveneous pipes transporting the condensates to the cold reinjection line, deposition of elemental sulfur in the cooling tower and spray nozzles in the condenser that minimize the efficiency of the cooling circuit and increase consumption of NaOH through time. Oxidation of dissolved H_2S in the circulating water to sulfuric acid and elemental sulfur through bacterial action or inorganic means produces hydronium ions and elemental sulfur precipitates that decrease the pH of the condensates to unacceptable level and pose potential debris in the cooling circuit, respectively.

3.0 METHODOLOGY

Two modeling strategies were applied in the numerical simulation: one box and multi-box models. The 'one box' model determines the effects of steam compositions to the condensate chemistry in the outlet of the turbine. On the other hand, the 'multi-box' model represents the cooling circuit and determines the distribution of gases, the chemistry of the circulating water, and the effects of dissolved H_2S oxidation to pH and the amount of NaOH needed to neutralize the acid generated.

3.1 One box Model: Turbine Outlet

The input file for the one box model is easier to create than the multi-box model. However, the one box model is limited only to a single component of the cooling water system thus multiple inputs need to be integrated to a single input by heat and mass balance.

The one box model can be directly applied to the turbine outlet. Modeling of the turbine outlet can be used to assess the effect of steam composition on the pH of the condensate. It will also give the baseline composition of the turbine condensate without considering the effect of the cooling water circuit.

There are two options offered by CNDSR in simulating the carbonate chemistry. The first option deals with partitioning of CO_2 between liquid and vapor considering the kinetics of CO_2 dissolution or hydration. This can be used if the residence time of the fluid in the turbine outlet is known. The other option is the full equilibrium calculation that assumes that CO_2 in the liquid reaches the equilibrium concentration (maximum solubility) and CO_2 hydration proceeds to completion. The option selected will -greatly affect the results because the dissolution of CO_2 is a slow reaction ***(Weres,*** 1983). In modeling the chemistry of the condensate at the outlet of the steam turbine, the first option is selected because the residence time of the fluid in the turbine is small so that full equilibration of the CO_2 gas in the liquid phase does not exist. This is justifiable because the ratio of vapor to liquid is very high in the turbine outlet and formation of the condensate happens in a split of a second. This leads to incomplete liquid-vapor contact.

3.2 Multi-box Model: Cooling Circuit

CNDSR models gas partitioning and transport in the cooling water circuit using the box configuration shown in Figure 2. The boxes represent the different parts of the reaction path and the mixing points in a simplified process flow diagram illustrated in Figure 1.

The steam gas ejector and the intercondenser are combined in a single box. The main condenser is divided into two parts, the condenser and hotwell showing the actual design wherein the mixtures of condensed steam and cooling water are separated from the residual steam plus NCG by baffles. A dummy box named 'RXN BOX' is added in the model to simplify the simulation of chemical reactions. This eases the calculation involving other external inputs to the system e.g. sodium hydroxide dosing.

The heat content of each box is maintained and the heat is removed only in the cooling tower through the discharged of the heated air into atmosphere so the atmosphere above the cooling tower represents the heat sink. This assumption implies that all of the piping in the power plant is fully insulated. Thus changes in

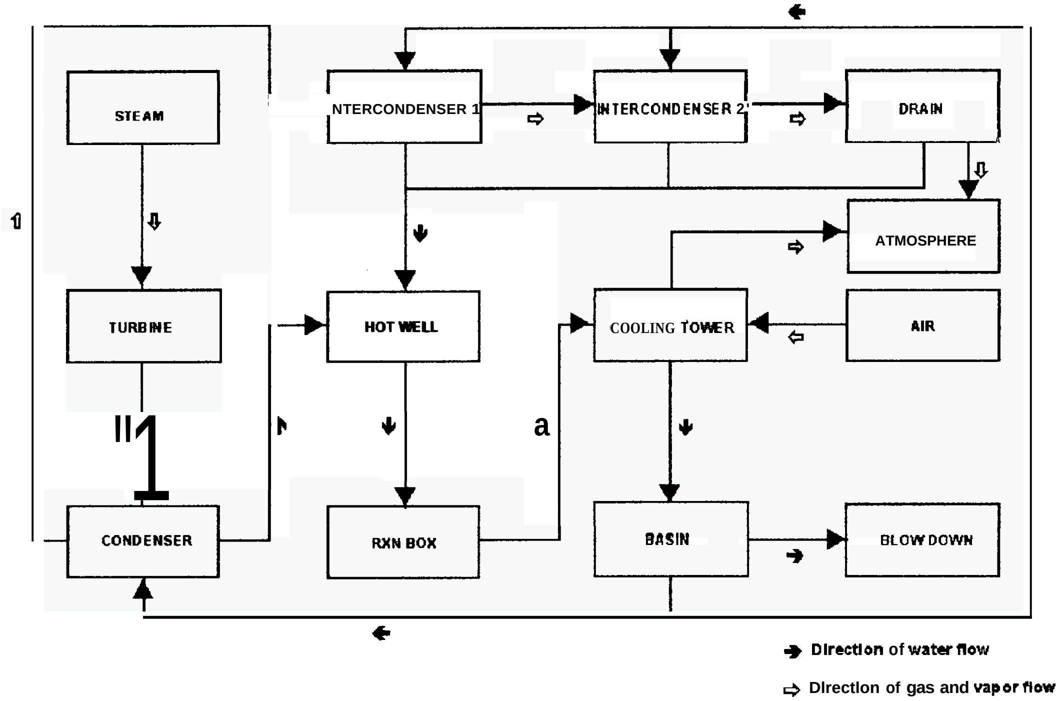

Figure 2. Mindanao-1 power plant multi-box model for CNDSR input file.

temperature are simply, functions of mass and temperature of the cooling water and steam (+ air in case for cooling tower). All of the calculation results are normalized using one-kilogram steam entering the turbine.

The option selected in this modeling is full equilibration with respect to CO_2 starting from the condenser box. The program calculates CO_2 partitioning without invoking kinetic data. This approach is reasonable because the liquid in the condenser, intercondensers and cooling tower are always in close contact with the vapor phase, which allows sufficient time for CO_2 to equilibrate. Furthermore, assessment of kinetic effects of CO_2 hydration requires the residence times of the fluid in all of the boxes and these data are not available.

The natural steady state chemistry of the cooling water circuit was initially modeled. This determined the effects of the present steam chemistry and the designed operating parameters to the distribution of gases in the system and the acidity of the cooling waters at different parts of the cooling circuit. The succeeding simulations invoked oxidation of H_2S at different levels. There are many possible products of H_2S oxidation and these are thiosulfate, elemental sulfur and sulfuric acid. The oxidation process is either aided by bacteria or through inorganic means. Inorganic oxidation is a slow reaction thus bacterial oxidation is a dominant pathway in most of the cases. The first level of dissolved sulfide oxidation is 5% this value was determined experimentally by Glover (1979) where bacteria were killed by biocide. This level of oxidation can be considered as the maximum extent of inorganic oxidation. The second and third levels of dissolved sulfide oxidation are 10 and 30%, these range of values were established by *Weres* (1983) as the common range of total dissolved sulfide oxidations (inorganic and bacterial oxidations) based on his previous works. The oxidation of dissolved sulfide produces sulfuric acid in all of the cases simulated. Aside from oxidation, the amount of NaOH needed to neutralize the acid produced due to H_2S oxidation and the effect of adding NaOH to the chemistry of the cooling water were also determined.

4.0 CHEMICAL AND PHYSICAL PARAMETERS

The data shown in Table 1 are the calculated mean values obtained from steam composition data for three consecutive years of operation. All sampling of steam and gas analyses were done by PNOC-EDC. The residual gases (He, H_2, N_2, CH_4 and Ar) are not included in the simulation because of the minimal effect to circulating water chemistry. In all simulations the same steam chemistry are used except when specified.

The physical parameters in Table 2 and the liquid flow rates in the circuit are taken from the heat balance diagram of the Mindanao-1 power station at 100% load. Other data like enthalpy at the exit of the turbine, wetness and mass of air in the cooling tower are calculated using the physical data provided.

5.0 RESULTS AND DISCUSSIONS

5.1 Chemistry at the Turbine Outlet

Removing one at a time the non-condensible gases from the input file for one box calculation, the effect of steam compositions to pH of the condensate at the outlet of the turbine was determined. The results are tabulated in Table 3. Calculation showed that the pH of the condensate is dependent on the amount of H_2S and NH3 gases present in the steam. The pH of the condensate decreased when NH3 was removed from the steam chemistry. In contrast, removal of H_2S gas from the steam input increased the pH of the condensate. There was no significant change in the pH when CO_2 gas was not included in the calculation. Absence of non-condensible gases gave a pH value of 6.70 while presence of these gases gave a highly alkaline pH of 8.21. This high pH value is due to high solubility and buffering effect of NH_3 gas.

The amount of dissolved H_2S in the condensate is governed by the partial pressure of H_2S, which is proportional to the influx of H_2S gas in the steam (Table 4). Increased concentration of dissolved H_2S is observed in the resutt of simulation when the amount of H_2S gas in the steam is increased. Another factor that affects the concentration of dissolved H_2S is the amount of NH3 gas (Table 5). The solubility is enhanced due to neutralization reaction of dissolved NH_3 and H_2S. The extent to which dissolved NH_3 affects the solubility of H_2S depends also with pH. At pH 6.7, dissociation doubles the solubility of H_2S; at pH 8.7, it increases the solubility a hundred fold (*Weres,* 1983). The CO_2 gas has

Table 1. Mean compositions of major constituents

	c02 mmol/100 mol	H_2S mmol/100 mol	NH_3 mmol/100 mol
M1GP Interface	250±50	7.50±2	0.30±0.1

'able 2. General physical parameters.

Steam flow from turbine	
Rate (kg-H_2O/s)	103
Enthalpy (kJ/kg)	2119
Wetness (%)	19
Exit pressure (bars abs.)	0.097
Motive Steam Enthalpy (kJ/kg)	2232/2344
Wet bulb temperature (°C)	18.3
Dry bulb temperature (°C)	26.7
Relative Humidity, %	98
Atm. pressure (bar abs.)	0.85
Mass of air in the cooling tower, kg per kg steam inlet	–30

Table 3. Predicted pH of the condensate at turbine outlet.

Scenarios	pH @ 45°C
With all NCG	8.21
NH_3 removed	6.38
CO_2 and NH3 removed	6.41
H_2S and NH3 removed	6.63
Without NCG	6.70

H_2S mmol/100 mol	pH @ 45°C	Dissolved H_2S ppm
7.5	8.21	0.65
10.0	8.16	0.77
15.0	8.09	0.98
25.0	7.99	1.33
30.0	7.95	1.48

Table 5. Effect NH3 content in steam to condensate pH and dissolved H_2S at turbine outlet.

NH_3 mmol/100 mol	pH @ 45°C	Dissolved H_2S ppm
0.30	8.21	0.65
0.40	8.27	0.73
0.50	8.32	0.83
0.60	8.36	0.90
0.80	8.42	1.03

CO_2 mmol/100 mol	pH @ 45°C	Dissolved H_2S ppm	Dissolved Co_2 ppm
250	8.21	0.65	0.28
300	8.21	0.65	0.34
350	8.21	0.65	0.38
400	8.21	0.65	0.45
450	8.21	0.65	0.51

BOX	t°C	pH	Water Flow kg/s	CO_2	H_2S	NH_3
				mg/kg		
Turbine Outlet	45	8.21	0.19	0.29	0.64	0.57
Condenser	44	6.28	41.8	12.0	0.53	2.34
Intercondenser 1	55	5.66	0.87	31.3	1.85	2.29
Intercondenser 2	51	4.73	0.72	251	15.1	2.33
Drain separator	73	4.16	6.7E-5	499	31.9	0.13
Hotwell	45	6.05	43.4	16.3	0.79	2.34
Cooling Tower	33	7.56	43.4	6.10	0.01	2.33
CT Basin	31	8.66	42.4	3.81	0.008	2.28

little effect to the amount of dissolved H_2S (Table 6). The solubility of CO_2 gas in the condensate is also governed by its partial pressure. Thus, increasing the influx of CO_2 gas in the steam increases the amount of C02 dissolved in the condensed steam. High amount of dissolved CO_2 will lower the pH of the condensate. At lower pH, NH_3 exist as NH_4^+ ions and reaction of H_2S to NH_3 is not possible. Theoretically, increasing the amount of CO_2 gas will decrease the H_2S solubility however, since kinetic dictates that the hydration of CO_2 gas is a slow process the effect of CO_2 gas to the amount of dissolved H_2S is not observed.

5.2 Steady State Chemistry of the Cooling Water Circuit

The results of the calculation are shown in Table 7. The chemistry in the turbine outlet is significantly different compared to the parts of the power station that are involved in the cooling circuit. The condensate has alkaline pH and very low amount of dissolved gases. This could have been the typical chemistry of the cooling water if it is not circulated back to the system. However, due to absence of large amount of fresh water source because the project is situated in the mountainous area and limited reinjection wells, circulation of cooling water is a practical choice.

Hart (1980) pointed out that there are two regimes that control the solubility of non-condensible gases in the cooling water circuit. These are the absorption and stripping regimes. The absorption regime dominates in the high pressure and low temperature environment while the stripping regime dominates in the low pressure and high temperature environment. In the stripping regime the solubilities of gases are lower while higher in the absorption regime. In agreement with these, the high concentrations of dissolved gases occurred in the intercondensers and the drain separator due to high pressure and low temperature. Lower calculated pH values were also obtained in these locations since increasing the solubility of gases decreases the pH due to dissociation of weak acids. The water in the drain separator has the highest aqueous concentration of gases (except NH_3). This makes the liquid in the drain separator the most acidic in the cooling circuit. However, due to very low water flow, the effect to the whole cooling water circuit is minimal. The amount of dissolved gases in the intercondenser 2 is relatively high compared to hotwell and intercondenser 1. The reason for this is the increase in pressure to 0.48 bar abs, which is twice the value of intercondenser 1 and the temperature decline to 51 °C. The increase in pressure coupled with temperature decline greatly increased the concentration of the dissolved gases. Controlling the amount of cooling water going to the intercondenser 2 might lower the amount of dissolved gases in the hotwell.

BOX	t°C	pH	Water Flow kgls	CO_2	H_2S	NH_3	SO_4
				mg/kg			
Turbine Outlet	45	8.21	0.19	0.29	0.64	0.57	
Condenser	44	5.75	41.8	7.81	0.44	4.84	11.9
Intercondenser 1	55	5.16	0.87	27.4	1.77	4.75	11.6
Intercondenser 2	51	4.42	0.72	245	15.2	4.81	11.7
Drain separator	73	4.16	6.7E-5	502	32.8	0.12	
Hotwell	45	5.51	43.4	12.2	0.72	4.86	11.8
Cooling Tower	33	6.96	43.4	1.76	0.004	4.82	11.9
CT Basin	33	6.96	42.4	1.80	0.005	4.92	12.1

BOX	t°C	pH	Water Flow kgls	C02	H_2S	NH_3	SO_4
				mg/kg			
Turbine Outlet	45	8.21	0.19	0.29	0.64	0.57	
Condenser	44	4.72	41.8	6.25	0.41	7.73	22.6
Intercondenser 1	55	4.56	0.87	26.0	1.75	7.58	22.1
Intercondenser 2	51	4.21	0.72	244	15.4	7.66	22.4
Drain separator	73	4.15	6.7E-5	502	33.2	0.12	
Hotwell	45	4.69	43.4	10.7	0.69	7.72	22.6
Cooling Tower	33	4.70	43.4	0.34	0.002	7.88	23.2
CT Basin	31	4.70	42.4	0.34	0.002	7.85	23.2

Ammonia behaves differently from the other non-condesible gases because of its high solubility to water. The concentrations of dissolved NH_3 in all of the boxes have similar values except for the drain separator. The absence of NH_3 in the drain separator is due to complete absorption of this gas in the liquid separated in intercondenser 2. Complete absorption of NH_3 gas from the vapor is possible because of the acidity created by dissociation of acid gases (H_2CO_3 and H_2S). The solubility of NH_3 gas in intercondenser 2 is now governed by the chemical reaction, not simply due to partial pressure and temperature, and the reaction of this gas to hydronium ion almost proceeds to completion to form NH_4^+.

There is a sharp drop in concentration and total amount of gases in the cooling tower water compared to the upstream chemistry (hotwell). This section of the power plant may also operate in the stripping regime, but under circumstances different from the one described by *Hart* (1980). The cooling tower may be divided into three horizontal sections:top, middle and bottom, to explain the step by step the mechanisms of stripping. In the top section of the cooling tower the unionized species (CO_2 and H_2S) and 'free' species (NH_3) are immediately stripped away. When the degassed fluid goes to the middle section, the fluid adjusts to a new equilibrium condition by favoring the reaction path that produces the chemical species that are being taken out from the liquid. This leads to decrease in hydronium ion concentration and increase in the pH. These newly produced unionized and free species will be stripped again in the bottom section. Thus the highest pH is observed in the cooling tower basin wherein the most concentrated dissolved gas is NH_3.

5.3 Oxidation of H_2S to H_2SO_4

The products of dissolved sulfide oxidation are thiosulfate, elemental sulfur and sulfuric acid. All of these oxidation reactions produced hydronium ions that decrease the pH of the cooling water in the circuit. It this paper, oxidation of dissolved sulfide to H_2SO_4 was calculated because it is easy to quantify the actual extent of oxidation by measuring the level of sulfate in the cooling water. However, the projected oxidation level might be the minimum value since other oxidation products were not taken into account.

The chemistries of the cooling water circuit at different oxidation levels were tabulated in Tables 8 to 10. Generally, the pH of the condensates in all of the sections of the cooling circuit decreases as the oxidation level

- The pH in the hotwell, considering only the gas distribution of gases and the composition of steam has a slightly acidic value of around 6.0.
- Five percent oxidation of dissolved H_2S in the hotwell will give a pH value of 5.5 while oxidation to 10 and 30% give pH values lower than 4.5.
- Oxidation of H_2S to 30% matched the level of actual sulfate concentration in the power plant condensate, suggesting that the level of oxidation is close to this value.
- Increasing concentration of H_2S in the cooling water circuit will be expected in the future due to increasing trend of H_2S in the steam.

REFERENCES

Glover, R.B. (1979). Some aspects of experimental chemistry of the direct contact condenser and cooling tower circuit pilot plant at Ohaaki. Proceedings N.Z. Geothermal Workshop, Part 1, 227-232.

Glover, R.B. and Mroczek, E.K. (1993). Impact of steam chemistry on power plant development at Ohaaki, Mokai, Rotokawa and Tauhara geothermal fields. Proceedings 35th N.Z. Geothermal Workshop, pp. 133-138.

Hart, W. (1980). Control of gas absorption in geothermal steam direct contact condenser. Geothermics, 9, 271-277.

Mroczek, E.K. and Glover, R.B.(1995). Impact of fluid chemistry on power development at Rotokawa, New Zealand. WGC.

Sanada, N., Y. Kurata, H. Nanjo, J. Ikeuchi and Kimura, S. (1998). Corrosion in acidic geothermal flows with high velocity. Proceedings 20th NZ Geothermal Worshop.

Weres, O. (1983) Documentation for CNDSR. Report LBL-11377. Lawrence Berkeley Laboratory, Berkeley, California LBID-622

Weres, O. (1983). The partitioning of hydrogen sulfide in the condenser of Geyser unit 15. Geothermics, 12(1), pp. 1-15.

Weres, O. (1984). Numerical evaluation of contact and hybrid condensers for geothermal power plats. Geothermics, 13, pp. 305-318.

Weres, O. (1984). Numerical evaluation of surface condensers for geothermal power plants. Geothermics, 13, pp.