IMPACT OF STEAM CHEMISTRY ON POWER DEVELOPMENT AT OHAAKI, MOKAI, ROTOKAWA AND TAUHARA GEOTHERMAL FIELDS

R.B. GLOVER AND E.K. MROCZEK

Institute of Geological and Nuclear Sciences Ltd., Wairakei

SUMMARY - Power station chemistry in a direct contact condenser and binary plant heat exchanger was modelled using gas compositions typical of steam from Ohaaki, Mokai, Rotokawa and Tauhara geothermal fields at an arbitrary flow rate of 100 tonnes/hr. The partitioning of gases and the condensate chemistry was directly related to the gas partial pressures and the concentration of ammonia in the steam. Oxidation of 30% of the dissolved sulphide to sulphuric acid in the direct contact condenser circuit required dosing with 20 kg/hr NaOH for Rotokawa, 11 kg/hr for Mokai and 7 kg/hr for Tauhara and Ohaaki type steam to maintain acceptable pH values (about 6) around the circuit. Mokai and Tauhara steam condensed in the heat exchanger to form acidic solutions at pH 4 and 4.5 respectively. Ohaaki and Rotokawa steam contains higher concentrations of ammonia so this type of steam condensed to form a less acidic fluid at pH 5.

1. INTRODUCTION

The transport and partitioning of geothermal gases in a geothermal power plant is greatly influenced by the steam chemistry as well as the condenser design.

To illustrate the effects of steam composition on power station chemistry, steam from Ohaaki, Mokai, Rotokawa and Tauhara geothermal fields is used to model the chemistry (a) in a simplified direct contact condenser and cooling water circuit loop and (b) in steam condensate in a heat exchanger of a binary plant.

The main components of steam extracted from these geothermal fields which are all located in the Taupo Volcanic Zone are carbon dioxide (CO_2) with lesser amounts of hydrogen sulphide (H_2S), ammonia (NH,), nitrogen (N_2) and methane (CH_4). All these gases dissolve in solution in proportion to their partial pressures. This was proved experimentally in the Ohaaki Pilot Plant by Glover (1979). However since ammonia is highly soluble it completely dissolves in the condensate. As a consequence the total solubility of the acid gas H_2S is increased by reaction to form bisulphide (HS^-). Oxidation of the dissolved sulphide species to sulphuric acid can result in a low condensate pH (< 3) which would require expensive remedial biocide or caustic dosing. CO, is also an acid gas which would counteract the effect of ammonia by decreasing the solubility of H_2S. However at very short residence times the effect of carbon dioxide may be limited by the slow rate of hydration of dissolved CO, to form carbonic acid (Weres 1983a). Therefore the proportion of ammonia to the acid gases is important in determining the condensate chemistry.

Condenser design and operation are also critically important for achieving low absorption of gases and minimizing oxidation of H_2S. In a direct contact condenser low gas absorption is difficult to achieve because of the large ratio of cooling water to steam. Maintaining the saturated vapour pressure of water (SVP) within 10 mba of the condenser pressure reduces gas absorption (Glover 1979, Hart 1980). Designing the cooling water sprays to efficiently strip dissolved oxygen from the aerated condensate minimizes downstream oxidation. Weres (1983a, 1984) found that in a surface condenser the venting of gases in proportion to the amount of steam condensed at different stages greatly improved the partitioning of H_2S into the vapour phase.

2. POWER STATION MODELS

2.1 Introduction

Recently various prospective developers have applied to develop Tauhara and Rotokawa geothermal fields for power production. The documents (Works Geothermal 1992a, 1992b) presented as part of the planning consent process contained details of the proposed generation schemes as well as the likely steam compositions from the various fields. Generally two power generation options were proposed. In the first option steam passes through a high pressure (HP) turbine then into a heat exchanger low pressure (LP) turbine binary plant loop. In the second option, after the HP turbine, the steam passes into a LP turbine and is condensed in a direct contact condenser. The condensate then circulates through a direct contact cooling tower to strip out the dissolved gases.

An estimate of typical Mokai gas chemistry was obtained from Henley and Glover (1982), Plum and Henley (1983), Henley and Middendorf (1985) and IGNS open files. As no operating or performance data of the Ohaaki power station has been published the steam chemistry was estimated from an 1978 average steam well composition (IGNS 1978).

The two generation options were simplified and modelled using the computer programs HOTCOND, COCO (Glover

1982) and CNDSR (Weres 1983b). As a basis for comparison the same set of typical operating conditions at an arbitrarily chosen flow rate of 100 tonnes/hr LP steam was used in the calculations for all the geothermal fields. No account was taken whether 100 tonnes/hr was a reasonable rate of steam flow from these fields.

2.2 Chemical and Physical Input Parameters

The composition of steam from the various fields is presented in Table 1. The total gas content varies from a high of 4% for Ohaaki to less than 0.2% for Tauhara steam.

The simplified conceptual model of the direct contact condenser and cooling tower circuit is presented in Figure 1 and the physical parameters are listed in Table 2. The flow of air through the cooling tower was initially adjusted to provide a condensate temperature at the condenser outlet a few degrees lower than the temperature corresponding to a saturated vapour pressure of 0.1 ba. Once determined, the air flow was fixed at the same level for all the calculations. This meant that the blowdown, evaporation and condensate flows throughout the circuit were similar in each of the four direct contact condenser models. Temperatures throughout the circuit varied slightly between the models for reasons which are discussed below.

The binary plant heat exchanger model was much simpler than the contact condenser model. It was assumed that the steam was cooled, in one step without venting of gas, to a final total pressure of 2 ba and a final temperature of 50°C.

2.3 Types of Calculations

In the direct contact condenser the partitioning of water, heat and each gas between the liquid and vapour phases was calculated simultaneously with the acid base equilibria assuming each part of the circuit was in steady state thermal and chemical equilibrium. The results of these calculations are presented in Tables 3 to 6. The second set of calculations involved oxidizing 30% of the total sulphide to sulphate in the combined flow from the condenser and gas coolers. The resulting sulphuric acid (H_2SO_4) was exactly neutralized with sodium hydroxide (NaOH) to raise the pH back up to unoxidized levels. The rates of NaOH dosing and final concentrations of $SO_4^=$ and Na+ are presented in Table 8. The quantities of gas stripped from the condensate in the cooling tower and vented to atmosphere from the aftercooler are presented in Table 9 and the final output partitions of the total incoming gases are given in Table 10.

The gas partitioning and condensate chemistry in the binary plant heat exchanger was calculated assuming chemical equilibrium. The total enthalpy of the steam was reduced until the final temperature was 50°C at a total pressure of 2 ba. The chemical data for the binary plant heat exchanger is listed in Table 11.

Table 1 : Gas Flows (kg/hr). Total steam flow 100 tonnes/hr.

	CO,	H_2S	NH_3	N_2	CH_4
Ohaaki	3912	41	3.7	13	18
Mokai	612	23	0.2	14	3.0
Rotokawa	2189	76	3.4	27	18
Tauhara	185	10	0.9	5	

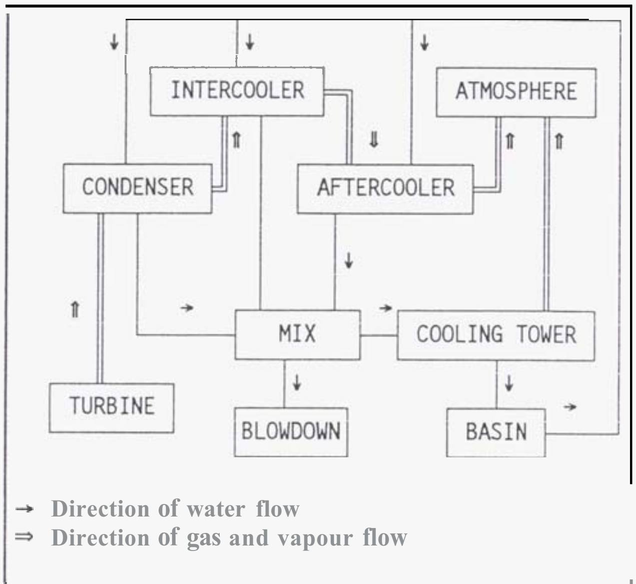

Figure 1 : Direct Contact Condenser Cooling Water Circuit

Table 2 : Direct Contact Condenser Physical Parameters

Pressure (bars absolute) :-	
- Condenser	0.1
- Intercooler	0.3
- Aftercooler	1.05
Steam flow (tonnes/hr)	100
Steam enthalpy (kj/kg)	2263
Condensate flow (tonnes/hr) to :-	
- Cooling tower	4500
- Blowdown	34
- intercooler	178
- aftercooler	178
- evaporation	66
Wet Bulb ("C)	7.5
Dry Bulb	12

Table 3 : Ohaaki Direct Contact Condenser Circuit Chemistry

	t (°C)	pH	H_2S	NH_3 (ppm)	CO_2
Condenser	42.5	6.7	0.9	15.0	53
Cooling tower	31.5	8.1	0.2	14.4	33
Intercooler	53.8	5.8	4.1	13.9	148
Aftercooler	36.6	4.9	29	14.3	1077
MIX*	42.7	6.1	2.1	15.0	97

* Combined flow from condenser, intercooler and aftercooler

Table 4 : Mokai Direct Contact Condenser Circuit Chemistry

	t (°C)	pH	H_2S	NH_3 (ppm)	CO_2
Condenser	43.4	6.1	1.1	2.4	15
Cooling tower	31.5	7.4	0.1	2.4	6.4
Intercooler	38.6	4.8	17	2.4	194
Aftercooler	31.7	4.3	48	2.4	886
MIX	42.3	5.4	3.5	2.4	56

3. RESULTS AND DISCUSSION

3.1 Direct Contact Condenser

3.1.1 Circuit Temperatures

The same heat and mass fluxes should result in comparable temperatures in the circuit when utilizing steam at the same enthalpy from the four geothermal fields. However the calculated temperatures in the condenser and intercooler are lower and higher respectively for Ohaaki and Rotokawa steam. For steam with a higher gas content there is a higher non-condensable gas flux and consequently a higher flow of residual water vapour and heat from the condenser to the intercooler. Thus the calculated steady state temperature in the condenser is lower, and, in the intercooler higher, than for steam with the same enthalpy but with a lower gas content. Controlling the temperature (or total pressure) in the condenser is critical for minimizing absorption of gas in the condensate (Hart **1980).** This is because the partial pressure of the gases decreases as the vapour pressure of water approaches the condenser pressure. The change in dissolved gas solubility with increasing temperature for the Rotokawa circuit is listed in Table **7.** Between **40** and **45** "C the total dissolved sulphide concentration decreases from **3.3** to **1.7** ppm. Although **this** may seem like a negligible amount the difference is equivalent to **7** kg/hr less H_2S dissolved in the cooling water. Potentially there is considerably less sulphide available for oxidation to sulphur and sulphuric acid. Minimizing CO_2 adsorption also has the beneficial effect of raising the condensate pH.

Table 5 : Rotokawa Direct Contact Condenser Circuit Chemistry

	t (°C)	pH	H_2S	NH_3 (ppm)	CO_2
Condenser	42.8	6.7	2.5	14.1	47
Cooling tower	31.5	8.1	0.4	13.6	31
Intercooler	48.6	5.7	15	13.3	174
Aftercooler	33.4	4.8	84	13.4	1075
MIX	42.7	6.1	6.2	14.1	92

Table 6 : Tauhara Direct Contact Condenser Circuit Chemistry

	t (°C)	pH	H_2S	NH_3 (ppm)	CO_2
Condenser	43.5	6.7	1.2	5.8	20
Cooling tower	31.5	7.8	0.1	5.8	14
Intercooler	34.6	5.3	12	5.8	157
Aftercooler	31.6	4.9	15	5.8	414
MIX	42.7	6.0	2.1	5.8	41

Table 7 : Change in Direct Contact Condenser Chemistry as Water Vapour Pressure Approaches 0.1 ba.

t (°C)	pH	H_2S (ppm)	CO_2 (ppm)	p_g (ba)
Rotokawa				
40.2	6.5	3.3	58	0.026
41.3	6.6	3.0	54	0.021
42.9	6.8	2.4	47	0.014
44	7.0	2.0	42	0.009
44.9	7.2	1.7	38	0.005

3.1.2 pH Values

The change in condensate pH around the circuit is similar for Ohaaki, Rotokawa and Tauhara. In the condenser the absorption of CO_2 is balanced by the dissolved ammonia resulting in a near neutral pH. In the Mokai circuit the lower concentration of ammonia (dissolved molar ratio CO_2:NH_3 **3** times higher than for the others) means that the condensate pH is **1** pH unit lower around the circuit. In the cooling tower the process occurring in the condenser is reversed with the gases being stripped out of solution with a consequent rise in pH. Conditions in the intercooler and particularly the aftercooler are much more severe with lower condensate pH and very high concentrations of dissolved gas due to the higher gas partial pressures. Since the flow through these parts of the circuit is only 8% of the total flow there is only a moderate effect on the combined flow from the condenser and gas coolers. The actual conditions in the gas coolers may be less severe than the calculated

Table 8 : Oxidation of 30% H_2S in MIX, pH Adjusted to Unoxidized Levels by Dosing with NaOH

	NaOH Dose Rate (kg/hr)	$SO_4^=$ (ppm)	Na^+ (ppm)
Ohaaki	6.8	245	117
Mokai	11.3	409	196
Rotokawa	19.8	709	340
Tauhara	6.7	242	116

Table 9 : Gas Flows (kg/hr) To Atmosphere from the Aftercooler and Stripped from the Condensate in the Cooling Tower

	Aftercooler		Stripped	
	H_2S	CO_2	H_2S	CO_2
Ohaaki	32	3612	6.2	292
Mokai	6.9	387	11	225
Rotokawa	50	1901	18	277
Tauhara	0.7	61	6.4	122

Table 10 : Output Partitions (%) of Total Gas Flow - Direct Contact Condenser

	Atmosphere	Blowdown	Oxidation
Ohaaki			
H_2S	92.9	0.1	7.0
NH_3	85.7	14.3	
CO_2	99.9	<0.1	
Mokai			
H_2S	78.3	0.3	21.4
NH_3	60.9	39.1	
CO_2	99.9	0.1	
Rotokawa			
H_2S	88.8	0.2	11.0
NH_3	84.6	15.4	
CO_2	99.9	0.1	
Tauhara			
H_2S	70.9	0.5	28.6
NH_3	79.5	20.5	
CO_2	99.9	0.1	

equilibrium conditions because of the relatively shorter condensate residence time and large gas to condensate ratio compared to the main condenser. The gas partial pressure in the condenser controls the concentrations of dissolved H_2S and CO_2. The flux of H_2S in Ohaaki steam is approximately double that of Mokai steam, yet the total dissolved H_2S concentration for the latter is higher even though the total dissolved NH_3 is considerably less. The partial pressure of H_2S in the condenser for Ohaaki steam is approximately 1% of the total gas compared to 3% for Mokai steam.

3.1.3 Oxidation of Sulphide

The absolute concentration of dissolved sulphide in the condensate is however very important because the oxidation of sulphide to sulphur can lead to deposition of sulphur in pipes and nozzles throughout the circuit and require removal prior to reinjection. Further oxidation of sulphur to sulphate or direct oxidation of sulphide to sulphate can result in highly corrosive condensate. The formation of sulphur is most favoured in the gas coolers due to a decrease in pH or in the cooling tower where a combination of cooling and evaporation could result in supersaturation with respect to elemental sulphur. The rate of inorganic oxidation of sulphide through to sulphate is much slower than bacterial oxidation by sulphur oxidizing bacteria (mainly Thiobacillus thio oxidans). In pilot plant studies Glover (1979) showed that by dosing with biocide less than 5% of the total oxidized sulphate was formed by inorganic means.

No kinetic data is available to adequately model the oxidation of sulphide. Practical experience indicates that between 30 and 60% of the total sulphide entering the hotwell ("MIX" in Figure 1) may be expected to be oxidized to thiosulphate and sulphate. In these models it was assumed that 30% of the dissolved sulphide in MIX was oxidized to sulphate. Under these conditions the pH of the condensate from all the fields was calculated to be between 2.1 and 2.5.

3.1.4 NaOH Dosing

The quantities of NaOH required to bring the pH back up to unoxidized levels are shown in Table 8. Rotokawa steam required about 20 kg/hr dosing with NaOH, 11 for Mokai and 7 for both Ohaaki and Tauhara. The unoxidized pH in MIX for Mokai was 5.5 so more NaOH would be required if the pH were to be increased to 6, the level found for the other fields. Again the NaOH dosing rate is correlated with the gas partial pressures not to the absolute flux of H_2S.

3.1.5 Output Gas Partitions

In the low gas steam a greater fraction of the total gas is dissolved in the cooling water. For Mokai and Tauhara approximately 61% and 90% H_2S respectively of the total H_2S gas exiting to the atmosphere is stripped out in the cooling tower, compared to 16% and 26% respectively for Ohaaki and Rotokawa (Table 9). The remaining gas is vented directly to atmosphere from the aftercooler.

It follows that for Mokai and Tauhara a greater fraction of the total incoming H_2S is oxidized, 21 and 29% respectively, compared to 7% and 11% respectively for Ohaaki and Rotokawa (Table 10).

For all the models over 99.9% of the total incoming CO_2 finally ends up in the atmosphere. Because of the higher solubility between 60 and 89% of the NH_3 ends up in the atmosphere the rest being removed in the blowdown. A higher equilibrium pH in the cooling tower results in more NH_3 being stripped out of the condensate.

3.1.6 Effect of Steam Ejectors

If a steam ejector is used between the main condenser and the intercooler then extra steam and gas would be added to the cooling water. The result would be a higher condensate temperature (assuming no change in cooling water flow to the intercooler) which would lower the partial pressure of the gases. The net effect would be to lower CO_2 and H_2S, and rake NH, and pH. The effects of adding the steam ejector at this point in the circuit and between the intercooler and aftercooler can be calculated using CNDSR.

3.2 Binary Plant Heat Exchanger

All the relevant condensed steam chemistry and gas flows are given in Table 11. As in the direct contact condenser the concentrations of dissolved H_2S and CO_2 are in proportion to the gas partial pressures and all the ammonia dissolves in the condensed steam. In all cases the pH of the condensed steam is very low, pH 5 for Rotokawa and Ohaaki and pH 4.5 and 4 respectively for Tauhara and Mokai. The lower pH values for Mokai and Tauhara are directly related to lower ammonia concentrations. Lower concentrations of dissolved CO_2 in the latter two cases are not sufficient to raise the pH. These low pH values may cause unacceptable corrosion in downstream piping as well as in well casings. If the gas phase was removed the pH of Mokai condensed steam (at 2 ba) could be increased from 4 to 6 by adding 0.56 kg/tonne NaOH and slightly less at 0.52 kg/tonne for Rotokawa condensed steam. Venting gas at different stages during the cooling cycle will reduce total dissolved gas concentrations but would result in greater heat loss. Diluting the condensed steam with flashed geothermal water would also help to reduce the corrosivity. These options are not modelled.

One major benefit of a closed system however is the absence of oxygen so sulphur or sulphuric acid are not produced. This means that biocide or extra dosing with NaOH would not be required.

The total gas flow to atmosphere for Ohaaki or Rotokawa binary models are not greatly different from the direct contact models (Tables 10 and 11). Gas flows for Mokai and Tauhara binary models are less because a greater fraction of the total gas is dissolved in solution.

3.3 Comparison Between the Contact and Binary Models

The direct condenser models all give acceptable circuit chemistry with NaOH/biocide dosing. The low partial pressure of H_2S in both Ohaaki and Tauhara steam means that the condensate in these fields required approximately one third NaOH than Rotokawa and half the quantity required at Mokai to neutralize the expected formation of sulphuric acid. The very low total gas content of the Tauhara steam (0.2% vs. Ohaaki at 4%) greatly eases the difficulty of maintaining low condenser pressures and results in low gas emissions to the atmosphere. Based on chemistry alone Tauhara would be the preferred field to develop using a direct contact condenser circuit. However chemistry is only part of assessing the economics of power station development. Economic considerations are outside the scope of this study, but for example Mokai required more NaOH dosing than Ohaaki even though the lower gas content (0.6%) and H_2S flux gives it an advantage over Ohaaki-type steam, particularly if H_2S abatement needs to be considered. Rotokawa had the highest dissolved H_2S gas concentrations which would require expensive dosing to control the circuit chemistry.

Table 11 : Binary Plant Physical and Chemical Parameters

Physical Parameters

Steam Flow (tonnes/hr)	100
Final pressure (ba)	2
Final temperature (°C)	50

Condensed Steam Chemistry (ppm)

	pH	H_2S	NH_3	CO_2
Ohaaki	5.0	54	38	1835
Mokai	4.0	121	2.0	1642
Rotokawa	5.0	157	34	1725
Tauhara	4.5	93	8.7	1492

Gas Flow at 2 ba (kg/hr) to Atmosphere and as a Fraction of the Total Gas

	H_2S	CO_2	$\%H_2S$	$\%CO_2$
Ohaaki	36	3728	87.0	95.3
Mokai	11	448	46.7	73.2
Rotokawa	61	2016	79.4	92.1
Tauhara	0.7	34	69.1	18.7

Traditionally for economic and efficiency' reasons binary plants were used for small scale developments and to exploit low temperature geothermal resources. Increasingly they are being considered for processing higher enthalpy fluids. In these models the low gas content steam from Mokai and Tauhara resulted in the most acidic condensed steam at pH 4. Ohaaki and Rotokawa condensed steam was at pH 5 with similar dissolved CO_2 concentrations. The Rotokawa condensed steam contained 3 times more dissolved H_2S than Ohaaki. Unlike the direct contact condenser situation this is not a problem here because of the absence of oxygen

If power station chemistry and the above stated operating conditions were to be the only criteria for developing these fields for power production the best options would be
- Tauhara, Mokai and Ohaaki: Direct Contact Condenser
- Rotokawa: Binary Plant Heat Exchanger

4. CONCLUSIONS

1. The concentration of ammonia in the steam and the partial pressures of the acid gases controls the condensate chemistry and gas partitioning for both the direct contact condenser and heat exchanger.

2. A low gas partial pressure in the direct contact condenser minimizes gas absorption.

3. 30% oxidation of the dissolved sulphide to sulphuric acid in the direct contact condenser circuit would require dosing with 20 kg/hr NaOH for Rotokawa, 11 kg/hr for Mokai and 7 kg/hr for Tauhara and Ohaaki type steam. These dosing rates, which would maintain acceptable pH values (about 6) around the circuit, are directly related to the H_2S steam partial pressure not the absolute flux of gas. A lower gas flux is however important for minimizing H_2S gas emissions to atmosphere.

4. In the heat exchanger, steam from Mokai and Tauhara with gas contents less than 0.2% and low ammonia concentrations condensed to form acidic solutions at pH 4 and 4.5 respectively. Based on chemistry alone a direct contact condenser appears to be the most favourable option for these fields.

5. Condensing Ohaaki or Rotokawa steam in a heat exchanger also results in an acidic fluid at about pH 5. The low partial pressure of H_2S in Ohaaki type steam suggests that a direct contact condenser would be preferable over a heat exchanger. However the opposite is true for Rotokawa steam where a high partial pressure of H_2S results in high dissolved sulphide concentrations. Based on chemistry alone a heat exchanger may be preferable to extract energy from this steam because the absence of oxygen in the system avoids the problem of dissolved sulphide oxidizing to sulphur and sulphuric acid.

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