Impact of fluid chemistry on power development at Rotokawa, New Zealand

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ABSTRACT

Power station chemistry in a HP turbine with two types of direct contact condenser systems and in a HP turbine with a binary plant heat exchanger were modelled using gas compositions from well RK5 in the Rotokawa geothermal field. For all three options a steam flow rate of 90 tonnes/hour was input to the model. The partitioning of gases and the condensate chemistry in each option was directly related to the partial pressure of the carbon dioxide, hydrogen sulphide, and other sparingly soluble gases, and to the concentration of ammonia in the steam. For the direct contact options oxidation of 30% of the total dissolved H_2S produced sulphuric acid that required biocide dosing or 12 and 5 kg/hr of NaOH to maintain an acceptable pH value (about 6) around the circuit. Dosing can be minimised by using the second design in which the water flow from the ancillary gas coolers was directed to the condenser and by optimising the operating conditions. In a binary plant the acidity is mainly due to CO_2 and 0.5 kg/tonne of NaOH (45 kg/hr) is needed to achieve a pH value of 6. A silica saturation index of 1.02 is calculated for a separation temperature of 210°C at a pressure of 19 bA. Mixing the separated water at 210°C with 45°C condensate from the outlet of the binary plant is a viable option as the silica saturation index is not changed.

1. INTRODUCTION

Before a geothermal development can proceed in New Zealand a "Resource Consent Application" has to be lodged with the appropriate authorities and consent obtained to discharge and dispose of well fluids. In part this consists of detailing the characteristics of (a) the extracted fluid, (b) the atmospheric discharge, (c) the waste fluids disposed of by reinjection and/or at the surface, (d) the receiving environment for the waste fluids. The first three aspects are dependant on the chemistry of the geothermal fluid supplying the well(s) and the design of the power station.

Glover and Mroczek (1993) illustrated the effects of steam composition on power station chemistry. Steam from Ohaaki, Mokai, Rotokawa and Tauhara geothermal fields was used to model the chemistry for two condensing options: (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.

In this paper we examine the control silica and calcite exercise on the separation pressure, cooling and mixing possibilities, and the consequences of operating either of three different design options with the Rotokawa steam.

The main components of steam extracted from Rotokawa which is located in the Taupo Volcanic Zone are carbon dioxide (CO,) with lesser amounts of hydrogen sulphide (H_2S), ammonia (NH,), nitrogen (N,) and methane (CH,). All these gases dissolve in solution in proportion to their partial pressures according to Henry's Law. This was verified experimentally in the Ohaaki Pilot Plant condensate by Glover (1979b). In addition to the Henry's Law solubility, the total solubility of the acid gas H_2S is increased by reaction to form bisulphide (HS). This is enhanced by the presence of ammonia which increases the pH. CO, is an acid gas which could counteract the effect of ammonia, 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_2 to form carbonic acid (Weres 1983a). Oxidation of the dissolved sulphide species to sulphuric acid can result in a low condensate pH (< 3). Oxidation which usually occurs by bacterial action (Glover, 1979b) can be minimised by biocide treatment. Alternatively the acid formed can be neutralised and the pH controlled by caustic dosing. Both these treatments can be expensive.

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 0.01 bA of the condenser pressure reduces gas absorption (Glover 1979b, Hart 1980). Designing the cooling water sprays to efficiently strip dissolved oxygen from the aerated condensate minimizes downstream oxidation.

2. CHEMISTRY OF THE RK5 WELL DISCHARGES ASSOCIATED WITH POWER PRODUCTION

2.1 RK5 well chemistry

2.1.1 "Safe" Separation Pressure

Fluid chemistry from the RK5 discharge in 1985 (IGNS files,1985) at an enthalpy of 1490 J/g was used to calculate liquid and vapour chemistry used in two basic scenarios. Table 1 shows the composition of water separated at 210°C (19 bA) and 180°C (10 bA). The silica saturation index (concentration of monomeric silica / solubility of amorphous silica) is 1.02 and 1.26 at these temperatures. The RK5 water will thus become supersaturated if the separation temperature or the temperature of the water after separation drops below 210°C. This will be true whether the temperature decrease is due to further steam loss or conductive cooling. Thus a "safe" separation pressure of 19 bA was chosen with a turbine inlet pressure of 18 bA. In piping geothermal water containing silica near or above saturation the rate of deposition is all important. In a deposition test at RK4, (Mroczek and McDowell, 1990) 180°C water with a saturation index of 1.4 deposited 60 to 100 mg cm^{-2} year-'. The deposit was a vitreous silica with a density of 2 gm cm^3. Thus over a 20 year period the scale thickness would be 6 to 10 mm. However this can only be used as a guide and fluid specific tests are needed for any planned development.

2.1.2 Calcite Deposition

Calcite is usually deposited when the partial pressure of carbon

TABLE 1: RK5 Liquid Chemistry (concentrations in mg/kg)

	pH	Li	Na	K	Ca	Cl	SO,	Tot B	Tot SiO_2	NH,	Tot HCO,	Tot H_2S	SiO_2 Sat	Log Q_{CC}	Log K_{CC}
RK-5 separated at 210°C	7.32	6.0	434	122	1.6	725	7.7	18.9	1052	5.0	209	18.3	1.00	-9.93	-9.80
RK-5 separated at 180°C	7.43	6.5	466	131	1.7	780	*8.2*	20.4	1133	5.7	156	12.7	1.34	-9.41	-9.15
Interturbine "wetness" @ 5.2 bA	6.41							5.04		7.63	36.4	3.5			

Totally condensed steam @ 2 bA and 44.6°C from binary heat exchanger

pH	Tot B	NH,	Tot CO_2	Tot H_2S	N,	CH_4	H_2
5.0	0.43	31.8	1737	156	0.6	0.4	0.01

dioxide, $P(CO_2)$, is reduced as the CO, is removed from the water during steam formation. If log $[Ca^{*} HCO_3^{2-}/P(CO_2)]$ = log Q, is greater than the equilibrium constant log K_{CC} then the solution is supersaturated with respect to calcite and deposition will occur.

Multi component calculations using the ENTHALP computer code show that for separation at 210°C log Q_{CC} = -9.93 and log K_{CC} = -9.80; i.e. close to but under saturation. Similarly, for water separated at 180°C log Q_{CC} = -9.41 and log K, = -9.15; i.e. less saturated than at 210°C. Cooling the 210°C water conductively to 180°C lowers the saturation due to the retrograde solubility of calcite; i.e. it is more soluble at lower temperatures. Lower saturation results also from cooling by dilution with steam condensate (see later).

3. POWER STATION MODELS

3.1 Introduction

Recently Tauhara North Number 2 Joint Venture have applied to develop the Rotokawa geothermal field for power production. The initial documents (Tauhara North Number 2 Joint Venture, 1992) presented as part of the planning consent process contained details of the proposed generation schemes as well as the likely steam and water compositions. 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. In this paper we consider also a modification of the second option which closely models the condenser system eventually chosen.

The three 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 a flow rate of 90 tonnes/hr HP steam was used in the calculations for each option.

3.2 Chemical and Physical Input Parameters

The composition of steam is presented in Table 2.

The simplified conceptual model of the direct contact condenser and cooling tower circuits for the "Original" and "Final" options are presented in Figures 1 and 2.

The basic units in the "Original" system (Figure 1) were:
HP Turbine and LP Turbine (TURBINE), CONDENSER, Hotwell (MIX), INTERCOOLER, AFTERCOOLER, COOLING TOWER, and Cooling Tower Basin (BASIN). "Wetness" produced in the HP Turbine was removed and reinjected. Both INTERCOOLER and

Table 2 : Gas Flows (kg/hr). Total steam flow 90 tonnes/hr.

	CO,	H_2S	NH,	N,	CH,
Rotokawa	1799	63	2.9	*21*	16

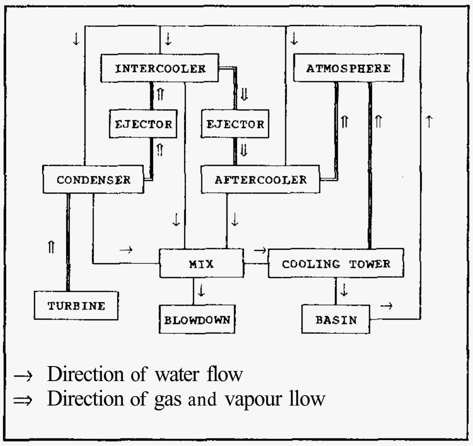

Figure 1 : Original Direct Contact Condenser Cooling Water Circuit

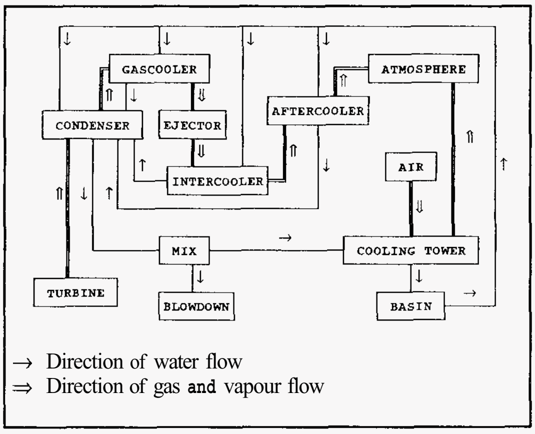

Figure 2 : Final Direct Contact Condenser Cooling Water Circuit

Table 3 : Direct Contact Condenser Physical Parameters

Pressure (bars absolute) :-		
- Condenser	0.08	
- Gascooler	0.08	
- Intercooler	0.35	
- Aftercooler	1.05	
	"Original"	"Final"
Steam flow (tonnes/hr)		
- to Turbine	84.8	87.4
- to Ejectors	2x 2.6	2.6
Condensate flow (tonnes/hr) to :-		
- Cooling tower	2282	2282
- Condenser	2016	1480
- * Mix	2315	2315
- Gascooler		640
- Blowdown	32	33
- intercooler	104	104
- aftercooler	104	10
- evaporation	58	59

* In "Original" located in hotwell
In "Final" located in main condenser

Wet Bulb (°C)	7.5
Dry Bulb ("C)	12

Table 4 : Original Direct Contact Condenser Circuit Chemistry

	t (°C)	pH	H_2S	NH, (ppm)	CO,
Condenser	37.0	6.7	3.0	17.0	59
Hotwell (MIX)	37.4	6.08	7.65	17.0	113
Gascooler					
Intercooler	46.8	5.6	21	16.5	236
Aftercooler	35.6	4.9	86	16.7	1170
CT Basin	18.2	8.2	0.1	15.8	39

AFTERCOOLER were powered by steam ejectors (EJECTOR) and their water outflows were combined with the water outflow from the CONDENSER in the Hotwell (MIX). The combined flow was circulated through the COOLING TOWER and reinjection (BLOWDOWN) of the excess fluid could be taken before or after the cooling tower.

The "Final" system (Figure 2) had very significant differences: The condenser contained a gascooler (GASCOOLER) as a second stage of cooling with its own cooling water supply but located within the body of the main condenser. The steam ejector driven AFTERCOOLER was replaced with an electrically driven exhauster with a liquid ring pump. Finally the liquid outflow from the INTERCOOLER and the small flow from the AFTERCOOLER were fed into the main CONDENSER. Thus the flows from the initial and GASCOOLER stages of the main CONDENSER and from the INTERCOOLER and AFTERCOOLER all finally equilibrated in the bottom of the Condenser, (MIX), **at the low pressure and high temperature** existing there. In each case the gases from the AFTERCOOLER and those released in the COOLING TOWER were vented to ATMOSPHERE above the cooling cower.

Table 5 : Final Direct Contact Condenser Circuit Chemistry

	t (°C)	pH	H_2S	NH, (ppm)	CO,
Condenser	37.0	**6.7**	3.2	16.8	59
Gascooler	20.5	6.1	7.8	16.2	113
MIX	37.0	6.7	3.2	16.8	59
Intercooler	35.1	5.4	30	16.6	340
Aftercooler	26.2	4.8	121	16.0	1325
CT Basin	18.1	8.2	0.05	15.6	39

Table 6 : Oxidation of 30% H_2S in HOTWELL, pH Adjusted to Unoxidized Levels by Dosing with NaOH

	NaOH Dose Rate (kg/hr)	SO^{-}_4	Na^+
		ppm	
Original	12.6	470	225
Final	5.3	193	93

Table 7 : Gas Flows (kg/hr) to Atmosphere from the Aftercooler and Stripped from the Condensate in the Cooling Tower

	Aftercooler		Stripped	
	H_2S	CO,	H_2S	CO_2
Original	45	1631	12	174
Final	55	1758	5.1	47

The physical parameters are listed in Table 3. 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 0.08 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 two 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 condensed in one step, without venting of gas, to a final total pressure of 2 bA and a final temperature of 45°C.

3.3 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 4 and 5. 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 to unoxidized levels. The rates of NaOH dosing and final

Table 8 : Output Partitions (%) of Total Gas Flow - Direct Contact Condenser

	Atmosphere	Blowdown	Oxidation
Rotokawa Original			
H_2S	91.1	0.3	8.6
NH_3	79.3	20.7	
CO_2	99.8	0.2	
Rotokawa Final			
H_2S	96.4	0.1	3.5
NH_3	79.9	20.1	
CO_2	99.9	0.1	

Table 9 :Binary Plant Physical and Chemical Parameters

Physical Parameters				
Steam Flow (tonnes/hr)			90	
Final pressure (ba)			2	
Final temperature ("C)			45	
Condensed Steam Chemistry (ppm)				
	pH	**H_2S**	**NH_3**	**CO_3**
Rotokawa	5.0	156	31.8	1737
Gas Flow at 2 ba (kg/hr) at Atmosphere and as a Fraction of the Total Gas				
	H_2S	**CO,**	**%H_2S**	**%CO_2**
Rotokawa	48.6	1643	77.6	91.3

Table 10 : Change in Direct Contact Condenser Chemistry as Water Vapour Pressure Approaches 0.08 ba.

t (°C)	**pH**	**H_2S (ppm)**	**CO,**	**NH, (ba)**	**P_g**
Rotokawa					
35.3	6.55	3.8	65	16.9	0.0229
37.0	6.69	3.23	58	16.9	0.0172
38.8	6.89	2.6	52	16.9	0.0109
39.7	7.07	2.25	48	16.9	0.0074

concentrations of $SO_4^=$ and Na^+ are presented in Table 6. The quantities of gas stripped from the condensate in the Cooling Tower and vented to atmosphere from the Aftercooler are presented in Table 7 and the final output partitions of the total incoming gases are given in Table 8.

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 45°C at a total pressure of 2 bA. The chemical data for the binary plant heat exchanger is listed in Table 9.

4. RESULTS AND DISCUSSION

4.1 Direct Contact Condenser

4.1.1 Circuit Temperatures

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. Dissolved gas solubility decreases with increasing water temperature and constant condenser pressure. Table 10 shows changes of chemistry with temperature for the final Rotokawa circuit with a constant condenser pressure of 0.08 bA. Between 35.3 and 39.7°C the total dissolved sulphide concentration decreases from 3.8 to 2.25 ppm, and the pH rose from 6.55 to 7.07. Although this may seem like a negligible amount the difference is equivalent to 40% or 3.6 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, adsorption also has the beneficial effect of raising the condensate pH.

4.1.2 pH Values

The change in condensate pH around the circuit is shown in Tables 4 and 5. In the condenser the absorption of CO, is balanced by the dissolved ammonia resulting in a near neutral pH in each of the two direct contact condenser models. 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 (in the original model) the flow through these parts of the circuit is only 9% 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 equilibrium conditions because of the relatively shorter condensate residence time compared to the main condenser. This is observed at Ohaaki (Mroczek et al., 1995). The gas partial pressure in the condenser controls the concentrations of dissolved H_2S and CO,.

4.1.3 Oxidation of Sulphide

The absolute concentration of dissolved sulphide in the condensate is 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 (1979b) 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 was calculated to be about 2.25.

4.1.4 NaOH Dosing

The quantities of NaOH required to bring the pH back up to unoxidized levels are shown in Table 6. The "Original" and "Final" models require 12.6 and 5.3 kg/hr dosing with NaOH. The NaOH dosing rate is correlated with the gas partial pressures not to the absolute flux of H_2S.

4.1.5 Output Gas Partitions

A greater fraction of the total gas is dissolved in the cooling water for low gas compared with high gas steam, (Glover and Mroczek, 1993). For the "Original" and "Final" Rotokawa systems approximately **21** and 8.5% H_2S respectively of the total H_2S gas exiting to the ATMOSPHERE is stripped out in the COOLING TOWER (Table 7). The remaining gas is vented directly to ATMOSPHERE from the AFTERCOOLER.

Given these partitioning values it follows that 8.6 and 3.5% of the total incoming H_2S is oxidized, (Table 8).

For both designs over 99.8% of the total incoming CO_2 finally ends up in the atmosphere. Because of its higher solubility only 80% of the **NH,** ends up in the atmosphere the rest being removed in the blowdown. The stripping out of CO_2 and H_2S in the cooling tower raises the pH which assists the removal of NH,.

4.1.6 Effect of Steam Ejectors

When a steam ejector is used instead of a mechanical pump, extra steam and gas is added to the cooling water. The result is a higher condensate temperature (assuming no change in cooling water flow) which would lower the partial pressure of the gases. The net effect is to lower CO_2 and H_2S, and raise NH, and pH.

4.1.7 Effect of Non Equilibrium in the System

If equilibrium is not attained in the gas coolers due to short residence time then the dissolved gas would be lower than calculated, i.e. beneficial. If. in the "Final" system, the water from the ancillary gas coolers does not re-equilibrate to the lower pressure and temperature, more gas will stay dissolved, and the MIX will be more aggressive. This failure for cold water with high gas content to re-equilibrate at the lower pressure and higher temperature end of the condenser was noted in early condenser tests (Glover. 1979a). However. the "Final" design will still have less dissolved gas than the "Original".

4.2 Binary Plant Heat Exchanger

All the relevant condensed steam chemistry and gas flows are given in Table 9. 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. The pH of the totally condensed steam (calculated by COCO) is very low, pH 5, which may cause unacceptable corrosion in the downstream piping and in well casings if the fluid is reinjected without treatment. If the gas phase was removed, the pH of Rotokawa condensed steam (at 2 bA) could be increased to 6 by adding OS2 kg/tonne NaOH. 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. As noted above the water is saturated with silica at 210°C and any cooling by conductive heat loss or by evaporation will increase the saturation (to 1.26 and 1.34 respectively, at 180°C). However, calculations show that mixing the separated water with 45°C condensate does not effect the silica saturation significantly. Mixing in any proportion may be used up to and including recombining the 90 t/h of condensate with the 200 t/h of water yielding a mixture temperature of 160°C.

One major benefit of a closed system 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 the Rotokawa binary model is not greatly different from the direct contact model (Tables 7 and 9).

4.3 Comparison Between the Contact and Binary Models

The direct condenser models both give acceptable circuit chemistry with NaOH/biocide dosing. However the "Final" option has a number of advantages. Firstly, the pH of the fluid in the "MIX" is higher (6.7 versus 6.1). To adjust the pH from 6.1 to 6.7 in the initial design could not be achieved by biocide dosing and would require caustic addition (not calculated). Secondly, to adjust the pH of the MIX to the values before oxidation, i.e. 6.1 and 6.7 in the initial and final designs, would require 12.6 and 5.3 kg/hr respectively. Even with this higher dosing the initial design would still have a lower pH in the MIX. Thirdly, and most importantly the dissolved H_2S in the MIX in the final design is only 40% of that in the original design. Thus for the similar operating temperatures and pressures there is 10.3 kg/hr less sulphide available for oxidation in this part of the circuit. However chemistry is only a part of the economic assessment of power station development and other parameters such as net power output were also considered in arriving at the final design.

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. Rotokawa condensed steam was at pH 5. Further decrease in pH is not likely, as in the oxygen free system the high concentration of H_2S is not oxidised to sulphuric acid. It is also likely that the potential for sulphur production will be much lower in the oxygen free environment. Thus it was concluded that the Binary system had the more favourable chemistry compared with the original direct contact condenser design. However, this advantage was lessened with the final direct contact design. Following commercial assessment by the developer, the final direct contact system was chosen.

5. CONCLUSIONS

1. Available silica concentrations in well RK5 indicate that the water will become supersaturated if the pressure is reduced below 19 bA.

2. RK5 fluids should present no calciting problems at the surface.

3. The proportion of ammonia to the acid gases and the gas partial pressures control the condensate chemistry and gas partitioning for both the direct contact condenser and heat exchanger.

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

5. The second direct contact condenser system evaluated, in which the outflow from the gas coolers is led into the main condenser, is superior. A higher pH occurs in the flow to the cooling tower and less dissolved H_2S is available for oxidation to sulphur or sulphuric acid. 30% oxidation of the

dissolved sulphide to sulphuric acid in this direct contact system would require dosing with 5.3 kg/hr NaOH for Rotokawa.

6. Condensing Rotokawa steam in a heat exchanger also results in an acidic fluid at about pH 5. A high partial pressure of H_2S results in high dissolved sulphide concentrations but the absence of oxygen in the system avoids the problem of sulphur and sulphuric acid production.

7. Condensate may be mixed with separated water without changing the silica saturation.

6. ACKNOWLEDGEMENTS

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