Ohaaki Power Station Cooling Water Chemistry - Predictions and Reality

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ABSTRACT

The principal factors controlling the circuit chemistry in the direct contact condenser/cooling tower of the Ohaaki geothermal power station had been identified by a comprehensive series of pilot plant studies and theoretical calculations (Dutton and Palmer 1980, Glover 1979). This work provided design recommendations as well as valuable pre-commissioning operation data for the power station. During the commissioning trials in 1989 the chemistry of the incoming steam, off-gases, circuit water chemistry as well physical parameters such as temperatures and flows were monitored over one day. In this study we report the comparison of these results with the previous predictions. The main finding was that the total dissolved hydrogen sulphide (H_2S) and carbon dioxide (CO_2) in the condenser and the intercooler were undersaturated with respect to the calculated equilibrium concentrations. In the condenser the measured H_2S and CO_2 concentrations were *52%* and 92% of the equilibrium values respectively and 59% and 62% of the intercooler equilibrium concentrations. In the condenser the lower total dissolved H_2S concentration was most likely due to the precipitation of sulphur. Oxidation of 60% of the sulphide entering the hotwell could account for the dissolved levels of thiosulphate and sulphate. The degree of oxidation was higher than previous predictions.

1. INTRODUCTION

New Zealand's second geothermal power plant (100 MW), located at Ohaaki uses a closed cycle circulating water system to condense steam in a direct contact condenser. The heat in the cooling water is dissipated by evaporative cooling in a natural draught tower and the excess steam condensate is disposed in the blowdown. In a direct contact condenser the turbine exhaust comes into direct contact with sprays of cooling water. The bulk of the non-condensible gases pass out through the vacuum exhaust with the remainder being dissolved in the cooling water.

During commissioning of the power station in September 1989 the chemistry of the cooling water circuit was measured to determine whether the chemistry occurring in the condenser and cooling water circuit was within the expected limits. In this study we compare the measured values against circuit chemistry calculated using the condenser chemistry modelling program CNDSR (Wercs, 1983) as well as against the previous predictions.

The main components of Ohaaki steam are carbon dioxide (CO_2) 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. However, since ammonia is highly soluble it completely dissolves in the condensate. As a consequence of the increase in pH, the total solubility of the acid gas H_2S is increased by reaction to form bisulphide (HS^-). Oxidation of the dissolved sulphide species to sulphur and/or sulphuric acid can result in precipitated sulphur throughout the circuit and low condensate pH (< 3) which would require expensive remedial dosing with biocide to control bacterial activity or with caustic to raise the pH. Therefore controlling the cooling water circuit chemistry to limit fluid corrosivity and the propensity for sulphur precipitation is of fundamental importance for maintaining proper functioning of the power station.

New Zealand's only other geothermal power station located at Wairakei does not contain a recirculating water circuit. When the decision was made to proceed with the development at Ohaaki there was little experimental data and no operating experience on which to base a condenser and cooling water circuit design specification. To help clarify the uncertainties a comprehensive series of small and large scale pilot plant studies were conducted in conjunction with theoretical calculations (Dutton and Palmer 1980, Girardin and Jamieson 1982, Glover 1978, Glover 1979, Hart 1980, Hart *et al.*, 1980). This work enabled the circuit chemistry to be predicted under different operating conditions and allowed the likely problems and their solutions to be defined.

2. PREVIOUS WORK

A series of experiments have been conducted on condensers. In December 1977 (Glover 1978) a model condenser using 1860 mm of 100 mm diameter pipe with a "barometric leg" was operated in a once through counter current flow mode. The aim of the work was to determine the effect on the gas concentrations in the condensate resulting from the following factors: a) the position of the steam entry; b) different steam/cooling water ratios; c) packing with a 400 mm bed of Raschig rings: and d) acidifying the solution in the condenser. It was concluded that: a) all the ammonia is dissolved in the condenser; b) a longer residence time resulted in more H_2S in solution; (c) packing assists solution of H_2S in the cold part of the condenser; d) the total sulphide dissolved is greater than the equilibrium H_2S value due to HS^- in solution; and e) acid treatment eliminated the HS^-.

Following these experiments a direct contact condenser/cooling tower circuit pilot plant was set up at Ohaaki (Dutton and Palmer 1980). This involved a 500 mm diameter condenser, run in co-current and counter current modes, with a once through cooling water flow. Subsequently a 7 metre high forced draught cooling tower circulating system was included. The effect of an aftercooler on top of the main condenser was also investigated. The pH, sulphide species, carbonic species, ammonia species, and sulphate were analysed around the circuit.

From these detailed experiments (Glover 1979) it was concluded that: a) it was possible to operate a direct contact condenser at Ohaaki without producing low pH conditions by using a high condensate outlet temperature and an aftercooler in the exhaust gas line; b) gas stripping in the cooling tower was approximately equal to the concentration of the unionised species, CO,, H_2S,and NH,, and resulted in an increase in pH of about 1 unit; c) most of the HS was oxidised to SO;; and d) only occasional (not constant) dosing with a biocide would be necessary. Since then Giggenbach and Sewell (1985) assessed the potential for sulphur deposition in the cooling water circuit at Ohaaki by considering the thermodynamics of the sulphur/water system and the effect of bacterial activity. They concluded that the probability of crusty, hard to remove sulphur depositing in the auxiliary coolers was very low. Deposition was most likely in the cooling tower pond, possibly on the spray nozzles in the cooling tower, or within the intercooler or its barometric leg due to lower pH values.

From the pilot plant experiments a theoretical basis of calculating the circuit chemistry was derived:

For ammonia - virtually ail ammonia in the steam dissolves in cooling water in the main condenser and free **NH,** is lost to the atmosphere in the cooling tower.

For H_2S - the amount in solution leaving the condenser depends on the partial pressure of H_2S (p_{H_2S}), Henry's constant and the pH of the solution. It also depends on whether equilibrium between the vapour and liquid is reached, which involves kinetics. Equilibrium is more likely to be attained in the water leaving the condenser when p_{H_2S} at the cold end of the condenser is closer to p_{H_2S} at the hot end of the condenser, and also as the residence time in the condenser increases.

For CO, - the same controlling parameters apply as for H_2S. Thus it is likely that the concentrations of CO, and H_2S at the hot outlet of the condenser tend to exceed equilibrium values.

Using the above data a relatively simple computer program (CONDEN) was designed to calculate the expected chemistry of the cooling water at the hotwell and in the cooling tower basin. This program was used to calculate the range of chemical compositions expected in the condensate and re-cooled water.

3. CONCEPTUAL MODEL

3.1 Physical Data

The physical data collected during the chemical sampling is listed in Table 1 and the model developed for the Ohaaki cooling water circuit is depicted in Figure 1. The circuit was modelled by CNDSR as a once through system excluding the cooling tower. This simplification substantially reduced computational time. The gas exhausters have no effect on the chemistry and were not explicitly modelled.

In the model the BASIN was filled with the appropriate mass, heat and chemical fluxes derived from the known basin chemistry. Flow from the HOTWELL in excess of the 3000 kg/s flow to the cooling tower was directed to BLOWDOWN, i.e. the condensate reinjection system. The steam flow into the power station minus the reinjection flow theoretically equals the amount of evaporation occurring in the cooling tower, in this case about 74.2 kg/s. The sum of the flows of water from the basin into the condenser, gas cooler and intercooler (Table 1) was lower by about 106.4 kg/s than calculated from the flow to the cooling tower minus the evaporation. This relatively small flow (3.6% of the total) may be an artifact of the uncertainties in the large flows to the condenser and cooling tower. In the model this flow was bypassed from the BASIN directly to the HOTWELL. This assumption makes little difference to the chemistry and was made purely to obtain internal consistency in the flows around the circuit.

3.2 Chemical Data

Samples of steam entering and gas leaving the power station were collected and water samples were taken at strategic points around the circuit. The analytical condensate results are presented in Table 2. The concentrations of the major gases in the steam were CO, 1775, H_2S 23.3, NH, 3.71. N, 20.3 and CH, 37.3 mM/100 M H_2O.

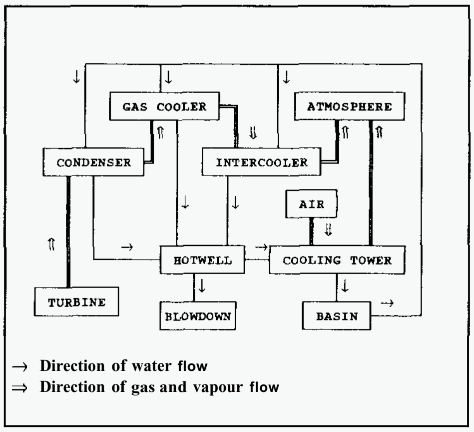

Figure 1 : Direct Contact Condenser Cooling Water Circuit

Table 1 : Direct Contact Condenser Physical Parameters

Pressures (mbars absolute) :-	
Condenser	99.3
Intercooler	406
Flows (kg/s)	
Steam (excluding gas)	101.4
Steam enthalpy (kj/kg)	2263
Gas per 101.4 kg steam	4.7
Gas from Exhauster to CT	3.51'
Condensate flow to :-	
- Condenser	2500
- Cooling tower	3000
- Blowdown	27.2
- Intercoolers	144.4*
- Gas Cooler	175
Temperatures (°C) (at point of sampling)	
Basin	18
Hotwell	34
Condenser	35
Intercooler	24

+ Calculated from pressure and temperature data
* Flow evenly split hetween two intercoolers

Table 2 : Ohaaki Cooling Water Circuit Chemistry (concentrationsin mg/kg), Sampled 22/9/89 11:30-12:30.

	Intercooler (Nth)	Intercooler (Sth)	Hotwell	Condenser	Basin
t(°C)	24	23	34	35	18
pH	5.94	5.92	6.78	7.08	1.15
H_2S *	8.65	8.9	1.72	1.24	.09
$SO_3^=$ *	0.5	0.5	NIL	0.2	NIL
SO;	43.4	45.6	44.6	41.3	45.4
$S_2O_3^=$	4.5	4.7	6.3	4.6	4.1
$CO_3^=$ *	608	561	232	211	188
NH, *	59.1	57.4	59.4	59.4	60.2

* Total Dissolved Concentrations

4. EVALUATION OF PHYSICAL DATA

The reliability of the mass flows, pressures and steam enthalpy and the correctness of the assumed vapour and flow fields were gauged by comparing the calculated and measured temperatures around the circuit. Except in the intercooler the temperatures agreed well indicating that there were no major inconsistencies in the data nor in the way the mass flow fields were set up in the model. The measured temperature in the intercooler was 2 degrees higher than the calculated temperature. There was no reason to account for this difference which may have been caused by extra heat added to the gas stream during compression in the low pressure exhauster or through steam carryover from the main condenser. Although a 2°C rise makes little difference to the overall chemistry (results in approximately a 4% drop in the calculated equilibrium dissolved total carbonate concentration) the temperature in the INTERCOOLER was increased to 23°C by an additional heat input.

Inspection of the analytical data indicated that only about 2% of the total gas dissolved in the cooling water which would suggest that 4.6 kg/s gas should have been leaving the power station. The measured value of 3.5 kg/s was significantly lower. The difference between the "measured" and calculated flows was well outside the analytical and physical data measurement uncertainties.

5. EVALUATION OF CHEMICAL DATA

5.1 Comparison of Measured and Calculated pH Values

The CNDSR program was used to calculate the equilibrium pH using the analytical data of the samples collected around the circuit. Close agreement between measured and calculated pH values indicated internal consistency in each set of analytical results.

5.2 Sampling Problems and Analytical Uncertainties

There are a few other features of the analytical data listed in Table 2 which require preliminary clarification and evaluation. Of particular concern is inconsistencies between the sulphur species around the circuit. The distribution of these species must be consistent with mass flows of liquid and vapour around the circuit, the partitioning of gases between the phases, the protolytic equilibria and the sulphide oxidation reactions. Unfortunately, it was not possible to collect gas samples from the intercoolers (and condenser) on the day of the sampling with which to correlate the water chemistry.

In the condenser and intercooler there appears to be less sulphate than would have been expected by dilution of basin condensate with steam. The data suggest that most of the oxidation occurred in the hotwell as this was the only point in the circuit where an increase in sulphate and thiosulphate was observed. In the condenser and intercooler a higher rather than lower sulphate concentration would be expected due to sulphide. oxidation. The mass flows listed in Table 1 suggested that there should be about a 3.7% dilution from the basin to the condenser. The observed change in the chloride concentration (1.28 to 1.23 ppm) was in close agreement with this value but the calculated sulphur flux entering the hotwell (Table 3) was 0.2 moles/s less and 10.2% of the total measured flux.

The measured total H_2S concentration in the hotwell was higher than calculated from the combined mass flows into the hotwell. This must have been due to sampling errors in the condenser and intercooler as there is no simple mechanism why the H_2S could increase. The condenser and intercooler samples were collected in the barometric leg (i.e. not in contact with the off-gas) and reactions to produce elemental sulphur could only further reduce the aqueous phase sulphide concentration. Only a small increase of 0.2 mg/kg in the condenser concentration would bring the calculated hotwell sulphide up to that measured. However this presupposes that there was no loss of hotwell sulphide due to oxidation. This was not the case as there was a significant increase (over dilution) of the sulphate and thiosulphate concentration values. This implies that the measured hotwell sulphide would have been even higher in the absence of oxidation in the hotwell. One possible reason for the discrepancies is that the hotwell sample was not well mixed at the point of sampling. However, as discussed below, this was not borne out by the carbonate chemistry.

The intercooler samples were collected near the bottom of the barometric leg at atmospheric pressure and the condenser was sampled close to the top of the barometric leg using a sampling pump. Sampling from the condenser at low pressure may contribute to errors in the sulphide concentration but is unlikely to have affected the nonvolatile sulphate and thiosulphate concentrations. Boiling off during sampling should have increased the concentrations of the nonvolatile components. Gas bubbles were observed in the intercooler barometric leg but the measured total dissolved gas concentrations were well below equilibrium, suggesting the gas was entrained and not due to exsolution. The low flow from the intercoolers means that the imprint of the intercooler chemistry on the hotwell is limited.

Compared to the sulphur chemistry the carbonate chemistry in the cooling water was uncomplicated, as only protolytic equilibria and partitioning into the vapour phase needed to be considered. The calculated total carbonate concentration in the hotwell agreed well with the measured value. This result implies that the hotwell sample was consistent with the intercooler and condenser samples and also that the hotwell was relatively well mixed at the point of sampling. The carbonate concentrations were significantly higher than the sulphide concentrations which would make for more precise analysis.

These difficulties highlight the problem of attempting to understand a complex system from only one set of samples taken at one point in time. As the control of the sulphur chemistry is so important to the quality of the cooling water and ultimately to the performance of the power station, the reasons for the sulphur mass balances and speciation need to be well understood. There was no obvious reason for the inconsistencies found in the sulphur chemistry around the circuit.

6. CONDENSER CHEMISTRY MODEL RESULTS

6.1 Assumption About Sulphide Oxidation in the Circuit

The CNDSR program cannot predict the degree of sulphide oxidation around the circuit and this information had to be estimated from the analytical data. The extent of sulphide oxidation occurring in the HOTWELL was assumed to bring the sulphate and thiosulphate values up to the values measured in the hotwell.

Oxidation of sulphide to sulphate and thiosulphate was not modelled in the intercooler or condenser as there was no analytical evidence that this was occurring. Also the measured drop in sulphate from the basin to the condenser (Table 2) is not certain and was not included in the model. Production of colloidal sulphur can be modelled simply by removing sulphide. However removal of dissolved sulphide in the intercooler and condenser, even at levels greater than 60%. has little effect on the dissolved sulphide concentration. This is because there is a large surfeit of H_2S in the gas phase and under steady state conditions dissolved sulphide is replenished from the gas phase at the same rate it is removed. The data shows that on the day of the tests the difference between the theoretical (without oxidation) and measured dissolved sulphide concentrations in the hotwell could be adequately accounted for by only considering the increase in sulphate and thiosulphate concentrations.

6.2 Results

The results of the condenser chemistry model are in listed in Table 3 and 4. Two main calculations were performed, one without oxidation anywhere in the circuit and the other with oxidation in the hotwell. The calculated pH values were within 0.1 to 0.3 pH units of the measured values. However, the calculated dissolved gas concentrations appeared to be higher than those measured indicating that the latter were undersaturated with respect to the vapour phase concentrations. This was contrary to the pilot plant measurements.

6.3 Condenser

The CNDSR total carbonate concentration in the condenser was calculated to be higher by 19 mg/kg than the measured value of 217 mgikg. This suggests that the condensate was undersaturated with respect to CO, gas in the vapour phase. However the difference is small (8%) and considering the complexity of the system is probably not significant. The uncertainty in the analytical measurement was estimated to be about 3-4%.

The CNDSR total sulphide value at 2.3 mgikg was almost double the measured value. As discussed above, the measured condenser sulphide concentration was not consistent (i.e. apparently too low) with that measured in the hotwell, so that the difference between the CNDSR and actual value was probably less than 1.1 mgikg. The analytical data showed that oxidation *to* thiosulphate and sulphate could not account for the low measured sulphide values. If there were no sampling problems (which canna be totally discounted) then the lower measured sulphide value could only have arisen if the dissolved sulphide was not in equilibrium with the vapour phase or if there was oxidation to sulphur. A 1.1 mg/kg drop in H_2S corresponds to a increase of 1 mgikg S and would imply a colloidal sulphur production rate of 10.4 kg/hr. In reality probably both processes are occurring as measurements after these test were completed showed high concentrations of dissolved oxygen in the condenser condensate.

The conclusion is that the dissolved gases in the condensate were undersaturated with respect to equilibrium with the gas in the vapour phase. The effect was more apparent for the sulphide because at the pH of the condenser, substantially more of the carbonate is dissociated. This result is surprising as there are other physical mechanisms, *e.g.* entrainment of gas bubbles, which would tend to increase dissolved gas values above equilibrium concentrations. The result is also opposite to that observed by Glover (1979) where the concentrations of CO, and H_2S at the hot outlet of the condenser tended to exceed equilibrium values. The model and analytical data showed that the assumption that all the ammonia dissolves in the condenser was correct.

6.4 Intercooler

The measured total dissolved sulphide and carbonate concentrations were significantly lower than the CNDSR calculated values by 41% (6 mgikg) and 38% (358 mgikg) respectively. As in the condenser the increase in measured sulphate/thiosulphate concentrations was negligible and not sufficient to account for the lower sulphide concentrations. The decrease in pH favours the formation of sulphur and the lower measured total sulphide may arise if sulphur precipitation was much faster than the gas dissolving in solution. A 6.1 mg/kg drop in sulphide without an increase in other sulphur oxyanions would have to be balanced by a 5.7 mgikg increase in colloidal sulphur (equivalent to 3 kg/hr). However, it is significant that the total measured carbonate concentration was also substantially lower than the calculated equilibrium value. This strongly suggests that the measured sulphide value is lower primarily because of undersaturation rather than due to removal by oxidation to sulphur. For equilibrium at the pH of the intercooler about 95% of the total dissolved sulphide and 81% of the dissolved carbonate are undissociated. The intercoolers are considerably smaller than the condenser and it is plausible that the residence time is too low to attain the high theoretical dissolved gas concentrations. The practical significance of the lower values on the circuit chemistry is **less** than may be expected because of the small fraction of condensate flow through the intercoolers.

Table 3 : Comparison of the Condenser Chemistry Model with Analytical Data'

	pH	H_2S	$CO_3^=$	NH_3 (mg/kg)	$SO_4^=$	$S_2O_3^=$
Basin Chemistry						
Analytical	7.7	0.09	188	60.2	45.4	4.1
Intercooler						
CNDSR	5.7	14.9	943	59.9	45.2	4.1
Analytical	5.9	8.8	585	58.3	44.5	4.6
(averaged Nth and Sth)						
Condenser						
CNDSR	6.8	2.3	236	59.3	43.8	4.0
Analytical	7.1	1.2	217	59.4	41.3	4.6
Hotwell						
CNDSR	6.6	2.79	268	59.4	43.9	4.0
Calculated*		1.56	234		41.8	4.6
Analytical	6.8	1.72	232	59.4	44.6	6.3
Oxidation'	6.6	1.12	268	59.4	44.6	6.3

§ total dissolved concentrations

* calculated assuming that the analytical concentrations in the intercooler, condenser and basin (small bypass) are additive in simple proportion of the mass flow rates given in Table 1.

\+ SO; and $S_2O_3^=$ up to measured levels in the hotwell

Table 4 : Calculated Partitioning (%) Between Dissociation States Of The Dissolved Gases Around The Circuit

	pH		H_2S/HS	H_2CO_3/HCO_3^-	NH_3/NH_4^+
Hotwell	6.6	unds	62	33	<1
		1st	38	67	>99
Intercooler	5.7	unds	95	81	<0.1
		1st	5	19	100
Condenser	6.8	unds	51	24	<1
		1st	49	76	>99
Basin	7.7	unds	17	4	2
		1st	83	96	98

unds = undissociated, 1st = first dissociation

6.5 Hotwell

The CNDSR total dissolved carbonate was 11% higher than the measured value and this was primarily due to the higher CNDSR equilibrium values calculated in the condenser and intercooler.

The CNDSR total sulphide value without oxidation was 2.79 mg/kg versus the measured value of 1.72 mgikg. The corresponding CNDSR sulphate and thiosulphate values (with no oxidation effectively diluted basin values) were 43.9 and 4.0 mg/kg, respectively, versus the measured values of 44.6 and 6.3 mg/kg. The increase in sulphate and thiosulphate clearly indicated that oxidation was occurring in the hotwell. Oxidation was modelled so that the CNDSR sulphate and thiosulphate concentrations were increased by 0.7 and 1.7 mg/kg, respectively, to the values measured in the hotwell sample. Under these conditions the total hotwell sulphide was reduced by 60% to 1.12 mg/kg, 0.6 mg/kg lower than the measured value of 1.72 mg/kg. Oxidation of sulphide to thiosulphate results in a greater sulphide decrease than oxidation to sulphate because of the different stoichiometry. The thiosulphate concentration in blowdown from the hotwell, sampled at the reinjection wellhead, was lower by 1 mg/kg than in the hotwell itself. This reduces the calculated fraction of sulphide oxidized to 33% (Webster 1989). The initial CNDSR models which incorporated a cooling tower assumed 30% oxidation of the total sulphide entering the hotwell (Mroczek and Glover 1988).

These results show that the simple assumption of about 33-60% sulphide oxidation to thiosulphate and sulphate adequately explains the observed sulphide levels. The complexity and uncertainties in the sulphur chemistry around the circuit did not warrant modelling more complex oxidation schemes or assumptions about gas lost from the hotwell which was open to the air.

6.6 Basin

Other than steam, the only other chemical input in the model was derived from the measured basin chemistry. In the basin about 4% of the total measured carbonate was undissociated while at the measured hotwell pH of 6.8 about 23% was undissociated. The observed change in total carbonate between the hotwell and basin was about 19% which supports Glover's original deduction, also borne out by pilot plant experiments, that most of the undissociated gas fraction would be lost in the cooling tower. The measured pH change of 0.9 units was also close to the predicted value of 1 pH unit.

7. COMPARISON OF PRESENT DATA AGAINST ORIGINAL. THEORETICAL PREDICTIONS

The original predictions of condenser/cooling tower circuit chemistry were made using the CONDEN program (based on Glover 1978). The differences between CONDEN and CNDSR can be attributed to different approaches to the problem. In CONDEN H_2S was assumed to be lost to the atmosphere in the cooling tower and all HS^- was oxidised to $SO_4^=$ in the cooling tower basin. The proportion of ionised to non-ionised species was assumed to be controlled by the incoming (i.e. the hotwell) pH. Conversion of ionised to non-ionised species, as the latter were lost to the atmosphere, was ignored. In reality the pH increases through the spray and packing and more NH_3 was lost than calculated. This explains the somewhat lower measured ammonia concentrations compared with the calculated values. All the NH_3 from the incoming steam was dissolved in the condenser plus a proportion of the incoming CO_2 and H_2S, depending on the partial pressure of each of these gases.

Results of past and present (Table 1) conditions are shown in Table 5. In the 1983 calculations the equilibrium values for CO_2 and H_2S (in the first column) used were 2 and 3 times equilibrium for CO_2 and H_2S, respectively (in column 2). Complete oxidation of HS^- was assumed, i.e. F=1, and this implied that there was no biocide dosing. The results showed that "acceptable" conditions of pH could be obtained without dosing.

The 1989 data indicated that the equilibrium pH with no biocide was lower (6.46 to 7.0). This was mainly due to the higher p_{gas} value (double that used in 1983).

In 1989, the calculated values were obtained: a) with total oxidation of HS^- (F=1); and b) with 15% oxidation of HS^- (F=0.15) i.e. taking into account the suppression of oxidation by biocide dosing. The latter values are closer to the measured data and the values calculated by CNDSR. The concentration of 56 mg/kg $SO_4^=$ assumes the only oxidized sulphur species present was $SO_4^=$.

Table 5 : CONDEN Predictions of The Cooling Water Chemistry (concentrations in mg/kg)

	1983		1989		
	Condenser		Condenser		C.T.Basin
Input Data					
t (°C)	40.5	40.5	36.3	36.3	18
b	0.012	0.012	0.0091	0.0091	
F	1	1	1	0.15	
Q H_2S	1	3	1	1	
Q CO_2	1	2	1	1	
Calculated Data					
p_{gas} (mbars)	20.5	20.5	38.8	38.8	
pH	7.0	6.2	6.46	6.80	7.78
Tot $CO_3^=$	105	62	106	230	173
Tot NH_3	86	95	94	70	69
Tot H_2S	0.5	2.0	1.9	2.5	0.85
$SO_4^=$	185	200	199	56	57

t = temperature in °C.
b = reinjection flow / flow through cooling tower.
F = fraction of HS^- oxidised.
Q = actual amount of unionised gas dissolved / theoretical equilibrium amount of unionised gas dissolved.
p_{gas} = partial pressure of the gas at the outlet of the condenser (excluding water vapour).

8. SULPHUR FORMATION IN THE COOLING WATER CIRCUIT

The chemical conditions required for the formation of sulphur in the circuit have been described by Giggenbach and Sewell (1985). The precipitation of sulphur is most favoured in the intercooler or its barometric leg due to acidification or in cooling tower spray nozzles/basin where access to oxygen and a combination of cooling and evaporation would result in supersaturation with respect to elemental sulphur.

The results indicate that no sulphur precipitation occurs in the cooling tower (Webster 1989). Assuming that the condenser and intercooler are in thermal and chemical equilibrium then the lower than expected dissolved sulphide implies that a significant portion of the dissolved H_2S is reacting immediately with dissolved oxygen to form sulphur by reaction 1.

$$H_2S_{(aq)} + 0.5O_2 \;=\; S_{(s)} + H_2O$$

However the calculated equilibrium dissolved oxygen concentrations in the condenser and intercooler are very low, 0.009 mg/kg and 0.12 mg/kg, respectively. The exsolution rate of dissolved oxygen from the basin fluid (9 mg/kg dissolved O_2) under these conditions was expected from the design specifications to be rapid. Therefore, it was thought that the inconsistencies in the sulphur mass balances could not be accounted for by colloidal sulphur formation in these parts of the circuit. Nevertheless, the oxygen levels of the condensate in the condenser were experimentally checked some weeks after these tests were completed and were found to be 2.1 to 2.4 mg/kg, substantially higher than the calculated equilibrium values. Following this extensive modifications of the condenser spray nozzles were attempted to increase the stripping of dissolved air. This shows how critical condenser design is to enable efficient stripping of oxygen from the aerated condensate. In the intercooler a significant part of the difference between the theoretical and measured dissolved gas concentrations was most likely a result of undersaturation (see 6.4) rather than as a consequence of sulphur precipitation.

The HS^- and a fraction of the $H_2S_{(aq)}$ will oxidize without precipitating sulphur. Oxidation proceeds through intermediate $S_2O_3^=$ ions to form SO; by reactions 2-4. Minor HSO; may form by the disproportionation of $S_2O_3^=$ but it is rapidly oxidized to SO; as shown in reactions 5 and 6. There may also be direct oxidation of $S_2O_3^=$ to SO; with the formation of HSO; as an intermediate species.

$$2H_2S + 20, = S_2O_3^= + H_2O + 2H^+ \qquad (2)$$

$$2HS^- + 20, = S_2O_3^= + H_2O \qquad (3)$$

$$S_2O_3^= + 2O_2 + H_2O = 2SO_4^= + 2H^+ \qquad (4)$$

$$S_2O_3^= + H^+ = HSO_3^- + S_{(s)} \qquad (5)$$

$$HSO_3^- + 0.50, = SO_4^= + H^+ \qquad (6)$$

Reactions 2, 3 and 5 would appear to take place mainly in the intercoolers and condenser while reaction **4** is likely to contribute SO; formation in the hotwell (Webster 1989).

The effect of bacterial activity has been excluded from the above discussion because the circuit was being dosed with biocide for some weeks prior to sampling. Inorganic oxidation of dissolved sulphide to elemental sulphur is faster than oxidation of sulphur to sulphate. Bacteria have a catalytic effect in accelerating oxidation of dissolved sulphur species to sulphate which is thermodynamically the most stable sulphur species. The bacterial counts which were lower than 10^3/ml, would have very little effect on the circuit chemistry.

9. CONCLUSIONS

1. Previous theoretical and experimental work predicted. within the assumptions, the observed chemistry throughout the cooling water circuit. In the present study the comparison of measured data with calculated results from the modelling provided a fundamental understanding of the circuit chemistry. However, interpretation was difficult because of the inconsistencies in the measured analytical data.

2. The modelling results show that the measured concentrations of dissolved gases in the condenser and intercooler were below chemical equilibrium. In the condenser the lower dissolved H_2S concentration was most likely due to the precipitation of sulphur while in the intercooler it appeared the H_2S and CO, in the vapour were not in chemical equilibrium with the condensate. Previous predictions had indicated that oversaturation of condensate was likely in the condenser.

3. The observed hotwell concentrations of dissolved total sulphide, thiosulphate and sulphate could be accounted for by assuming between 33 and 60% oxidation of the total sulphide calculated to be entering the hotwell. This was higher than previously assumed in the CONDEN calculations where only the bisulphide was assumed to be oxidized. A full chemical flow model, incorporating a cooling tower, assumed 30% oxidation of total sulphide entering the hotwell.

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