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CHANGES IN THE CHEMISTRY OF WAIRAKEI FLUIDS, 1929 TO 1997

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SUMMARY – Development of the Wairakei geothermal resource has resulted in changes to the chemistry of the discharged fluids which continue to provide challenges in both interpretation and plant operation.

1. INTRODUCTION

The chemistry of the fluids at Wairakei has been studied and changes in physical and chemical characteristics have been observed over 39 years

Spring data for the pre-1959 period are given by Herbert (1921), Grange (1937), Gregg and Laing (1951), Healy (1951) and in reports by Wilson. Prior to 1959 well chemistry was sketchy due to the lack of established and comprehensive sampling and analytical techniques. By 1959 systematic analysis of geothermal fluids was being carried out at Wairakei.

Analytical data from Wairakei well discharges and natural features from 1950 to 1982 have been compiled by Henley et al (1984). Ellis (1962), Mahon (1962) and Glover (1970) have interpreted the gas chemistry. Mahon and Glover (1965) provide a summary of early chemistry at Wairakei.

2. INITIAL CHEMICAL STATE OF THE RESERVOIR

2.1 Well Chemistry

The fluid encountered in production wells at depths greater than 400 m was a near neutral pH, alkali chloride water with a concentration of up to 1680 g/t chloride. Dilution and cooling of the deep reservoir fluid by unmineralised groundwater result in dilute chloride waters such as those originally discharging in Geyser Valley and also encountered by some of the early shallow wells.

The chemistry of the highest temperature wells later suggested that the principal upflow feeding the field lay to the west of the Western Production Field, in the Te Mihi area (Glover and Mroczek, 1988). The parent fluid was considered to be heated to about 265°C with a chloride concentration of 1680 g/t. Boiling of this fluid, with the associated steam loss, led to a fluid at a temperature of about 260°C with a chloride concentration of about 1700 g/t flowing towards the Western Production Field.

The resistivity (Risk, 1984) and chemical boundaries of the reservoir are correlated with less mineralized waters found in wells within and outside the resistivity boundary zone. For example WK223, in the west, had a chloride concentration at 1341m depth of less than 265 g/t in 1963. WK224, also in the west, had a chloride concentration at 274m of about 28 g/t in 1970. WK32 and WK33, in the northeast, had a chloride concentration of less than 7 g/t. Bicarbonate water was encountered in WK5, along with negligible chloride and 1000 g/t HCO_3. These bicarbonate waters arose from steam separating from the deep water followed by condensation and scrubbing out of the more soluble H_2S leaving CO_2 to rise and dissolve in the ground water. In the southwest WK208, in 1978, had a chloride concentration of 1347 g/t at 747m, indicating dilution in this well. Dilution was also seen in WK214 and WK220. At the resistivity boundary in the east dilution is demonstrated by a discharge sample from WK 305, collected in 1997, which had chloride and bicarbonate concentrations of 12 and 303 g/t respectively (Wood et al, 1997).

The Wairakei geothermal reservoir fluid was saturated with quartz. Hot water at 260°C reached saturation with amorphous silica when it was flashed to 6.6 ba (163°C). Initial H.P. separation was at 16.2 ba (202°C) and I.P. separation at 6.5 ba (162°C). Thus the water in the separators was not supersaturated. Saturation was only exceeded in the weirbox causing deposition (about 1000 tonnes per annum) in the drains throughout the borefield.

The pH in the deep aquifer before development was 6.3 resulting in the waters being slightly undersaturated with respect to calcite. As the gas

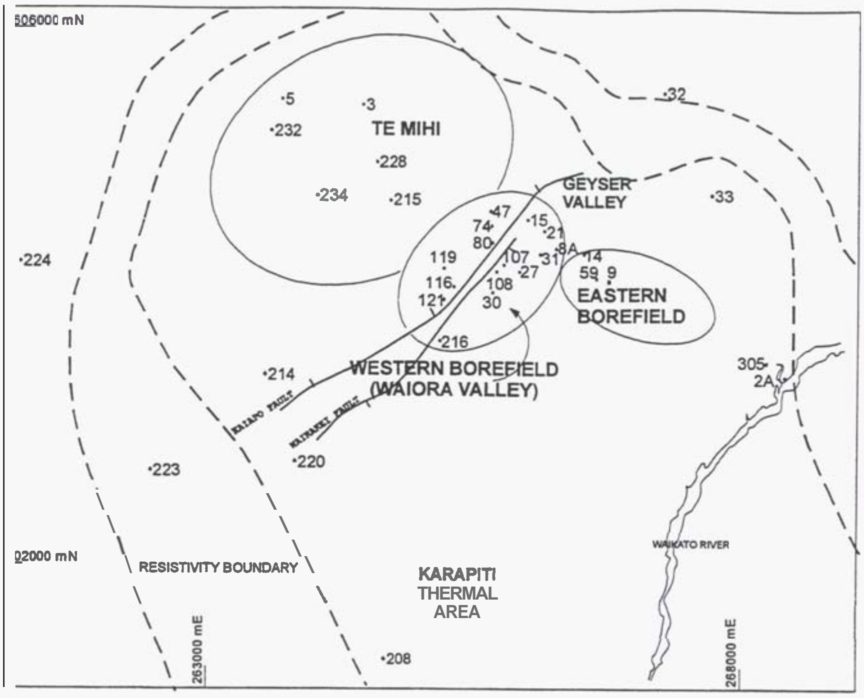

Figure 1 : Wairakei Geothermal Field.

content of the water is low, loss of CO_2 into the steam gave a small increase in pH as the water ascended a bore. This has caused no noticeable calcite deposition.

2.2 Spring Chemistry

Surface springs at Wairakei were located in two major areas, the Waiora Valley and the Wairakei Geyser Valley and typical analyses are shown in Table 1. Fluid from the main Geyser Valley features showed dilution of the deep chloride water from about 260°C to 210-220°C, followed by boiling as the fluid ascended from about 220m through the Huka beds to discharge at the surface.

Table 1: Wairakei Spring Chemistry

Spring	Date	pH	Cl g/t	SO4 g/t	Cl/SO4
Geyser Valley Springs					
S97	5/51	7.6	1771	25	190
S37	1/63	8.75	402	49	22
S197	2/67	3.75	28	268	2.8
Waiora Valley Springs					
Devil's Eye	1929	3	718	189	10.3
"	1951		665		
"	1984	2.75	296	690	1.2
"	1997	2.54	154	345	1.2

The Waiora Valley activity, situated at a higher elevation than the Geyser Valley springs, discharged acidic chloride-sulphate or acid sulphate waters. Devil's Eyeglass, the lowest elevation discharge in 1929 (Grange 1937), had a pH = 3.0, Cl= 718 g/t, SO, = 189 g/t and Cl/SO_4 = 10.3. There was a slight decrease of chloride to 665 g/t in 1951. In 1954 the total chloride flow in the Waiora Valley area was 9.3 g/sec (c.f. Geyser Valley = 154 g/sec) and the average chloride concentration was 200 g/t (1/10th of Geyser Valley).

2.3 Gas and Steam Chemistry

Ellis (1962), Glover (1970) and Giggenbach (1980) have shown that differences in gas composition of individual production wells are related to steam separation processes within the reservoir both in the natural state and due to the development of the reservoir.

The original CO, concentration of the deep fluid at Wairakei was deduced to be about 17.5 millimoles (mM)/100 moles of water with a CO_2/H_2S ratio of about 30 (Ellis, 1962 and Glover, 1970).

The wells were classified into four main types:

A. A well that discharges water that has not been modified (enthalpy of about 1140 kJ/kg (260°C), CO_2 = 15 - 22 mM/100 moles H_2O).

B. A well that discharges water that has lost steam (enthalpy of less than 1140 kJ/kg, CO_2 of less than about 15 mM/100 moles H_2O).

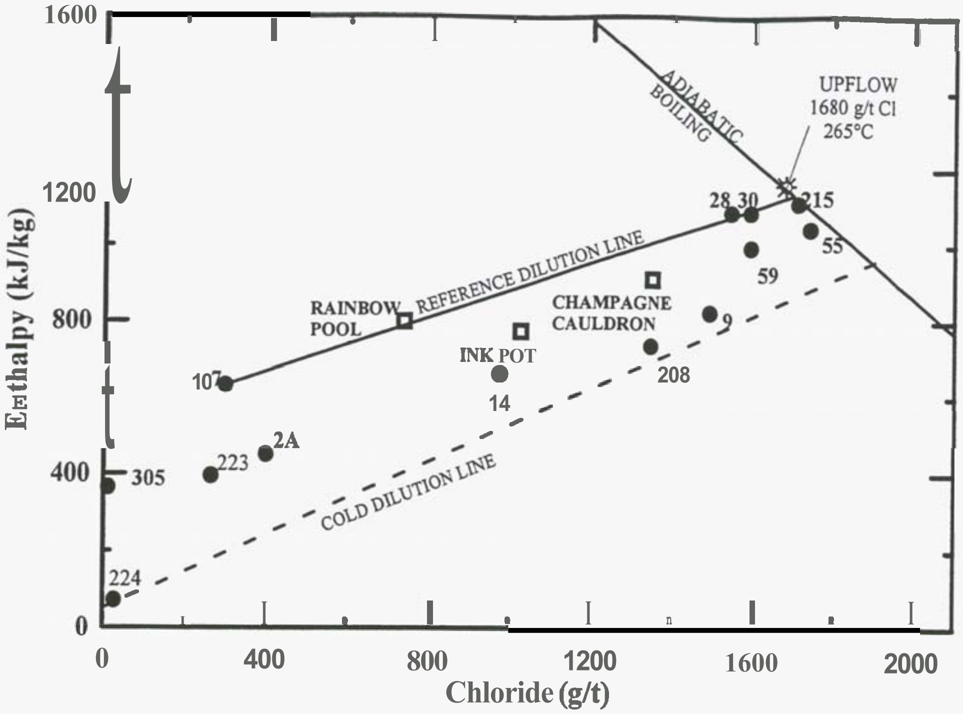

Figure 2: Enthalpy versus chloride of Wairakei well and spring waters.

C. **A** well that discharges separated steam only (enthalpy of about 2780 kJ/kg, CO, > about 150 mM/100 moles H_2O).

D. **A** well that discharges water that has lost steam initially and then regained steam while migrating through the country.

The existence of a mobile steam phase in the upper part of the reservoir before development may be deduced from a number of facts. Firstly, the occurrence of acid sulphate waters such as those in the Waiora Valley implies an underlying steam supply. Secondly, the CO_2 in the bicarbonate waters must have come from steam. Thirdly, the discharge of steam from the fumaroles in the Upper Waiora and the Karapiti Areas. Fourthly, some of the early wells in the Eastern Borefield produced a flow of steam only.

Steam zones have been exploited in both the Eastern and Western borefields since production commenced and are now being tapped in the Te Mihi area.

2.4 Interrelationship of initial fluids

Figure 2 is a conventional enthalpy-chloride mixing diagram showing the relationship between different water types in the Waiora and shallow aquifers. The well data are from the earliest available analytical data and the spring data from Glover (1977). The data are bounded by two mixing patterns, relative to the highest chloride fluid, with either unmineralised cold water of zero chloride, or steam heated waters at about 155°C such as encountered in wells WK3 and WK5. The end-member diluent of the reference dilution line is similar to the water found in WK107 in 1978 (Section 3.4). Mixing of chloride water and steam-heated waters with or without additional cold groundwater leads to hybrid hot dilute chloride waters such as that found in the outflow zone near the Waikato River (e.g. WK2A).

It is difficult to identify diluting fluids present in the undisturbed aquifers (pre-development). However candidates are steam heated waters (Cl = 0; t = 150°C), dilute chloride waters ($0<Cl<300$ g/t; $0<t<200$°C) or fresh groundwater (Cl = 0; t = 10°C). A chloride gradient with respect to depth occurred in the shallow aquifer and this is supported by spring data (Healy, 1951). Certainly by 1960, a vertical chloride gradient is apparent in parts of the borefield, e.g. shallow wells WK8A and WK9 showed dilution, having waters containing 1090 and 1700 mg/kg Cl, respectively, at atmospheric pressure.

3. RESPONSE TO DEVELOPMENT

3.1 Response of Springs

As development of the reservoir took place, spring activity declined accompanied by dilution of the spring waters by shallow groundwater. The geysers and flowing springs of high chloride concentrations were eventually replaced by steam heated waters (low pH and Cl and high SO,) of low or zero discharge and by fumaroles and steaming ground.

This was attributed to declining pressures in the geothermal reservoir which lowered the water level below the discharge point of the springs. Figure 3 shows changes with time of the mass flow of chloride into the Wairakei Stream in Geyser Valley, the average chloride concentration of the springs, the heat gain of the stream, and the mass output from the Wairakei bores. The first three parameters show an inverse relationship to the field output.

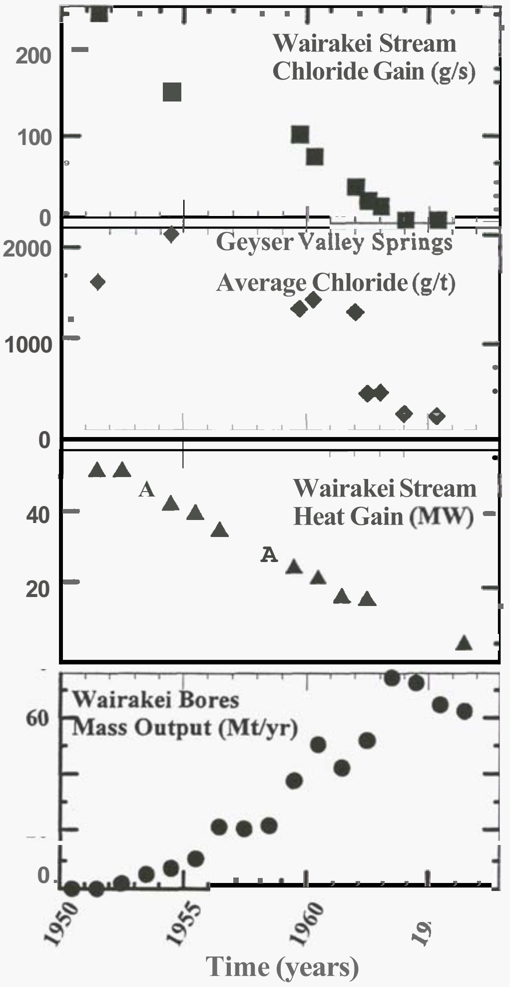

Figure 3: Changes in Wairakei Geyser Valley and in mass output of the Wairakei borefield (1950 – 1967).

While some changes in spring activity were noted prior to 1951 the major changes, including total cessation of hot neutral chloride water discharge in Geyser Valley, took place subsequent to large scale mass discharge from the wells. Much slower change took place in the Waiora Valley. By 1984 changes in the chemistry of the Devil's Eyeglass had occurred, in line with decreasing pressures, to pH = 2.75; Cl = 296 g/t; SO_4 = 690 g/t; Cl/SO_4 = 1.2, in 1997 further analyses gave pH = 2.54; Cl = 154 g/t; SO, = 345 g/t; Cl/SO_4 = 1.2 (Table 1). A possible explanation of the difference in the changes in Geyser Valley and the Waiora Valley may lie in the original chemistry of the two areas. Geyser Valley features mainly discharged deep chloride water having undergone a small amount of dilution by surface water. The Waiora Valley features originally had a much lower deep water component (<50%). Being near to a high upflow zone and at higher elevation than Geyser Valley, the Waiora Valley features discharged a mixture of steam, deep water and groundwater. The hot dilute chloride-sulphate water at relatively high elevation in the Waiora Valley is now slowly draining away and providing the water for the Devil's Eyeglass. In Geyser Valley, when pressures decreased, the deep chloride component flow was reduced and the features were invaded by ground water as the acid chloride-sulphate water was absent. Thus the chloride springs were rapidly quenched and the chloride water replaced.

3.2 Response of Wells

The first changes in well chemistry were observed in wells WK21 and WK31 which started to decline in chloride concentration in January 1961 and 1962 respectively. These changes suggested development of a dilution zone in 1965 extending from Geyser Valley to the production wells. In simple terms the channel supplying Geyser Valley in the pre-development days was reversed and provided access for cooling and diluting water to reach the wells. Obviously the depth of casing in a well influences the access of shallow diluting water into the well discharge. However the effect of structure is illustrated by comparing WK31 and WK108. These wells have almost identical casing configurations. WK31 showed dilution in 1962 whilst it was not seen in WK108 until after 1968. From 1965-1975 this dilution trend was more obvious with the strong effect of structure being clear as cold tongues of water penetrated from the NE along the Kaiapo Fault and along the Wairakei Fault.

In 1978 downhole samples fiom a downflow in WK107 indicated a diluting fluid of a chloride concentration at least 300 g/t and a temperature of 150°C. Downhole samples in some shallow water level holes in 1983 showed chloride concentrations up to 800 g/t within 15m of the surface, a general decrease of chloride with elevation and concomitant sulphate increase. These data confii that residual chloride contents of at least 300 g/t characterise surface zone waters over much of the production area. Change in the sulphate content and Cl/SO_4 ratio in production wells, e.g. WK15, WK21, and WK80, also suggest that steam-heated surface waters were the principle diluent.

3.3 Enthalpy and Chloride changes

General chemical trends can be represented on an enthalpy-chloride diagram (Figure 2) in which the apparent aquifer chloride concentration (fkom well discharge data) is plotted against the enthalpy of liquid at the quark geothermometer temperature. On such a diagram, changes with time appear as vectors reflecting the dominance of boding, dilution, or transient conductive heat transfer processes.

Between 1961 and 1971 the Western Borefield wells showed mainly a dilution trend while the Eastern Borefield wells showed mainly a boiling trend. **Similar** trends for the Western Borefield were apparent in the 1971-1981 period but the magnitude of dilution was larger and more wells were involved than during the earlier period. Wells in the Eastern Borefield also showed dilution trends in this latter period.

The use of enthalpy-chloride diagrams, although useful for interpreting initial well discharges, is not appropriate for quantifying trends in an exploited field such as Wairakei. The time series for some wells **may** mimic field trends but other wells can exhibit contrary or variable behaviour that often **masks** field trends.

3.4 Corrected chloride (Cl')

Brown et al. (1988) determined that in order to compare chloride concentrations in different wells they must be referred to a baseline condition. **A** theoretical reference dilution line (Figure 1) was constructed between the initial composition of the water entering the western production area at depth: i. e. 1700 g/t chloride, enthalpy of 1134 kJ/kg (approx. 259°C), and a diluting water containing 300 g/t chloride at 632 kJ/kg (approx.150°C). **All** chloride values were corrected for aquifer steam **loss** and recalculated to this reference line to give corrected chloride values (Cl').

Quartz geothermometer temperatures (T_{QTZ}) for the same time periods provide aquifer temperatures to +/– 2°C. The values show similar changes to the chloride concentrations but the silica temperature appears to respond more quickly to changes. **This** is because the temperature of the water reaching the well is changed by (a) dilution which affects Cl' also, and (b) by boiling which does not affect Cl'. Thus lower pressures, which occurred with large well discharges in the early **1960s,** led to reservoir boiling of the geothermal liquid before it reached the well. **The** silica concentration would adjust to the new (lower) temperature but Cl' would be unchanged or even slightly increased (due to steam enthalpy differences at high and low pressures).

From 1975 to the early 1980's the same trends continued. Wells WK47, WK74, WK116, and WK119 maintain the highest Cl' and **support** the suggestion of upflow in the Te Mihi Basin followed by movement east to the **main** Western Borefield. During the 1980's and 1990's the **quartz** temperatures in some of the Western Borefield production wells were relatively stable although the Cl' continued to decrease. This suggests that dilution is occurring below the depth at which boiling occurs to control the **quartz** temperature. This indicates flow down faults and/or wells and then horizontal flow rather than dilution by an even, downwards percolation of cold water.

3.5 Gross Changes in Cl'

Average chloride (Cl') values for production areas, weighted for well **output,** have been calculated (Figure 4). A steady decline of chloride

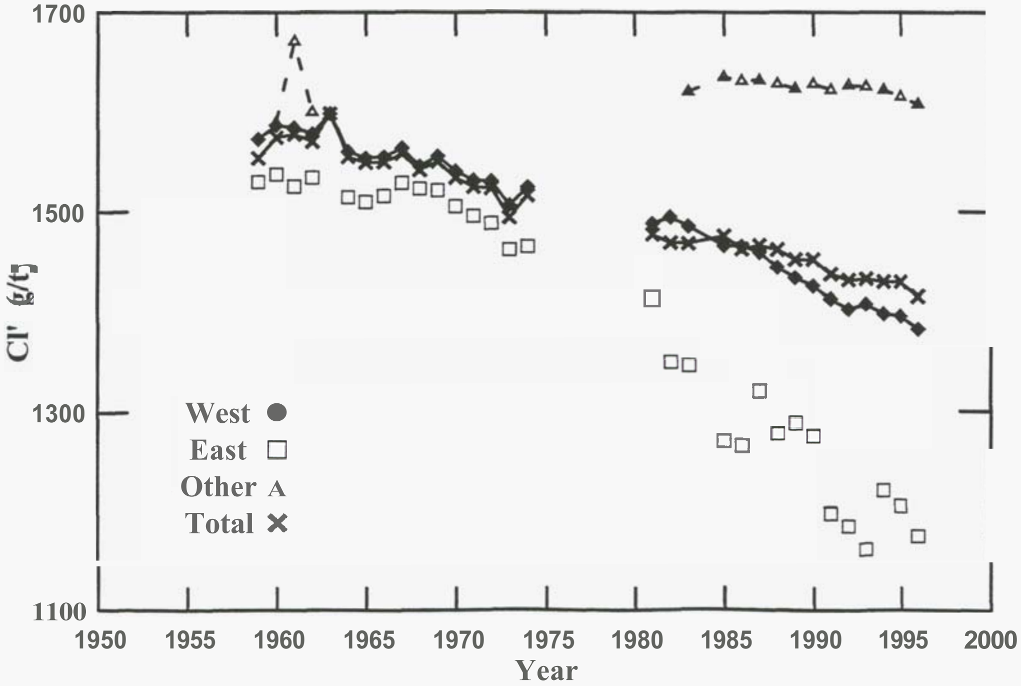

Figure 4: Changes in average corrected chloride (Cl') values for the Wairakei production areas.

concentration of approximately 5 g/t per year was observed between 1960 and 1983. It is noted, however, that the average depends on which wells are used and as the more diluted wells are taken out of production, so their effect (although small due to their low output) is removed. The major mass flow is from the West and thus the Total line is close to the West line. The East shows much more dilution than any other area and is more variable, probably due as much to the fewer and lower output wells here than elsewhere. Thus the East points have not been connected but the trend is obvious. The introduction of the Te Mihi liquid wells in 1985 is seen in the "Other" plot. The higher chloride concentrations in this part of the reservoir is reflected in the Cl' of about 1635 g/t in 1985 compared with 1466 g/t in the West. The difference is partly due to the Te Mihi wells being closer to the deep upflow and partly to the long production from the West wells resulting in pressure drawdown and infiltration of colder surface water in that area. The Cl' values for all the groups are still decreasing. The rate of decrease for the West (7.5 g/t per year) is greater since production commenced from the Te Mihi wells. This is due to some of the high chloride water supply from Te Mihi being produced in that area, rather than flowing to support production from the Western Borefield.

3.6 Chloride Mass balance for the Wairakei Production Field

Brown et al. (1988) modelled the mass and chemical flows in the Wairakei field. The mass flows were (1) M_R, deep recharge fluid inflow, (2) M_I, cool surface water inflow, (3) M_D, drainage from the upper levels, **(4)** M_P, production outflow, and *(5)* M_O, non-production outflow. M_O is considered to be zero as there has been no surface outflow of water since the early sixties. Rigorous treatment would include the surface steam flow in M_O. Values of this steam flow are not known and have been neglected in the calculations except for 1993 and 1996. These latter values include the steam flow from the Te Mihi wells. M_D is calculated from the pressure and gravity changes (Allis and Hunt, 1986) and has been zero since 1987. Assuming constant chloride values for Cl_R, Cl_I, and Cl_D of 1700,300 and 1700 g/t respectively the percentage of cold inflow in the production fluid is calculated. This has increased with time (Figure 5).

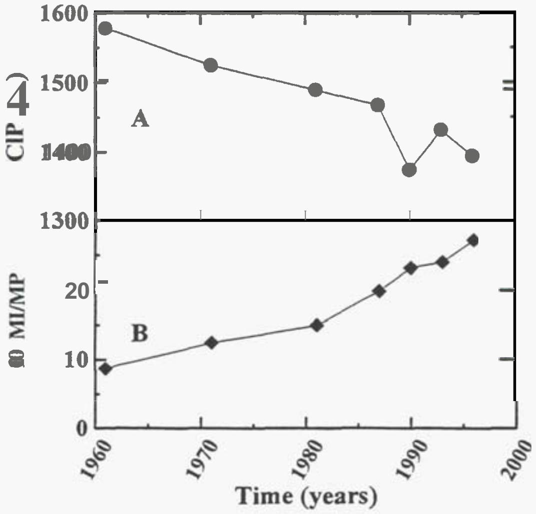

Figure 5A: Change in average chloride content of the production well fluid - ClP (g/t)
Figure 5B: Change in percentage of cold inflow in the production well fluid (100 x MI/MP)

3.7 Silica Changes

With dilution and cooling of the aquifer supplying the wells the maximum temperature is now 235-240°C. A number of wells show quartz equilibrium temperatures higher than the temperature equivalent to the discharge enthalpy. The suggestion has been made that the silica concentration is no longer controlled by the quartz solubility (Lovelock, 1995).

3.8 Gas Changes

Gas compositions may change relatively quickly with time. Reservoir boiling transfers gases *to* the vapour phase and this depletes the residual water. As further boiling occurs the gas in the steam is diluted and the gas in the residual water decreases further. The gas content of a particular well, therefore, depends on the extent of separation processes occurring and the proportions of steam and water entering the well at the feed zone(s). Initially, the steam separation process was related to a single stage equilibrium mechanism. Later observations showed that the low gas contents and CO_2/H_2S ratios (e.g. WK30 where, in 1967, C02 = 1.1 mM/100 moles total discharge and CO2/H2S = 5.8) could not be explained by a distinct one stage loss of steam. Thus a fifth type was defined, (Glover, 1970), involving "multistage" steam separation, in which early flashed steam escapes from the water phase and the final gas-in-steam to gas-in-water equilibrium is governed by the secondary flashed steam and not by the total steam flashed. Many Wairakei wells are in this category at present.

Generally, gas concentrations in both liquid and steam wells, and in the combined steam flow from all wells decrease with time. Gas concentrations in dry steam wells may increase if diluting water condenses some of the steam in the steam cap. At present gas concentrations in the total discharge from individual Wairakei wells vary from 2 to over 1300 millimoles CO_2/100 moles steam. High values are found in the Te Mihi "dry steam" wells. If the steam is close to the edge of the reservoir it is likely that cooling and condensation will occur thus increasing the gas concentration. This probably accounts for WK232 and WK234 being higher in gas content than WK228.

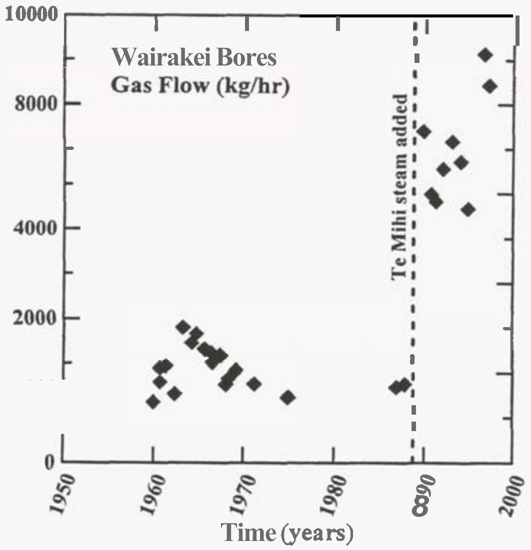

Figure 6: Total gas flow to the Wairakei Power Station (kg/hr).

The gas flow from the bores to the power station is shown in Figure 6. During the early 60's the flow rose as more wells were brought into service. From 1963 the gas flow decreased as the gas concentration in the wells decreased. The large increase in 1988 is due to the addition of the Te Mihi wells. At that time WK234 which produces about 150 t/hr contributed approx. 65% of the gas flow. This large gas flow provided new challenges with respect to balancing the gas flow to the 7 condensing sets and the upgrading of some of the gas extraction equipment at the station.

4.0 Future Challenges

No doubt the field will continue to provide challenges of interpretation and power station management. Large scale reinjection will affect interpretation of the changes in the water chemistry if reinjection fluid mixes with the present deep and diluting fluids. Decreases in the allowed discharge to the river may need modification of power station operation.

5.0 Acknowledgments

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