DEVIATIONS IN SILICA GEOTHERMOMETRY AT WAIRAKEI

Brian Lovelock

Electricity Corporation of New Zealand
Wairakei Power Station, Private Bag 2001, Taupo, New Zealand

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ABSTRACT

Analysis of feed-zone temperatures and discharge chemistry data for Wairakei production wells indicates that reservoir silica concentrations have departed from the quartz equilibrium that existed prior to development of the field and are now 50-100ppm oversaturated with respect to quartz. As a result quartz equilibrium temperatures are 10-20°C above measured feed-zone temperatures in 220-230°C liquid feeding wells.

Supersaturation occurs primarily as a result of boiling but the ingress of chalcedony-saturated waters may also be a contributing factor. Oversaturated conditions are sustained because the kinetics of silica precipitation are not sufficiently rapid to allow fluid to reequilibrate before it reaches the wellbore. The analysis suggests that while the geothermometer may be accurate in the early stages of development when reservoir conditions are stable, divergent temperatures may result when a system is in a more dynamic state.

The main implications of silica disequilibrium at Wairakei are that quartz geothermometer temperatures can no longer be used to accurately monitor changes in feed-zone temperature and can distort interpretation of reservoir hydrology when combined with chloride data in chloride-enthalpy plots. As with other fluid-mineral geothermometers, application of the quartz geothermometer should be circumspect and supported by regular verification against measured temperatures.

1. INTRODUCTION

1.1 Background to Study

Mahon (1966) compared silica geothermometer temperatures at Wairakei with maximum downhole temperatures and showed that the reservoir water, at that time, was close to equilibrium with respect *to* quartz. Subsequently, much of the geochemical analysis of reservoir hydrology and discharge-induced change at Wairakei has hinged on the use of the quartz geothermometer as an accurate measure of feed-zone temperature. The kinetics of quartz precipitation and dissolution were considered sufficiently fast to allow the geothermometer to be used to monitor relatively rapid changes in feed-zone temperature (eg: Ellis and Mahon, 1977).

Mahon and Finlayson (1983) reassessed the accuracy of the silica geothermometer at Wairakei after 20 years of field production and temperature decline. Although their analysis was based on only six wells they concluded that the silica geothermometer was still acceptable for monitoring purposes. However, they did note anomalously high silica temperatures in two out the six wells and attributed this to boiling. Confidence in the geothermometer at Wairakei has extended to its use in developing enthalpy-chloride diagrams (eg: Brown ***et al*** ,1987), a key technique for the analysis of boiling and dilution processes.

Since about 1968, downhole temperature surveys at Wairakei have been conducted routinely on discharging wells and this has allowed the feed-zone temperatures to be accurately measured in liquid-feeding wells. Monitoring during the past 5 years has shown that mean feed-zone temperatures in the main production area have stabilised at about 225-230°C (Bixley, 1990). In contrast, discharge silica concentrations equate to quartz equilibrium temperatures of 235-245°C. With a recent improvement in the precision of discharge enthalpy measurements this discrepancy has become apparent as a pronounced enthalpy "deficit" of between -50 and -100 kJ/kg for most liquid-feeding wells, ie: measured enthalpies are consistently lower than geothermometer-based enthalpies.

This study was undertaken primarily because of concern that ongoing, uninformed use of the quartz geothermometer at Wairakei

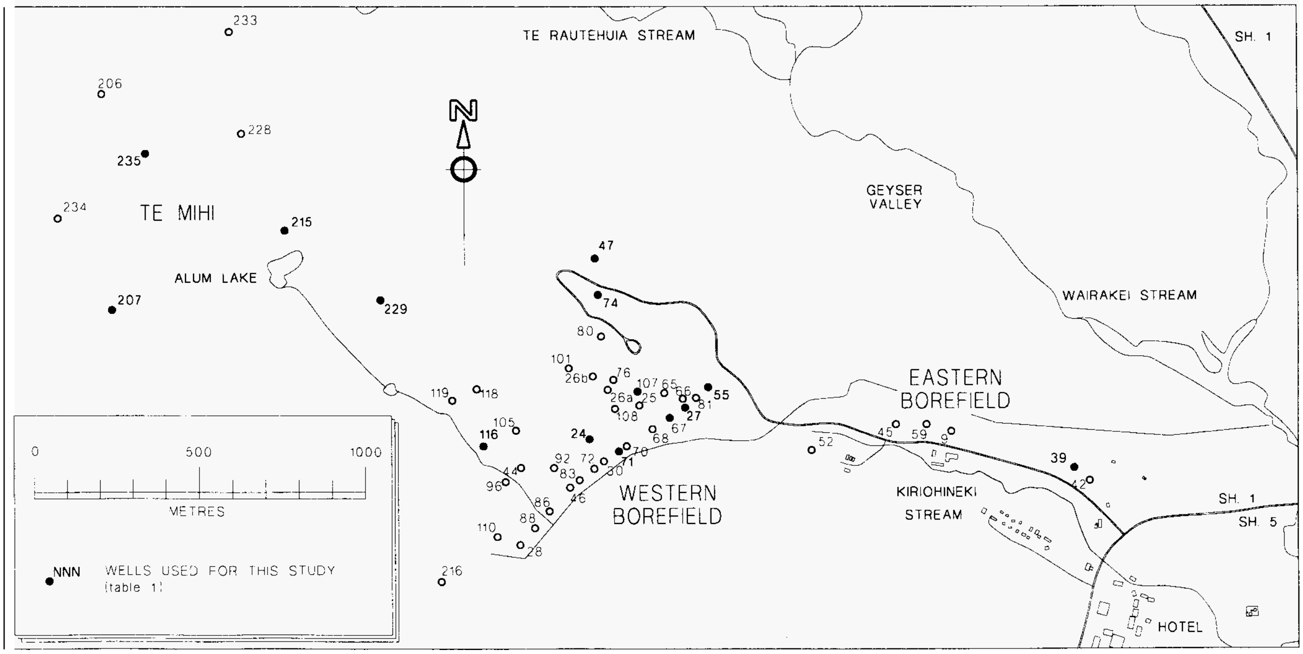

Figure 1. Map of the Wairakei Geothermal Field Showing Production Wells

could give rise to inaccurate interpretation of reservoir hydrology. Also, it is believed that the reliability of the quartz geothermometer has often been taken for granted, without sufficient consideration of the processes that can cause divergence in calculated temperatures, particularly in developed reservoirs.

The study first quantifies the quartz disequilibrium at Wairakei and then examines the distribution of saturation conditions in the reservoir. Interpretation of the data attempts to address two questions: (1) how do reservoir waters become oversaturated, and (2) how are oversaturated conditions sustained. The implications for the use of the geothermometer at Wairakei and other fields are also considered.

1.2 The Quartz Geothermometer

Of the many fluid-mineral geothermometers used in geothermal science, the quartz-based silica geothermometer is the best defined and most widely used. Since the early quartz solubility experiments of Kennedy (1950) and Morey *et al.*, (1962) the validity of the geothermometer has been confirmed in many fields (eg: Mahon, 1966; Fournier and Kowe, 1966; Arnorsson, 1975) and it is widely believed that silica saturation is attained in any high-temperature field where silica is present (eg: Fournier, 1985).

The original silica geothermometer of Fournier and Rowe (1966) was based on experimental data for the solubility of quartz. Equations were later fitted to this data and provided a rapid and convenient means of applying the geothermometer. Two equations, for use up to 250°C, are given by Fournier (1981); for water at equilibrium:

$$t\ ("C) = 1309/(5.19 - \log SiO_2) - 273.15, \qquad - (1)$$

and for discharge water after adiabatic steam loss to 100°C:

$$t\ ("C) = 1522/(5.75 - \log SiO_2) - 273.15, \qquad - (2)$$

where SiO_2 is the concentration in mg/kg. Using more recent quartz solubility data, Foumier and Potter (1982) produced an expanded and more flexible geothermometer for use up to 330°C. This geothermometer differs from the above equations by a maximum of about +4°C at 250°C.

Quartz saturation conditions are controlled by the activity of silicic acid (H_4SiO_4) but, because the concentration of dissociated silicate ion ($H_3SiO_4^-$) and other silica complexes is relatively minor in most geothermal reservoirs, the geothermometer can be accurately applied using total SiO_2 concentrations.

1.3 The Wairakei Geothermal System

A map of the Wairakei field including the location of production wells is shown in Figure 1. In its initial state, the reservoir was a liquid-dominated system with a base temperature of about 260°C and chloride water outflows to the surface in the Geyser Valley. The reservoir fluid at typical production depths had a neutral pH, Na-Cl composition with 1600-1700ppm Cl and a low gas content of 0.05% by weight (20 mmoles/100moles). Most wells are drilled to 600-700m and the bulk of production comes from 550-600m depth. This is near the base of the Waiora Formation, a thick sequence of pumice breccias and intercalated lacustrine sediments.

Physical changes to the reservoir, in response to exploitation, have been described by Bixley (1986, 1990). A rapid decline in reservoir pressures occurred in the period 1960-1965 accompanied by a parallel decline in reservoir temperature in line with saturation conditions. This led to the development of a vapor zone above the main borefield and a decline in water flow from surface springs. Wells located close to the Geyser Valley were quenched by the ingress of relatively cool groundwaters. This water appears to flow laterally into the Western borefield where it appears as internal downflows in several wells.

In 1994 about 80 production wells were supplying the Wairakei Power Station, of which about 35 produce from single-phase liquid feeds, 7 are shallow steam producers, and about 10 have excess enthalpy discharges (discharge enthalpies above the enthalpy of reservoir liquid). Vapor zones of varying pressure and distribution now exist over most of the Wairakei reservoir but liquid conditions still exist below a depth of about 550m. The gas content of this liquid is now less than 50ppm (0.005%) reflecting its boiled state. The steam cap overlies liquid water and most wells produce from either dry steam or single-phase liquid conditions. Two-phase (mixed steam and water) reservoir conditions appear to be of very limited extent and most of the excess enthalpy wells probably feed from separate steam and water feeds.

For liquid-feeding wells reservoir chloride concentrations can be accurately calculated and range between 1300 and 1800ppm. Water in the Western Borefield is diluted about 15% with respect to pre-exploitation values. A detailed analysis of the chemical response to production is given in the review by Brown *et al.* (1987).

Gravity surveys and heat flow calculations suggest that the reservoir is now in a state of dynamic equilibrium with mass withdrawal matched by recharge, at least half of which is considered to be deep 265°C water (Allis, 1981).

2. METHODS

The analysis of quartz disequilibrium in this study is based on a comparison of measured feed-zone temperatures and quartz equilibrium conditions for liquid-feeding production wells. In these wells the location and temperature of the feed-zones can usually be defined from downhole temperature surveys conducted under flowing conditions. Of the approximately 35 liquid-feeding wells at Wairakei, about half have had flowing temperature surveys which accurately define the feed-zone temperature. These temperature data are presented in Table 1. Temperature surveys were run using either Kuster instruments or continuous electrical logging. Included in Table 1 are two additional wells (WK215, WK235) which have slight excess enthalpies due to steam entering the bore above the main feed depth.

TABLE 1

Measured Feed-Zone Temperatures and Reservoir Chemistry for Wairakei Production Wells

Well No	Temp Survey Date	Measured Feed Temp °C	Feed Enthalpy kJ/kg	Sampling Date	Discharge Chloride mg/kg	Discharge Silica mg/kg	Discharge Enthalpy kJ/kg	Separator Pressure b.g	Xatm	Xsep	Xres	Reservoir Chloride mg/kg	Reservoir Silica mg/kg	TQTZ °C (1)	TQTZ °C (2)
39	6-May-89	192	817	14-Nov-88	1300	300	820	1.4	0052	0.128	0.000	1075	248	196	195
24	28-Mar-88	225	968	23-Nov-87	1918	564	960	5.4	0.119	0.139	0.000	1455	428	242	238
27	7-Feb-90	232	1001	30-Jan-90	1914	564	965	5.4	0.119	0.155	0.000	1426	420	240	237
47	29-May-91	223	959	23-Apr-91	2219	513	935	5.7	0.122	0.131	0000	1693	391	233	231
55	12-Feb-88	229	987	8-Oct-87	1820	559	940	5.2	0 116	0.150	0.000	1367	420	240	237
67	27-Feb-89	231	996	8-Nov-88	1932	598	970	5.3	0.117	0.154	0.000	1443	447	246	242
71	22-Feb-89	224	964	16-Nov-88	1914	579	990	5.5	0.120	0 136	0.000	1456	441	244	241
74	15-Oct-86	226	973	11-Dec-86	2240	585		5.8	0.123	0.137	0.000	1695	443	245	241
107	5-Jun-91	214	917	23-Apr-91	1659	501	930	5.4	0.119	0.114	0.000	1295	391	233	231
116	22-May-91	232	1001	14-May-91	2170	575	1000	5.7	0.122	0.151	0.000	1617	428	242	239
207	6-Mar-89	236	1019	12-Apr-89	2330	581	961	-	0.269	-	0.000	1704	425	241	238
229	5-Sep-86	221	949	7-Oct-87	2300	565	960	5 8	0.123	0.125	0000	1764	433	243	240
215	16-May-91	226	973	8-Mar-91	2370	544	1138	-	0.321	-	0.090	1768	406	236	234
235	15-May-89	242	1048	16-May-89	2304	600	1180	5.3	0.117	0.242	0.075	1667	434	243	240

Xatm - steam fraction to atmosphere

Xscp - steam fraction at separator pressure (where applicable)

Xres - steam fraction in reservoir

(1) - Foumier and Potter (1982)

(2) - Foumier (1981), no steam loss

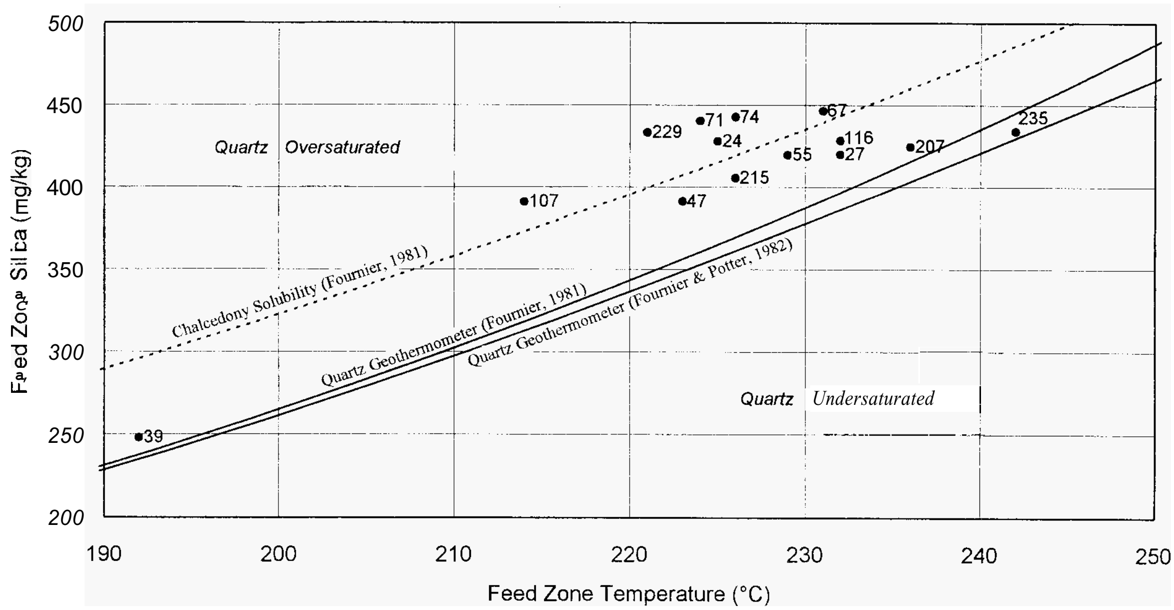

Figure 2. Calculated reservoir silica concentration versus measured feed-zone temperature for Wairakei production wells using data from Table 1

Included in Table 1 are discharge chloride and silica analyses for sampling dates closest to the temperature survey. For most of the wells, feed-zone temperatures and discharge chemistry had shown little or no change over the period the data span and temporal variations amongst the wells are considered small. The chloride and silica analyses are for water discharged at atmospheric pressure (ie: weirbox water) usually after prior steam separation at a higher pressure. Discharge enthalpy measured at the time of sampling is calculated from separated steam and water flows (for wells with production separators) or by the lip-pressure method.

Silica was analysed using the atomic absorption procedure of Giggenbach and Goguel (1986). A comparison of results with those from an an independent laboratory (using a common control water) showed agreement to within 2%. From experience in running laboratory control samples over a number of years, the method appears to be be reproducible to within about ±10 mg/kg at 500 mg/kg. The possibility of systematic errors in the analyses is considered unlikely. This is supported by the observation that discharge samples from the neighbouring Ohaaki geothermal field, when analysed alongside the Wairakei samples, do not show the same deviations in quartz temperatures.

All the wells in Table 1 are considered to have only one major feed-zone and the reservoir concentrations of silica and chloride were calculated using the feed-zone enthalpy (generally close to the measured enthalpy), correcting for steam loss at the separator and atmospheric pressures. In the case of WK235 and WK215, which have excess enthalpies. the reservoir concentrations are corrected for steam in the reservoir.

The selection of wells used in this study is considered representatative of the range of fluid compositions found at Wairakei. As can be seen from Figure 1, most production wells at Wairakei are located in the Western Borefield where feed-zone depth, temperature and chemistry are fairly uniform.

3. RESULTS

3.1 Reservoir Silica Concentrations

Calculated reservoir silica concentrations from Table 1, expressed as total SiO_2, are plotted in Figure 2 as a function of measured temperature, together with the quartz solubility correlations of Fournier (1981) and Fournier and Potter (1982). This plot clearly shows the departure of silica concentrations from quartz equilibrium with waters on average 50ppm oversaturated and up to 90ppm oversaturated in WK71, 74 and 229. Concentrations lie either side of the solubility line for chalcedony. although at the temperatures involved this is not considered to be a controlling mineral phase. The silica concentrations. in Fact, show. little or no trend with temperature and the impression gained from Figure 1 is that the cooler wells have simply retained the silica concentrations of the deeper, higher temperature water. Silica Concentrations are close to quartz equilibrium in WK235, located in the Te Mihi area, and in well WK39 which lies in a cooler. possibly more stable outflow position in the Eastern Borefield (Figure 1).

3.2 Quartz Geothermometer Temperatures

The deviation of quartz equilibrium temperatures from measured temperatures can be seen in Table 1. using the geothermometer correlation of Fournier and Potter (1982). This shows an average 10-15°C deviation from measured temperatures with a 20°C discrepancy in WK71, 74 and 229. Included in Table 1 are temperatures calculated using equation (1) from Foumier (1981) which are 1-4°C lower. Direct application of the adiabatic expression of Fournier (equat. 2) would give temperatures 3-5°C lower still. This is mainly because the steam flash factor inherent in the adiabatic expression is not consistent with the actual flash occurring. The consequence therefore, of using the adiabatic expression in oversaturated conditions, is that the discrepancy in quartz equilibrium temperatures tends to be underestimated.

3.3 Silica Speciation in the Reservoir

Reservoir waters that have high pH's may have anomalously high total silica concentrations as a result of the dissociation of silicic acid concentration (H_4SiO_4) to give $H_3SiO_4^-$. The reservoir pH at Wairakei increased from about 6.3 to 7.1 between 1958 and 1970 because of boiling and gas loss (Ellis & Mahon, 1977), and is currently about 7.2 in the Western Borefield reservoir.

Table 2 shows the chemical speciation in the reservoir of well WK67, calculated from separated water and steam samples collected at the same pressure (different to sample in Table 1). The discharge chemistry of this well, in particular the very low gas content, is typical of all liquid feeding wells in the Western Borefield. At the feed-zone temperature of 225°C the reservoir water has an alkaline pH of 7.2 (neutral pH = 5.4) and of the total silica content, 11ppm (as SiO_2) or 2.5%, is in the form of dissociated $H_3SiO_4^-$. Applying the quartz geothermometer in this case, using the total silica concentration, would overestimate the real quartz equilibrium temperatures (ie: that based on H_4SiO_4) by 2-3°C. This is relatively small compared to the discrepancy seen in Figure 2 (10-20°C) and suggests it is only a minor factor contributing to the elevated silica concentrations. The calculated silica speciation of Table 2 is sensitive mainly to the first dissociation constants of H_4SiO_4 and H_2CO_3 and the total concentration of CO_2, but over the range of uncertainty in thermodynamic data (taken from Arnorsson *et al.*, 1982 and Glover, 1982) and analytical methods, there was little variation in silicate ion concentration.

Under stable reservoir conditions, high pH's would be neutralised by reaction with formation clay mineral buffers (Fournier, 1985). However, at Wairakei neutralisation may be slow relative to fluid residence times, particularly where flow channels are coated with silica.

TABLE 2

Calculation of Chemical Speciation in Reservoir Water of Well WK67

Date: September 19, 1991
Discharge Enthalpy = 995 kJ/kg
Water Sampling Pressure = 5.50 b g
Steam Sampling Pressure = 5.50 b g

Discharge Water		Discharge Steam	
Analyte	malka	Analvte	mmol/100mol
pH/T	(8 45 123°C)	CO2	12 1
Na	977	H2S	1 60
K	142	NH3	0 52
Ca	16 7		
Mg	0 010		
Cl	1666		
SO4	30 0		
tHCO3	<5		
B	22 0		
SiO2	509		
H2Sw	0 82		
NH3w	0 50		

Calculated Reservoir Chemistry at 225°C

Species	Act Coeff	mmol/100mol	mg/kg
H+ (pH)	0 784	9.16E-08	(7 14)
Na+	0 730	3 61E-02	830 927
K+	0 716	3 11E-03	121 570
Ca++	0 321	2 93E-04	11 761
Mg++	0 357	3 00E-07	0 007
Cl-	0 716	4 01E-02	1420 757
HSO4-	0 730	3 85E-07	0 037
SO4=	0 281	1.87E-04	17 939
H2CO3	1 000	4 91E-04	30 424
HCO3-	0 730	3 90E-04	23 802
CO3=	0 281	1.62E-07	0 010
H3BO3	1 000	1.72E-03	106 508
H2BO3-	0 709	3 17E-05	1931
H4SiO4	1 000	7 13E-03	684 959
H3SiO3-	0 730	1.77E-04	16 794
H2S	1 000	6 15E-05	2 095
HS-	0 724	8 19E-05	2 708
NH4+	0 709	1.68E-06	0 030
NH3	1 000	6 35E-05	1081
NaSO4-	0 748	4 11E-05	4 895
KSO4-	0 748	2 16E-05	2 920
MgSO4	1 000	5 51E-08	0 007
CaSO4	1 000	1.93E-05	2 630
CaHCO3+	0 755	4 33E-05	4 378
CaCO3	1 000	3 13E-06	0 313
NaCl	1 000	4 51E-04	26 367

4. DISCUSSION

4.1 Historical Trends

As reservoir waters prior to 1964 were at equilibrium with respect to quartz (Mahon, 1966) it is clear that the oversaturated conditions that now exist have developed during the exploitation of the resource.

However, tracing the development of this disequilibrium is difficult because few wells have a continuous record of feed-zone temperatures and silica concentrations. In addition, discharge silica analyses prior to 1964 were inaccurate and generally too low (Mahon and Finlayson, 1983), and flowing temperature surveys were conducted only after 1968 (Bixley, 1986). Nevertheless, the impression gained from examination of the data is that the divergence of quartz temperatures occurred as reservoir temperatures declined, ie: although some decline in quartz temperatures occurred, this did not keep pace with the decline in reservoir temperature. In the work of Mahon and Finlayson (1983), discrepancies were recognised in two of the six wells studied (WK24 and 47) but because of the limited scope of the study (and possibly because of the use of maximum rather than feed-zone temperatures), an overall trend towards disequilibrium did not emerge.

4.2 Boiling and Mixing Processes

Boiling and mixing are both potential causes of silica supersaturation in geothermal reservoirs. However, boiling is likely to cause significantly greater supersaturation because of the combined effects of cooling and concentration of silica in the residual liquid. A comparison of the effects of boiling and dilution is shown in Table 3. For this calculation the diluting water is 150°C water saturated with respect to quartz or chalcedony. Cool (130-160°C) chalcedony-saturated waters are found at Wairakei overlying the Western Borefield reservoir and is probably responsible for the 15% dilution here with respect to Te Mihi water. It is unclear what the silica saturation condition of the cool water is by the time it reaches production depths but tracer injection into a downflow of such water in WK107 showed returns to production wells after several hours (McCabe *et ai.*. 1983).

Table 3 shows that the mixing of two quartz-saturated waters causes only a small degree of supersaturation. This is because quartz solubility as a function of enthalpy is fairly close to linear in the temperature range 150-250°C. Mixing with chacedony-saturated water causes greater super-saturation and could distort quartz geothermometer temperatures by 6-7°C. Boiling causes much greater supersaturation and would require significant deposition of silica to return concentrations to equilibrium with quartz. It is clear from this simple example that the quartz geothermometer is likely to "work" much better when declines in reservoir temperature are due to dilution (rather than boiling), because only a small adjustment in SiO_2 concentration is needed to restore the fluid to quartz saturation.

TABLE 3

Cooling of 240°C Quartz-Saturated Water to 220°C:

Cooling Mechanism	Final SiO_2 ppm	Oversaturation mg/kg
Dilution with 150°C quartz-saturated water	351	+10
Dilution with 150°C chalcedony-saturated water	363	+26
Adiabatic Boiling	441	+104

The importance of boiling and dilution processes at Wairakei can be examined by the use of a enthalpy-chloride plot (Figure 3) using the data from Table 1. Here enthalpy is derived from the measured feed-zone temperature (rather than the quartz temperature) and reservoir chloride is calculated from this derived enthalpy value. Included in the plot are an adiabatic boiling line passing through the Te Mihi wells and a dilution line extrapolated to a 300ppm chloride, 150°C shallow water, similar to that seen in cool downflows in the Western Borefield. Also shown in Figure 3 is the reference dilution line of Brown *et al.* (1987) defined by the 260°C, 1700ppm Cl water that was considered to be the original recharge fluid. Brown *et al.* (1987) interpreted the relative dilution of different waters by projecting the boiling line of each data point onto this reference line.

The enthalpy-chloride plot shows a clear grouping of wells along the dilution and boiling trends. Boiling is particularly pronounced in the Te Mihi area: the four Te Mihi wells produce from a range of depths and temperatures appear to be controlled by the boiling point for depth relationship. WK235 is the least boiled of the Te Mihi waters which is consistent with the accuracy of the quartz geothemometer in this well. The shallower, cooler waters (WK215 and WK229), with lower enthalpies and higher chloride concentrations, are clearly in a more boiled state with respect to the the deeper WK235 fluid. Wells WK47 and WK74, lying north of the Western Borefield are also in an evaporated position. The clear trend of data points along the boiling trend confirms that this is an important process in the Wairakei reservoir and a viable mechanism for causing quartz super-saturated conditions.

The cause of quartz over-saturation in the Western Borefield is less obvious. Here the waters are about 15% diluted with respect to the Te Mihi fluids but do not appear to be as strongly boiled. WK24 and WK71 compositions are displaced from the dilution line but WK27 and WK55 look to have undergone little boiling (although the very low gas content and overlying steam cap would suggest that this is not the case). A combination of boiling and mixing with chalcedony-saturated fluid may be contributing to the quartz saturated conditions here.

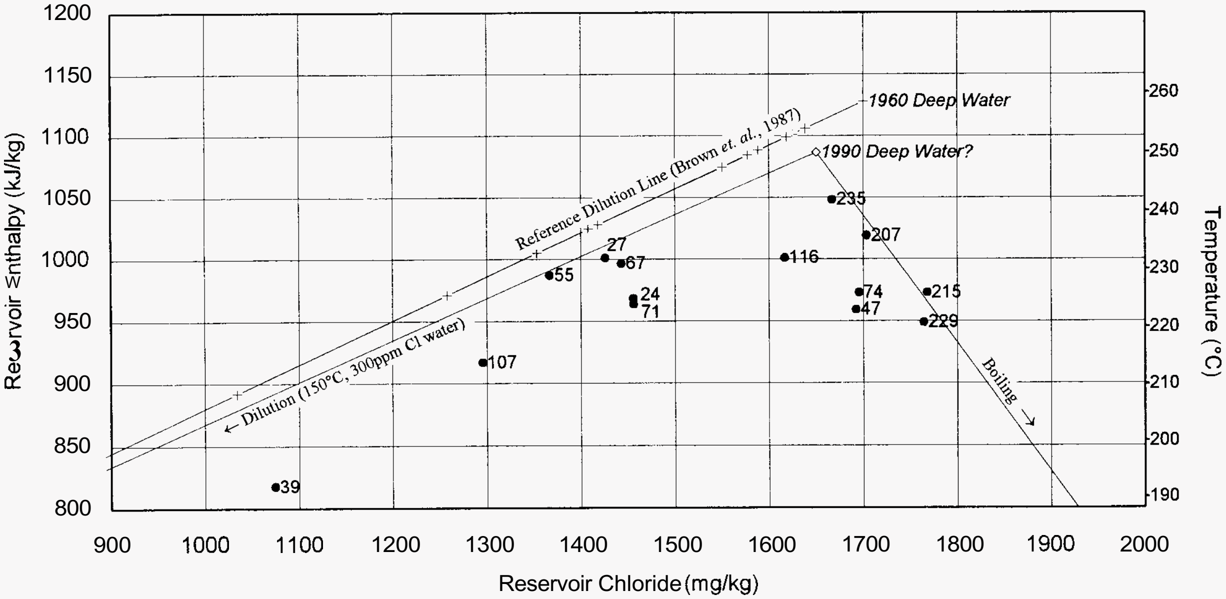

Figure 3. The enthalpy-chloride relationship of Wairakei reservoir water for the period 1986-1991 (data from Table 1).

The chloride-enthalpy data of Figure 3 can be used to analyse the hydrological relationship of Te Mihi and Western Borefield waters. It is clear from Figure 3 that the Western Borefield waters are not derived from the boiled Te Mihi waters (eg: WK215, 229) for this would require significant isothermal dilution: a process difficult to invoke in this situation. However, extrapolation of the dilution and boiling lines suggest that they may share a deeper common source of about 250°C and 1650ppm Cl (denoted "1990 Deep Water" in Figure 3). This is slightly removed from the position of the 1960 source water and suggests that after 35 years of production the deep recharge composition of Wairakei water may have itself shifted.

4.3 The Kinetics of Quartz-Water Reequilibration

The discussion above describes possible mechanisms for the development of silica disequilibrium in the Wairakei reservoir. How this disequilibrium is sustained until fluids are discharged is probably related to the kinetics of silica equilibrium and the nature of reservoir permeability and fluid flow. Silica reequilibration rates are controlled by kinetics which are reasonably well defined experimentally (eg: Rimstidt and Barnes, 1980) but are difficult to apply in natural systems. Ellis and Mahon (1977) suggested silica reequilibration at 250°C takes several hours or less while experiments by Rimstidt and Barnes (1980) indicated a period of days or weeks depending on the nature of permeability. In reinjection schemes where rapid returns to production wells occur, it has been shown that highly supersaturated injected waste water can totally reequilibrate with respect to quartz over a matter of hours (Harper and Jordan, 1985). Rimstidt and Barnes (1980) showed reequilibration rates to be directly dependent on rock surface area to mass ratios, with high rates of equilibration for movement through fine-grained sediments and lower rates for flow through wide fractures. However, because surface area to mass ratios are difficult to estimate in natural systems, and could easily vary over several orders of magnitude, it is clear that reequilibration rates are likely to be variable and site-specific.

Arnorsson *et al.* (1978) suggest that in wells where pressure drawdown has caused boiling and temperature decline, quartz equilibrium temperatures would fall to somewhere between the initial reservoir temperature and the current feed temperature. This is probably the case at Wairakei. In considering the application of the silica geothermometry to spring chemistry, Fournier (1985) suggested that reservoir water in the temperature range 230-250°C, rising rapidly to the surface, probably loses little silica through precipitation. It is reasonable, therefore, to imagine a similar situation occurring in the reservoir itself, where boiling oversaturated water moves rapidly to the wellbore without returning to equilibrium conditions.

The nature of fluid flow at Wairakei, and by inference permeability, is best interpreted from the results of radioactive tracer tests (eg: McCabe *et al.*, 1983) which have shown rapid (up to 17m/hr) but highly directional peak movement and high recovery rates (>10%). These results point to anisotropic, fault-dominated permeability with flow concentrated along open fractures. This permeability is superimposed on the more diffuse lithological permeability associated with the Waiora Formation. If the boiled oversaturated waters are in a continual state of withdrawal and recharge then kinetic disequilibrium is a viable mechanism for sustaining the oversaturated conditions.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Quartz Disequilibrium

This paper has quantified the degree of silica-quartz disequilibrium in the Wairakei reservoir and shown that the quartz geothermometer is no longer an accurate tool for monitoring changes in feed-zone temperatures. The main reservoir at 600m depth is oversaturated with respect to quartz by 50 to 100ppm SiO_2 and as a result quartz geothermometer temperatures are 10-20°C above actual temperatures. From historical data it is clear that quartz disequilibrium has developed since the start of exploitation: while reservoir temperatures have fallen 20-30°C in response to pressure decline and boiling, quartz temperatures have only partially reequilibrated.

The Wairakei reservoir is in a highly dynamic state and oversaturated conditions are reached primarily as a result of boiling and to a lesser degree by mixing with chalcedony-saturated waters. Consideration of the nature of fluid flow and permeability in the Wairakei system suggest that the kinetics of silica precipitation are not sufficiently rapid to allow the waters to reequilibrate before they reach the wellbore. This suggests that the way a reservoir responds to exploitation will have some bearing on whether reservoir water remains at equilibrium with quartz. Although the geothermometer may be shown to be valid in the early stages of resource development, when the chemical and physical state of the reservoir is stable, this does not mean that the geothermometer can be used with confidence throughout the life of the project.

5.2 Implications for the Use of the Silica Geothermometer

Care must be exercised when using the quartz geothermometer to construct enthalpy-chloride diagrams, both in the derivation of the enthalpy measurement and the recalculation of surface chloride data *to* reservoir conditions. At Wairakei, possibly because of the variable quality of enthalpy measurements in the past, it has been common practice, in the case of enthalpy deficits, to fall back on the quartz temperature as the more reliable indicator of discharge enthalpy (eg: Brown *et al.*, 1987). Unfortunately this can give rise to inaccurate chloride-enthalpy relationships and distort interpretation of reservoir hydrology. In WK229 for example. surface discharge (weirbox) water with 2300ppm Cl, flowing from a 220°C reservoir feed. equates to a feed-zone concentration of 1760ppm (Table 1). However, if an erroneous discharge enthalpy is used based on a 240°C quartz temperature then an unrealistically low feed-zone concentration of 1660ppm will be obtained. The overall effect of using unrealistically high geothermometer temperatures is to under-estimate the degree of boiling and over-estimate the degree of dilution.

The problems experienced with the geothermometer at Wairakei should not diminish its importance as a geothermometer. but should serve to highlight the need for more qualified and circumspect application. Like other fluid-mineral geotherniometers the quartz geothermometer should only be applied with full consideration of the physical conditions existing in the reservoir.

5.3 Validation of the Quartz Grothermometer

As a part of routine reservoir monitoring, efforts should be made to validate the quartz geothermeter whenever the opportunity arises. A check on the precision of the geothermometer requires a direct measure of the feed zone temperature. This may be possible during flowing downhole temperature surveys if the well has a single liquid feed and, ideally. if the flash point is within the casing. The discharge enthalpy in this case should equate closely to the measured temperature at the flash-point. Downhole samples collected from internal flows, in which the temperature is known. also provide an opportunity to verify the accuracy of the geothermometer. For liquid-feeding wells. a consistent discrepancy between measured discharge enthalpy and quartz-based enthalpies may signal divergent geothermometer temperatures.

An underlying lesson in the above is that interpretation of reservoir chemistry must not be conducted in isolation of well measurements and reservoir engineering information.

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