CALCIUM CARBONATE SCALING IN GEOTHERMAL WELLS AT OHAAKI

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ABSTRACT

Calcium carbonate scaling is a common occurrence in geothermal wells in Broadlands-Ohaaki. Broadlands-Ohaaki is a high temperature geothermal field in the eastern margin of the Taupo Volcanic **Zone** *(TVZ) in the North Island of New Zealand. The field provides the steam requirementsfor the 116 MWe Ohaakipower station.*

Using the chemical analysis of water and gas dischargedfiom the wells, the chemical changes associated with iso-enthalpic boiling and subsequentformation of calcite scales is modeled using SOLVEQ, a computerprogramfor computing aqueous-mineral-gas equilibria (Spycher and Reed, 1991), and CHILLER a reaction-path modeling computerprogram (Spycher and Reed, 1990). The model assumes the deep ***fluid*** *undergoes boilingfiom the initial reservoir temperature down to –150°C with every 5°C decrement. Saturatedgas and solid phasesformed remain in contact with the solution throughout simulating a closed-system reactionprocess.*

Maximum rates of calcite precipitationfiom modeling calculations are in the order ***of*** 10^{-4} *to* 10^{-3} *grams per kilogram of geothermal fluid and occur less than* ***20°C from*** *initial reservoir temperature. The scaling rates are consistent with inferred rates of calcite deposition in wellbores.*

1.0 INTRODUCTION

As early as 1970, there have been reports of calcium carbonate deposition in drilled boreholes in Ohaaki geothermal field. Aragonite was observed to form from the surface discharge of well BR6 (Browne, 1973) and in the steel casing of BR11, which resulted in rapid decrease in output from 500 to 260 k-lb./hour (Mahon and Finlayson, 1972). By the end of 1996, a total of 11 production wells have undergone continuous chemical anti-scalant injection to mitigate borehole clogging because of calcite deposition in the field. Although calcium carbonate scaling in the borehole has since been a common occurrence, scale management strategies employed by Ohaaki prevented the problem from grossly affecting the productivity of the field. The lessons learned from the experience of Ohaaki with respect to calcium carbonate scale management can be used as a valuable tool for new geothermal fields such as Mt. Apo in the Philippines, which at an early stage of production, have already experienced similar calcium carbonate scaling problems.

Broadlands-Ohaaki geothermal field is located on the eastern margin of the Taupo Volcanic Zone (TVZ) (Simmons and Browne, 1991) (Figure 1).

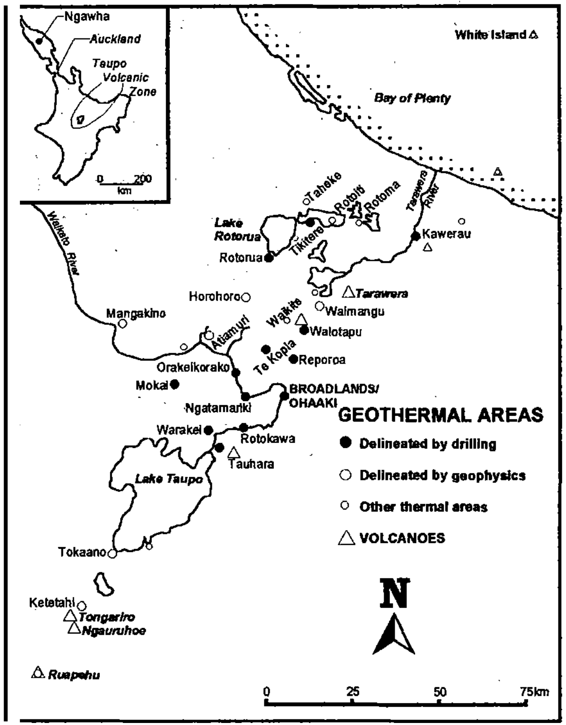
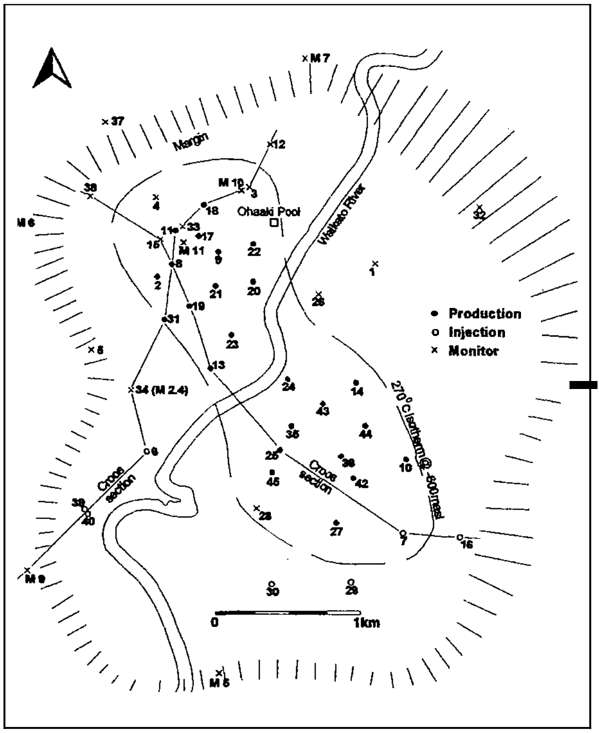


Figure 1. Broadlands-Ohaaki geothermal **field** in Taupo Volcanic Zone **(TVZ)**, **North** Isaland, **New** Zealand.



igure 2. Well location map of Broadlands-Ohaak geothermal field

The field extends some 3.6 km. along both sides of the Waikato River in the Taupo-Reporoa Basin, about 27-kin. northeast of Taupo (Mahon and Finlayson, 1972) (Figure 2). A total of 52 deep wells have been drilled in the area since 1967. At present, 21 production wells are used to supply steam to the 116-MWe (net) Ohaaki power station.

The fluids supplying the deep wells are neutral-pH chloride-bicarbonate type waters mainly coming fiom a heterogeneous formation of tuff-breccias and tuffs below a depth of 732 meters (Browne and Ellis, 1970). Faults are also suggested to function as permeable channels for the deep geothermal fluid The water has a temperature range from 260-285°C and typically contains less than 2000 mg/kg chloride (Mahon and Finlayson, 1972) and non-condensable gas content of -0.6 molal of which CO_2 constitutes more than 90% (Hedenquist, 1990). Hedenquist highlighted the existence of marginal CO_2-rich steam heated waters in the field. Tnis type of water accounts for the variation in chloride content (dilution) of the deep waters discharged from the wells. There is evidence that a liquid /vapor mixture exists at depth and supplies some of the discharges coming from the wellbore. The discharge enthalpies from these wells exceed the saturated liquid enthalpy of the highest downhole measured temperatures (Mahon and Finlayson, 1972). Fluid inclusion data also show that boiling has occurred in the reservoir (Hedenquist, 1990). The typical hydrothermal alteration encountered m the drillcores suggests an equilibrium assemblage of K-mica, K-feldspar, albite, chlorite, calcite and quartz. The precipitation of calcite and adularia and formation of epidote is linked to boiling (Browne and Ellis, 1970).

There is enough evidence fiom the location of calcite scale deposits in Ohaaki wellbores to show that the main mechanism for deposition is boiling. Tulloch (1982) cited the ‘development of platy calcite upwell of prismatic calcite resulted from a higher degree of flashing and correlates with two sharp drops in WHP in well BR19’. Usually scales are observed to form just above the flashpoint level in most wells. Boiling as the main mechanism for calcite scaling in boreholes have been documented in other geothermal fields all over the world such as Dixie Valley in Nevada (Benoit, 1988; Reed, 1988), Bolshe-Banny in Kamchatka (Kryukov and Larionov, 1970), Cesano and Latera in Italy (Corsi et. al., 1985).

In this report, the chemical changes in the typical fluid from Ohaaki during boiling and subsequent deposition of calcite will be modeled using the computer programs SOLVEQ and CHILLER The exercise Will highlight some significant chemical behavior of boiling geothermal fluid in conditions similar to those inside geothermal wellbores. The objective of this study is to determine if prediction of calcite scaling in the wellbore is possible using available surface discharge fluid chemistry.

2.0 METHODOLOGY

Five wells were selected for the study, BR8, BR13, BR19, BR25 and BR27. Four of the wells (except BR25) have confirmed calcite scaling in the wellbore. BR8 and BR13 have been worked-over to remove calcite scales in the slotted liner as early as 1987. Two ream-outs Using a drill rig were performed in BR19, one in September 1980 and the second in December 1992. In both cases, the work-over was to remove blockages due to calcite deposition. Similar ream-out operation was performed in BR27 in May 18,1995.

Table 1. Selected discharge chemistty used in modeling study. WHP stands for wellhead pressure at the time of sampling, TMF is the total massflow discharged from the well and WCP and SCP is the water and *steam* collection pressures respectively. A WCP value of zero bars **means** the water was collected from atmospheric flash of the discharge typically in the weirbox of the atmospheric discharge silencers. Water chemistry is expressed in milligrams per kilogram (ppm) while the gas chemistry is inmillimoles per 100 moles of steam. Enthalpies are discharge values calculated using the James Lip Pressure Method.

Well	BR8	BR13	BR19	BR25	BR27
Date	22 Jan 1990	08 Apr 1994	23 Jan 1990	07 Apr 1994	05 Apr 1994
WHP, bar g.	13.5	14.5	20.0	14.0	9.4
Enthalpy, J/g	1129	1175	1332	1238	962
TMF, ton/h	109	28.9	282	174	138
WCP, bar g.	0.0	0.0	0.0	0.0	0.0
Water Chemistry					
pH/T°C	8.88127	8.35119	8.47130	9.18121	9.13/18
Li	13	11.5	12	8.8	11.3
Na	1006	928	1044	880	1040
K	164	189	207	138	137
Ca	1.2	4.04	1.31	0.81	1.34
Rb	1.32	1.7	1.8	1.31	1.17
Mg	<0.01	0.008	<0.01	0.005	0.008
Cl	1434	1613	1702	1294	1436
Br		5.7		4.3	4.8
SO_4	44.1	7.3	5.1	11.7	10.2
$THCO_3$	451	193	233	268	408
B	39.8	44.4	47.5	41.8	55.8
SiO_2	603	672	800	754	508
SCP, bar g.	4.5	3.7	5.3	2.35	6.0
Gas Chemistry					
CO_2	1520	1863	1460	736	959
H_2S	21.5	26.5	21.3	13.4	9.37
NH_3	3.21	4.2	3.44	2.5	2.6
H_2	2.8	8.72	4.5	5.37	0.58
CH_4	25.8	30.4	27.1	12.9	13.4
N_2	20.1	15	13.7	7.87	6.67
O_2		0.018		0.00	0.00
Ar	0.049	0.038	0.036	0.0206	0.0158
He	4.19	0.003	0.005	0.002	0.001

Table 1 shows the chemistry of the well discharges from the five wells used for the study. Because changes have occurred in the chemistry of the fluids discharged from the well through time, the selected data correspond to periods of calcite deposition.

The chemistries shown are results of analysis of water and steam samples from the wells. Water samples were collected from the weirbox during atmospheric discharge to silencers. Steam is sampled using Webre mini-separators. A description of the updated analytical methods to analyze water and gas samples in Broadlands-Ohaaki can be found in Lovelock (1991).

To reduce the raw chemical analysis of the water and steam samples to downhole conditions the computer program SOLVEQ is used. SOLVEQ is a program that calculates equilibrium conditions in aqueous systems. It can be used to calculate the distribution of aqueous species and mineral saturation indices in natural waters and fiom hydrothermal experiments (Spycher and Reed, 1990). The chemistry in Table 1 cannot be inputted directly into SOLVEQ. A utility program GEOCAL produces a file called SOLRUN.DAT, which SOLVEQ uses to read the chemical data from. GEOCAL integrates the separate water and gas chemistries into one and computes the total molar amount of hydrogen ion (MTOT) fiom the in-situ pH measurements. Details of how to set-up the SOLRUN.DAT file is described in (Spycher and Reed, 1990). After the correct SOLRUN files are produced, the chemistry of the well discharge at the reservoir condition can be calculated in SOLVEQ. To do this, the temperature of the liquid in the reservoir must be known. In this report, the temperature of the fluid at depth is assumed to be that indicated by the TNaKCa (Fournier and Truesdell, 1973).

To model the boiling of geothermal fluids during ascent to the wellbore, the computer program CHILLER is used. CHILLER is a FORTRAN based Computer program for computing multi-component heterogeneous chemical equilibria among solids, gases and aqueous phase (Reed, 1982). The process used for modeling is boiling with the enthalpy constraint. This appears to be the most appropriate description of flashing inside the wellbore at the discharging state. Fluid flow is rapid such that heat-loss to the surroundings is negligible. With irreversible expansion and no heat loss the process is isenthalpic (Henley et al., 1984). To simplify the model, the total starting enthalpy of the fluid is assumed to be equal to the saturated liquid enthalpy at the reservoir temperature (as given by the TNaKCa).

The fluid is allowed to equilibrate at the starting temperature (TNaKCa) without boiling. Setting the fluid pressure to a very high value (500 bars) does this. Boiling is initiated in the fluid by setting the fluid pressure slightly less than the saturation pressure of the solution. Boiling occurs after every 5°C decrement in temperature starting from the initial reservoir temperature down –150°C. Although the supersaturated solid and gaseous phases precipitate or separate from the solution, they are not fractionated out but remains in contact with the boiling fluid during the entire length of the boiling run.

3.0 RESULTS AND DISCUSSION

Table 2 below shows some selected results of the deep chemistry calculations done by SOLVEQ on the well discharges.

Table 2. Results of deep chemistry calculation of discharge fluids **using SOLVEQ. Mineral saturation indices are expressed log Q/K where Q is the activity product and K is the mass action constant.**

Well	Temperature°C	deep pH	log Q/K calcite	Log Q/K quartz
BR8	279	6.63	-0.16	-0.03
BR13	283	6.08	-0.38	-0.01
BR19	294	6.34	0.00	-0.01
BR25	282	6.76	-0.26	+0.01
BR27	266	6.98	0.24	-0.01

Except for fluid discharged from BR27 the wells generally are slightly undersaturated with respect to calcite in the reservoir. This agrees with the results of previous calculations on Broadlands-Ohaaki fluids done by Ellis (1970) and Hedenquist (1990). With regards to *quartz,* the fluids are just about saturated, which agrees with the observation from most high temperature geothermal fluids. The pH of the deep water ranges from 6 to 7. Considering that the neutral pH (based on the dissociation of water) at 250°C is ***5.6*** (Henley et al., 1984). The deep fluids in these wells are alkaline. It is interesting to note that Ellis (1970) predicted calcite deposition in the reservoir of Ohaaki *occur* at pH range in excess of 6.5. This is validated by the results of calculation of log Q/K of calcite in well BR27. However, despite pH in excess of 6.5 in BR8 and BR25 the calcite remains under-saturated in the fluid

Figures 3 to 7 shows the graphical results of boiling simulation done for the wells. The bottom most graphs show the plots of saturation pressures, *steam* fractions and partial pressure of CO_2 against temperature during multi-step boiling. The saturation pressure *calculated for each* temperature is

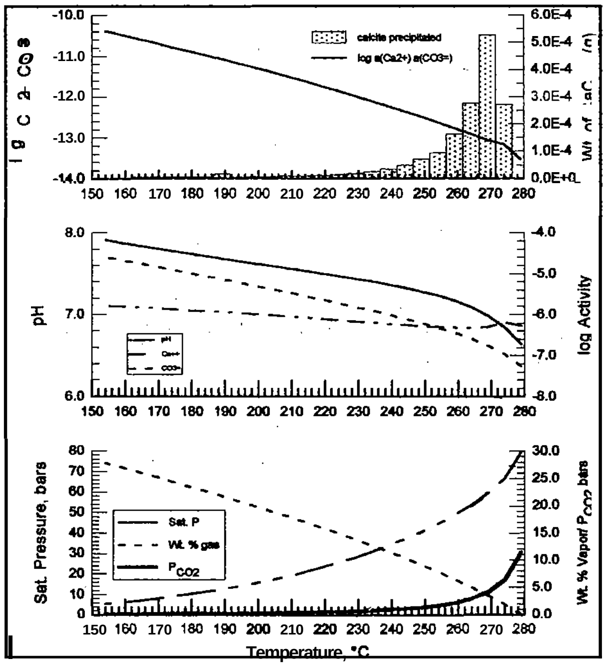


Figure 3. Well BR-8 boiling simulation.

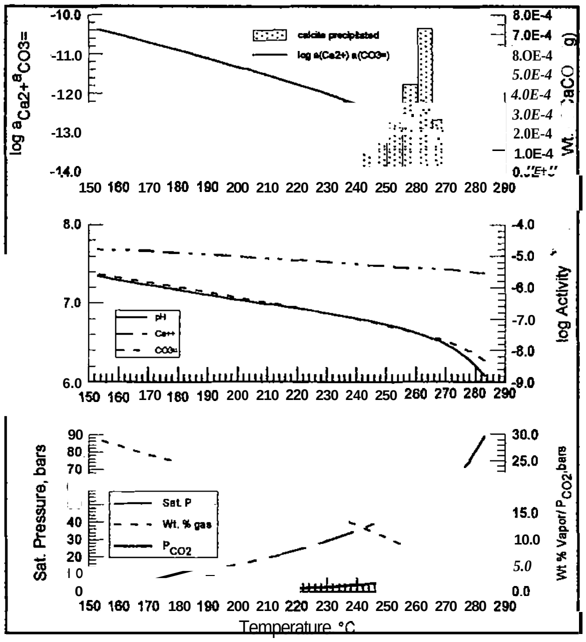


Figure 4. Well BR-13 boiling simulation.

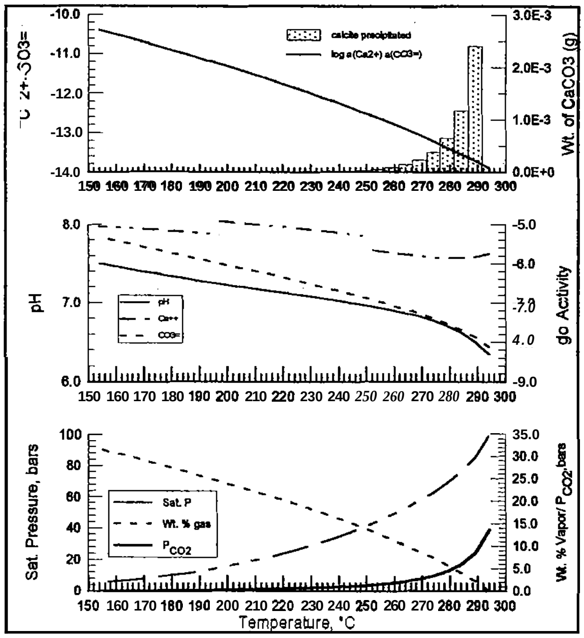


Figure 5. Well BR-19 boiling simulation.

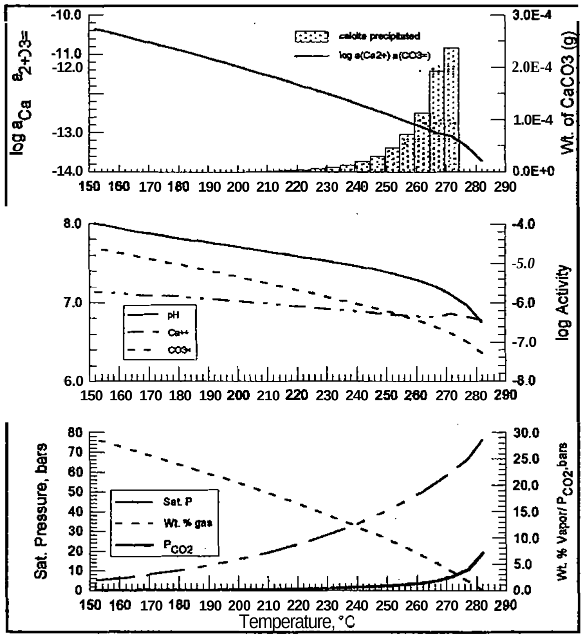


Figure 6. Well **BR-25 boiling** simulation.

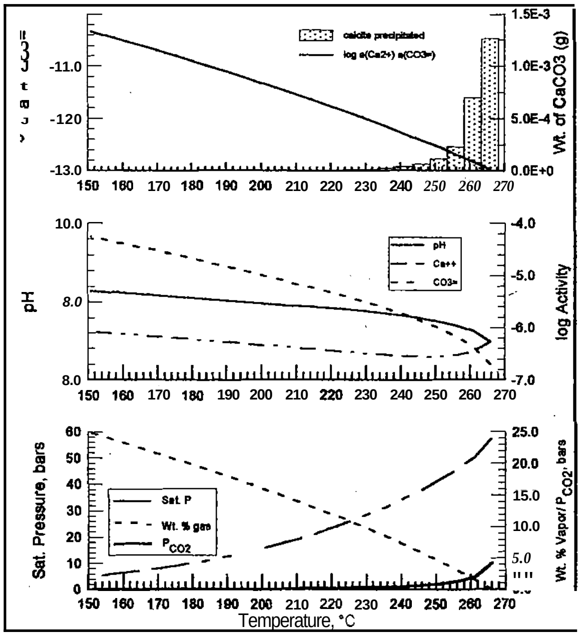


Figure 7. Well **BR-27 boiling simulation.**

generally higher than the saturation pressure of pure water because of non-condensable gas (primarily CO_2) partial pressure contributions (Sutton and McNabb, 1977). However, as more and more non-condensable gases are transferred to the steam phase as boiling proceeds (as shown by the decreasing P_{CO_2}), the saturation pressure of the system approaches that of pure water.

The middle graph shows the behavior of Ca^{2+} and $CO_3^{=}$ activities at decreasing boiling temperature. The changes can be correlated with the plot of pH of the liquid, All the fluids show increasing pH with increasing steam fraction. This is a direct result of gases that form weak acids in aqueous solution such as CO_2 and H_2S moving into the steam phase. Note that the sharp increase in pH corresponds to the steep decline in P_{CO_2} in the first 10°C drop in temperature. The increase in pH directly affects the formation of $CO_3^=$ ion as shown in the graph. The increasing trend in $CO_3^=$ activity results fiom dissociation of HCO_3^- ions forming H^+ and $CO_3^=$ as the fluid becomes more alkaline. The behavior of Ca^{2+} is more varied because of the effects of calcite being precipitated from solution and the 'concentrating effect' caused by the formation of steam.

The topmost graph shows the trend of the ion activity product of Ca^{2+} and $CO_3^=$ and the amount in grams of calcite precipitated from solution. The mass of the solution is approximately 1 kilogram. Table 3 shows a *summary* information on calcite precipitated fiom solution fiom the five wells studied.

Table 3. *Summary* **of calcite precipitation due to boiling based on simulation (complete results are in Appendix C. The flash-point depths were determined fkom flowing temperature and pressure surveys results** (data **from Clothworthy, pers.** comm.).

Well	TNaKCa °C	T@ max. scaling, °C	Max. Scale Rate mg/kg	Temp. Interval w/ Scaling,°C	Flash Point Temp. °C
BR8	279	269	0.5	<154-274	200
BR13	283	263	0.7	228-268	240,259
BR19	294	289	2.4	244-294	
BR25	282	272	0.2	207-272	
BR27	266	266	1.3	186-266	236,258

All the wells studied showed a potential to precipitate calcite even BR25. Note that that maximum scaling potential in multi-step boiling occurs not more than 20°C fiom the reservoir temperature. The temperature intervals where calcite scaling can happen are quite extensive. In well BR8 the potential for scaling *can occur* even less than 160°C. This temperature is close to the flash temperature in the separator. Assuming that the fluid fiom the well is transported in a single two-phase line to the separator and flashing occurs. It is expected that calcite scales will form in the pipes albeit in a very slow rate. In well BR19 at flash temperature below 240°C calcite scaling is not expected. Likewise, in BR13, BR25 and BR27, calcite will not precipitate at flash temperatures below 220°C, 200°C and 180°C, respectively.

Notice that the rate of precipitation is based on a solution mass of approximately 1-kilogram. If this rate is multiplied by the massflow rate of the discharge of the well a rough estimate of the mass of calcite precipitated in a given time period *can* be obtained. In well BR19, with a precipitation rate of 2.4 mg/kg and a mass flowate of 282 tonshour, about 0.7 kg of calcite will be deposited in one hour. This is in contrast to BR25 where only about 35 grams of calcite is deposited per hour at a mass flowrate of 174 tonshour.

In Ohaaki, a similar method is used to estimate the rate of calcite precipitation in the wells. The method is based on the difference noted in the concentration of Ca^{2+} in the weirbox. The stable concentration of Ca^{2+} is established when scaling is not occurring in the well. This condition is achieved when antiscalants are injected into the hole. Without antiscalant injection, the Ca^{2+} concentration in the weirbox drops sharply as a result of calcite formation. Assuming that all Ca^{2+} lost goes into the formation of calcite a rate of deposition *can* be established. Using this method Clothworthy and Lovelock (1993) were able to obtain a calcite scaling rate of *-0.55* tons/month in well BR8. Rased *on* the results above, the rate of deposition in BR8 is ~0.04 ton/month. The calculation in BR8 takes into account only one boiling temperature, which produced the lower estimate. By taking the cumulative rate for the range of temperature where calcite scaling occurs, the precipitation rate increases to –0.2 tons/month. In terms of order of magnitude estimates however, the values are reasonably close. Some leeway must be given to natural variations in the discharge chemistry through time.

It must be noted that the chemistry of BR19 as shown in Table 1, as it stands, will not produce calcite precipitation in the well during boiling. The calculated log Q/K of calcite in the reservoir as calculated by SOLVEQ unusually low compared to the other fluids. The reason for this is that the analyzed Ca^{2+} concentration is too low in comparison to the initial Ca^{2+} of the well during discharge test in 1968. It is possible that this decrease in Ca^{2+} is due to the formation of calcite (as discussed above). The problem of estimating the original Ca^{2+} concentration *can* be resolved in two ways, either use the value of Ca^{2+} during the 1968 discharge *or* allow SOLVEQ to compute the Ca^{2+} concentration assuming the fluid is in equilibrium with calcite in the deep fluid. The second method is used in this calculation. The Ca^{2+} concentration computed is in fact close to the data in 1968. By using the equilibrated calcium concentration, calcite precipitates when the fluid fiom BR19 is boiled.

4.0 CONCLUSION

Calculation of the deep composition of waters discharged from wells in Ohaaki showed the fluids are in equilibrium with quartz and just about saturated with respect to calcite. Results of isenthalpic multi-step boiling of the deep fluid causes the fluid to become supersaturated with calcite. Highly supersaturated conditions resulted from the sharp increase in the pH resulting from preferential movement of gases that form weak acids in solution such as CO_2 and H_2S into the vapor phase. The supersaturated solution precipitates calcite and forms 'platy calcite' scales in the wellbore upstream of the flashpoint level.

The rate of calcite deposition obtained from the modeling calculation range from 10^{-3} to 10^{-4} grams per kilogram of discharge fluid The maximum rates of deposition occur not more than 20°C below the assumed reservoir temperature of the fluid The temperature interval where boiling causes calcite to precipitate from the fluid varies for each well. Provided enough information on the physical processes occurring in the well are available, calcite scaling can be predicted and quantified using chemistries of fluids discharged from the wellbore.

REFERENCES

Arnorsson, S., S. Sigurdsson, and H. Svarvarsson, 1982. The chemistry of geothermal waters in Iceland. 1. Calculation of aqueous speciation from 0 to 370°C: Geochimica et Cosmochimica Acta, v. 46, p. 1513-1532

Benoit, W. R, 1989. Carbonate scaling characteristics in Dixie Valley, Nevada geothermal wellbores: Geothermics, v. 18, No. 1/2, 41-48

Browne, P. R L. and A.J. Ellis, 1970. The Ohaaki-Broadlands geothermal area, New Zealand mineralogy and related geochemistry: American Journal of Science, v. 269, p. 97-131

Browne, P. R L., 1973. Aragonite deposited from Broadlands geothermal drillhole water: New Zealand Journal of Geology and Geophysics 4,927-933

Clothworthy, A. and B.G. Lovelock, 1994. 1993 Annual Report on Reservoir Engineering and Scientific Monitoring: ECNZ Internal Report

Corsi, R, G. Culivicchi, and F. Sabatelli, 1985. Laboratory and field testing of calcium carbonate scale inhibitors: Geothermal Resource Council, Transactions, vol. 9, part II, p. 239-243

Ellis, A. J., 195%. The solubility of carbon dioxide in water at high temperatures: Am. Jour. Sci., v. 257,217-234

Ellis, A. J., 1959b. The solubility of calcite in carbon dioxide solutions: Am. Jour. Sci., vol. 257, p. 354-365

Ellis, A. J., 1963. The solubility of calcite in sodium chloride solutions at high temperatures: Am. Jour. Sci., vol. 261, p. 259-267

Ellis, A. J., 1970. Quantitative interpretation of chemical characteristics of hydrothermal systems: Geothermics, vol. 2, part 1, p. 516-528

Fournier, R O. and A.H. Truesdell, 1973. An empirical Na-K-Ca geothermometer for natural waters: Geochimica et Cosmochimica Acta, v. 37, p. 1255-1275

Fournier, R O. and RW. Potter, 1982. A revised and expanded silica (quartz) geothermometer: Geothermal Research Council Bulletin, v. 11, p. 3-9

Frear, G. L. and J. Johnston, 1929. Solubility of calcium carbonate (calcite) in certain aqueous solutions at 25°C: Am. Chem. Soc. Jour., v. 51, p. 2082-2093

Hedenquist, J. W., 1990. The thermal, and geochemical structure of the Broadlands-Ohaaki geothermal system: Geothermics, v. 19, p. 151-185

Holland, H. D., E.R. Segnit, and U.M. Oxburg, 1960. Carbonate solubility at high temperatures and pressures: Annual report N.S.F.- G6069, Princeton University

Kryukov, P. A. and E.G. Larionov, 1970. Physico-chemical sampling of high temperature wells in connection with their encrustation by calcium carbonate: Geothermics, vol. 2, part 2, p. 1624-1628

Lee, S. G., K. Roberts, B. Carey, and L. Bacon, 1998. 1996 Annual Report on Monitoring and Reservoir Performance: Contact Energy Geothermal Internal Report

Lovelock, B. G., 1991. The Ohaaki geothermal system: fluid chemistry, hydrology, and response to production in 1989-1990: Masters Thesis (Applied Geology) – University of Auckland.

Mahon, W. A. J. and J.B. Finlayson, 1972. The chemistry of the Broadlands geothermal area, New Zealand: American Journal of Science, v. 272, p. 48-68

Malinin, S. C. and A.B. Kanukov, 1971. The solubility of calcite in homogeneous H2O-NaCl-CO2 systems in the 200-600°C temperature interval: Geochemistry International, v. 8, p. 668-679

Miller, J.P., 1952. A portion of the system calcium carbonate, carbon dioxide, water: Am. Jour. Sci., v.250, p.161-203

Morris, C. and B.G. Lovelock, 1995. 1994 Annual Report on Reservoir Engineering and Scientific Monitoring: ECNZ Internal Report

Morris, C. J., P.F. Bixley, and B.G. Lovelock, 1997. Ohaaki geothermal field annual report on monitoring and reservoir performance 1995: ECNZ Internal Report

Reed, M. H., 1982. Calculation of multicomponent chemical equilibria and reaction process in system involving minerals, gases and an aqueous phase: Geochimica et Cosmochimica Acta, v. 46, p. 513-528

Reed, M. H. and N.F. Spycher, 1984. Calculation of pH and mineral equilibria in hydrothermal waters with application to geothermometry and studies of boiling and dilution: Geochimica et Cosmochimica Acta, v. 48, p. 1479-1492

Reed, M. J., 1988. Thermodynamic calculations of calcium carbonate scaling in geothermal wells, Dixie Valley geothermal field, USA: Deposition of solids in geothermal systems, Proceedings, Reykjavik, Iceland.

Simmons, S. F. and P.R.L. Browne, 1991. Active Geothermal Systems of North Island New Zealand: Geological Society of New Zealand Misc. Publication 57

Simmons, S. F. and B.W. Christenson, 1994. Origins of calcite in a boiling geothermal system: Am. Jour. Sci., v. 294, p. 361-400

Spycher, N. F. and M.H. Reed, 1988. Fugacity coefficients of H2, C02, CH4, H2O, and of H2O-CO2-CH4 mixtures: a virial equation treatment for moderate pressures and temperatures applicable to calculations of hydrothermal boiling: Geochimica et Cosmochimica Acta, v. 52, p. 739-749

Spychet, N. F. and M.H. Reed, 1990. Users guide for CMLLER: A program for computing water-rock reactions, boiling, mixing and other reaction processes in aqueous-mineral-gas systems: Revised Edition

Spycher, N. F. and M.H. Reed, 1991. Users guide for SOLVEQ: A computer program for computing aqueous-mineral-gas equilibria: Revised Preliminary Edition

Tulloch, A. J., 1982. Mineralogical observations on carbonate scaling in geothermal wells at Kawerau and Broadlands: New Zealand Geothermal Workshop, 4th, Proceedings p. 131-134.