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CHEMISTRY OF WELL DISCHARGES IN THE OLKARIA GEOTHERMAL FIELD, KENYA

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ABSTRACT

Representative chemical data from nine production wells in the Olkaria geothermal field, Kenya, were studied to assist in the evaluation of alteration minerals controlling fluid composition, processes causing excess discharge enthalpy in the wells and application of chemical geothermometry to map the lateral movement and locate upflow zones in the reservoir. Interpretation of overall composition of well discharges indicate that the high discharge enthalpy is largely caused by evaporation of degassed pore water in the rock rather than the relative permeability of steam and water in two phase flow. Chemical geothermometry has been applied, together with measured downhole temperatures and knowledge of the level of producing aquifers, to evaluate which aquifer dominates the discharge. Distribution of salinity and Na-K temperatures in the field indicate an upflow zone to the northwest of the drilled area and dilution during lateral movement either by mixing with cold water or condensate. The gas concentations are similar in all well discharges, indicating that the lateral flow occurs in a confined aquifer. Reservoir studies have indicated an upflow in the north of the presently drilled area, suspected to be associated with a fault, trending N 70° E about a km due north. The results of these earlier studies are based on data on permeable zones, producing aquifers and transmissivity tests on twenty wells (OW's 2 - 21), whereas the present geochemical model is based on chemical data from nine wells only (OW's 2, 5, 6, 7, 10, 11, 12, 20, and 21). Mineral equilibria studies indicate that the reservoir fluid is saturated with respect to calcite, fluorite and guartz and undersaturated with respect to anhydrite.

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1 INTRODUCTION

1.1 Scope of work

The author of this report was awarded a fellowship by the United Nations University (UNU) to take part in the UNU Geothermal Training Programme in Iceland. The Programme is organised by the National Energy Authority (NEA) of Iceland and jointly financed by the UNU and the Icelandic government. Lecturers and instructors are mostly staff the NEA and members of the University of Iceland (Fridleifsson, 1982).

During the training period, a total of sixty introductory lectures were given by renowned academics and geothermal energy experts. All major aspects of geothermal resources, ranging from prospecting, appraising, utilisation, possible environmental impacts, planning and economics of exploitations, were covered in considerable detail. A number of seminars on selected geothermal fields in Iceland were given mostly prior to or during study tours to the respective areas.

Practical training, assessment and interpretation of fluid chemistry was carried out under the joint supervision of Dr. Stefan Arnorsson of the University of Iceland and Dr. Einar Gunnlaugsson of the Municipal Heating Service of Reykjavik. This session included a revision on theory and application of chemical thermodynamics in the evaluation of geothermal fluid chemistry (2 weeks). Techniques for sampling hot/warm springs, fumaroles (one week in the Geysirarea) and wet-steam wells (two weeks at the Krafla geothermal field) as well as analytical methods for major components (three weeks) were practised. Experts from the NEA gave demonstrations in the laboratory and field and instruction on computer filing of geochemical data and various calculations using computer programmes took five weeks.

A part of the training programme curriculum involves execution of a specific project. This report describes the author's project, which took about one month to compile. It is based on data from the Olkaria geothermal field, Kenya. Twenty three wells have been drilled in this field and drilling is continuing. The wells give a two phase discharge and the aquifers have low permeability as depicted by the low output of the wells (2-4 MWe equivalent). Seven wells are being used to generate 15 MW; on line from June 1981, and seven others are scheduled to generate a further 15 MW in late 1982 (KPC, 1982b).

For this research project data from nine wells were used. Seven of these wells are the ones connected to the first 15 MW unit. These wells have wellhead separators and are throttled to a pressure of about 5 bars. Steam samples were collected from sampling taps fixed on the sides of the separators and water samples from the weirboxes. The other two wells, OW's 20 and 21 were being tested for discharge characteristics and did not have wellhead separators so a 2"-cyclone separator was used to collect steam samples. Fifteen samples in all were collected from these nine wells and analyses were carried out in Iceland, except for non-condensible gases, pH, CO2, and H2S which were analysed at Olkaria. The interpretation of data focuses on the of the fluid composition by control equilibria with alteration minerals, the effect of boiling in the formation on the discharge composition and deductions regarding the boiling mechanism and the hydrology of the reservoir.

2 SAMPLING AND ANALYTICAL METHODS

2.1 Sampling

Samples for the research project were collected from nine discharging wells at Olkaria. Two categories of wells were sampled: (a) wells on line, and (b) wells under test. The discharge from the wells on line goes through a master valve to a high pressure cyclone separator, where the water phase is separated from the steam phase. The steam is led to the turbine through a steel pipeline. The water is taken by another pipe past a weirbox to a conditioning pond from where after a transit time of three hours it is disposed into an infiltration lagoon. A V-notch is cut at the end of the weirbox which is used to measure the rate of water flow. A pressure gauge attached to the separator is used to measure the pressure at which the phases are separated. The steam flow rate is measured by installed meters. These measurements are used to evaluate the discharge enthalpy using the relation below :

H = h + xL

where H = discharge enthalpy; x = steam fraction = steam flow/water flow + steam flow; L = latent heat of vaporisation of water at separation pressure.h enthalpy of water saturated with steam at separation pressure. L and h are obtained from steam tables.

Steam was collected from a sampling valve fixed about a meter from the separator on the transmission pipeline from the separator to the turbine. Water samples were collected from the weirboxes at atmospheric pressure (0.8 bars at Olkaria) and treated as outlined in the Programme for Geochemical Data Collection and Monitoring of Well Discharges (Kenya Power Company, 1982a).

The wells under test were discharging through a horizontal delivery pipe of a known lip diameter into a rectangular

separator which separated the steam and water phases, but not as effectively as the cyclone separators. Water was led into a temporarily constructed weirbox and steam discharged into the atmosphere. Lip pressure and diameter of the delivery pipe were used to evaluate discharge enthalpy using the Russel James (1962) relation :

$$\frac{W}{783AP^{0.96}} = \frac{2673 - h}{h^{1.102}}$$

where W = water flow rate (kg/sec); A = section area of pipe (m2); P = critical lip pressure of pipe (bars abs.); h = discharge enthalpy (kJ/kg). Water samples were collected from the weirbox. Steam samples were collected from the delivery pipe using a 2"-cyclone separator. The separator was fixed onto a sampling tap made on the delivery pipe about a metre from the master valve.

2.2 Analytical methods

Gas samples were analysed at the Olkaria Geochemistry Laboratory. The Orsat apparatus was used for the analyses of hydrogen, methane, oxygen, and "inert gases". Hydrogen sulphide was determined by back titration with sodium thiosulphate in acid solution after addition of excess iodine. Carbon dioxide was analysed by determining excess sodium hydroxide solution; the sample had been collected in a known volume and strength of the alkali solution. Calculations were carried out to adjust the results to correspond to a sampling pressure of 0.8 bars, the pressure at which water samples were collected.

Water samples were analysed at the University of Iceland, Reykjavik, except for pH, carbon dioxide and hydrogen sulphide, which had been analysed at Olkaria because samples should be analysed immediately after sampling for these components. The analytical methods and procedures used are shown in Table 1 and the results of the analyses

are shown in Table 2. The methods used at the University of Iceland are similar to those used at Olkaria. There were, however, some advantageous technical approaches noted which are discussed at the end of this report under recommendations.

Table 1. Analytical methods used for the water samples.

Component Method

| Na | Atomic Absorption Spectrophotometry |
|------------------|-----------------------------------------------|
| | (with lithium as inhibitor to interference) |
| К | Atomic Absorption Spectrophotometry |
| | (with lithium as inhibitor to interference) |
| Ca | Atomic Absorption Spectrophotometry |
| | (with lanthanum as inhibitor to interference) |
| Mg | Atomic Absorption Spectrophotometry) |
| | (with lanthanum as inhibitor to interference) |
| Si02 | UV/VIS Spectrophotometry |
| | (Silico-molybdate complex) |
| В | UV/VIS Spectrophotometry |
| | (Methylene blue complex) |
| S04 | Titration with barium perchlorate |
| | (using thorin as indicator) |
| c02 | Titration with hydrochloric acid |
| | (using pH-Meter to mark end point) |
| H ₂ S | Titration with mercuric acetate |
| - | (using dithizone as indicator) |
| C1 | Chloride meter |
| F | Selective electrode. |
| | 2006년2017년 2012년2011년 - 11월212년2년 전·가·전·전·이 |

| Well No. | Date of sampling | Discharge Enthaloy | | | | | Wat | er sample | Gas sample | | | | | | | | | | | | |
|-------------|------------------|-----------------------|-------|------|-----|-------|------|-----------|------------|-------|------------------|--------|-------|-----|--------------|---------------|-------|--------------|-------|------|------|
| | | KT/kg | DH/20 | Si02 | Na | ĸ | Ca | Mg | CO2 | so4 | H ₂ S | C1 | F | В | Sampling | Liters | 00- | s Vo | lume | - | I No |
| | 16.1.82 | 2015 ^d | 6.88 | 868 | 625 | 107.9 | 0.52 | 0.011 | 30.50 | 42.9 | 0.51 | 755 | 58.4 | 4.3 | (bar) 4.8 | tond. 1,73 | 65.36 | H2S 19.61 | 13.07 | 1.31 | 1.95 |
| | 10.3.82 | 2013 | 8.70 | 751 | 482 | 72.3 | 0.77 | 0.013 | 78.90 | 34.5 | 0.90 | 819 | 66.4 | 5.7 | 4.3 | 1.56 | 82.56 | 6.4 | 8.3 | 0.90 | 1.90 |
| 5 | 17.1.82 | 2600 | 8.70 | 601 | 298 | 40.1 | 0.63 | 0.009 | 26.80 | 34.90 | 0.44 | 357.2 | 51.30 | 2.7 | 4.7 | 1.89 | 69.18 | 25.15 | 4.40 | 0.57 | 1.66 |
| ÷. | 20.3.82 | 2600 | 8.50 | 497 | 278 | 36.8 | 0.66 | 0.039 | 37.10 | 18.0 | 0.71 | 367.1 | 45.7 | 2.9 | 4.6 | 1.02 | 71.43 | 14.26 | 9.0 | 0.62 | 0 |
| 6 | 17.1.82 | 2350 | 9.25 | 741 | 498 | 69.10 | 0.81 | 0.013 | 49.60 | 41.10 | 2.58 | 365.1 | 49.9 | 5.4 | 5.2 | 1.91 | 73.17 | 18.29 | 6.09 | 1.20 | 1.24 |
| 6 | 11.3.82 | 2281 | 9.25 | 783 | 492 | 71.3 | 0.83 | 0.005 | 48.10 | 136.2 | 3.23 | 599.4 | 49.1 | 5.8 | 4.8 | 1.70 | 81.8 | 8.2 | 8.10 | 0.70 | 1.20 |
| 7 | 26.7.82 | 2260 | 8.70 | 760 | 598 | 114.1 | 0.86 | 0.030 | 27.40 | 34.0 | 1.60 | 1051.6 | 60.60 | 7.5 | 4.9 | 1.28 | 72.73 | 18.18 | 7.27 | 0.64 | 1.18 |
| 10 | 17.1.82 | 2400 | 8.55 | 785 | 783 | 148.3 | 0.84 | 0.029 | 25.80 | 39.40 | 0.55 | 1107.2 | 64.7 | 8.1 | 5.0 | 1.30 | 81.08 | 9.01 | 6.31 | 0.90 | 2.70 |
| 18) | 21.3.82 | 2355 | 8.6 | 684 | 686 | 146.5 | 1.0 | 0.034 | 42.90 | 20.80 | 0.68 | 1173.3 | 49.4 | 8.0 | 4.5 | 1.06 | 76.83 | 10.61 | 9.27 | 0.68 | 2.50 |
| 11 | 17.1.82 | 1920 | 8.94 | 820 | 456 | 83.3 | 0.72 | 0.018 | 28.1 | 33.80 | 0.40 | 644.8 | 66.7 | 4.7 | 5.6 | 1.12 | 77.78 | 7.78 | 8.89 | 0.89 | 4.56 |
| 11 | 31,3,82 | 1920 | 8.90 | 771 | 504 | 85.9 | 1.06 | 0.028 | 55.8 | 21.2 | 0.82 | 627.8 | 68.2 | 5.6 | 5.0 | 1.13 | 60.89 | 7.37 | 21.08 | 4.61 | 4.6 |
| 17. | 12.3.82 | 2178 | 9.20 | 853 | 485 | 73.9 | 0.59 | 0.017 | 76.80 | 32 | 1.8 | 620.8 | 68.30 | 6.7 | 7.8 | 1.08 | 72.15 | 12.56 | 12.77 | 0.60 | 1.90 |
| 12 | 19.1.82 | 2240 | 9.01 | 906 | 466 | 70.6 | 0.66 | 0.018 | 65.4 | 562 | 1.13 | 639 | 66.7 | 6.1 | 8.7 | 1.20 | 76.92 | 7.69 | 7.69 | 5.77 | 1.93 |
| 20 | 16.1.82 | 2400 | 9.02 | 710 | 617 | 111 | 0.78 | 0.016 | 10 | 64.7 | 1.22 | 828 | 81.2 | 5.9 | 5.3 | 0.84 | 78.95 | 11.84 | 7.89 | 0.39 | - |
| 21 | 18.3.82 | 2650 | 9.20 | 597 | 390 | 58.5 | 2.63 | 0.185 | 147.9 | 76.6 | 2.04 | 458.8 | 32.10 | 4.5 | 3.8 | 1.11 | 72.57 | 17.23 | 9.44 | 0.67 | 0 |

| Table 2. | Composition | of | water | and | steam | from | wells | at | 1 | atm | pressure. |
|----------|-------------|----|-------|-----|-------|------|-------|----|---|-----|-----------|

3 ENTHALPY AND FLUID COMPOSITION

3.1 Excess enthalpy and deep composition

When the discharge enthalpy of wells exceeds that of steam saturated water at the aquifer temperature (which is the case at Olkaria), it is often referred to as "excess enthalpy". Discharge enthalpy of wells in the Olkaria geothermal field ranges from 1900 to 2700 kJ/kg. The discharge enthalpy has been evaluated by monitoring steam and water flows after separation of the total discharge, by the critical lip pressure method and but also measurement of water flow. The high discharge enthalpy reflects two phase (steam and water) conditions in the reservoir and their partial separation in the aquifer before entering wells.

There are difficulties involved in evaluating the chemistry of reservoir water based on data from excess enthalpy wells. If the reservoir contains only water and the discharge enthalpy is that of steam saturated water it is easy to relate analysed composition of surface samples to that in the reservoir. On the other hand, if the inflow into the well is a two phase fluid with excess enthalpy, it is not possible to relate the surface fluid chemical composition to that in the reservoir without making some fundamental assumptions regarding boiling processes. 0ne of the causes of excess enthalpy of wells is that the steam and water phases are not transmitted through the formation in the reservoir with equal ease because the two phases properties (Stefansson have different flowing and Bjornsson, 1982). It is also conceivable that the excess enthalpy is due to evaporation of water by conduction of heat from the reservoir rock, but pressure drop caused by withdrawal of the fluid by discharging wells leads to cooling (by boiling) of this fluid and therefore conductive heat flow from the rock to that fluid. If the cause of the excess enthalpy is known then data can be evaluated effectively.

In this project the composition of water in the Olkaria geothermal reservoir was evaluated by assuming two possible causes for excess discharge enthalpy of wells: (a) transfer of heat from the rock and (b) relative permeability effects for flow of the steam and water Both models were considered to occur exclusively. phases. In the first case it was assumed that the heat transfer involved evaporation of degassed (i.e already boiled) water so that a gas free steam was added to that previously This model effectively assumes that the total formed. discharge represents a single water phase in the reservoir and that the excess enthalpy is due to non-isoenthalpic conditions in the reservoir between rock and fluid. In the second case it was assumed that the excess enthalpy was due to the relative permeability effect for the water and steam phases. Here, calculations of reservoir water compositions assume two phases (their proportion being dictated by the measured discharge enthalpy) to occur in the reservoir at the respective undisturbed aquifer temperature. This temperature was derived from the analytical sodium and potassium concentrations in the discharges applying the Na-K geothermometer. Deep fluid compositions for the respective models were obtained with the aid of the computer programme of Arnorsson et al. (1982a). In chapter 4 an attempt is made to evaluate the relative magnitude of the boiling processes as assumed for the two model fits models by studying which best certain solution/mineral equilibria in the reservoir.

3.2 Total discharge composition

Whereas the concentrations of the various components will vary in the individual phases (water and steam) depending on the pressure exerted on the discharge, the concentration in the total discharge remains constant for constant reservoir conditions. The components are distributed between the phases in accordance with the steam fraction, which is a function of pressure. Thus the total discharge is a characteristic of the reservoir and can hence be used

to monitor changes in the reservoir such as colder or hotter aquifer inteferences, temperature drops, etc. These compositions were calculated for all the samples using the following equation:

$$A_0 = A_w (1 - X_p) + A_s X_p$$

$$x_p = \frac{H_o - h}{L_p}$$

A concentration of component A
o subscript means in total discharge
w - water phase
s - steam phase
p - at sampling pressure
L latent heat of vaporisation of water
H enthalpy of fluid
h enthalpy of water saturated with steam

The results are shown in Table 3. The basic data required for the calculations are discharge enthalpy, (H_0) and the analysed concentrations of each component in the water (A_w) and steam (A_s) .

| Well No. | Sampling date | sio ₂ | Na | к | Ca | Mg | so4 | C1 | F | в | co2 | H ₂ S | Н2 | CH4 | ^N 2 | NH ₃ |
|-------------|------------------|------------------|-------|------|-------|--------|-------|-------|-------|-------|-------|------------------|-------|-------|----------------|-----------------|
| 2 | 82 1 17 | 246.4 | 177.4 | 30.6 | 0.15 | 0.003 | 12.18 | 214.3 | 16.6 | 1.22 | 1466 | 338.8 | 13.38 | 10.66 | 27.67 | - |
| 2 | 82 3 10 | 213.8 | 137.2 | 20.6 | 0.21 | 0.004 | 9.82 | 233.1 | 18.9 | 1.62 | 1680 | 99.8 | 7.7 | 6.6 | 24.3 | 0.0 |
| 5 | 82 1 17 | 15.9 | 7.9 | 1.1 | 0.02 | 0.002 | 0.92 | 9.44 | 1.36 | 0.07 | 229.2 | 645.1 | 6.69 | 6.9 | 35.13 | |
| 5 | 82 3 20 | 13.1 | 7.35 | 0.97 | 0.018 | 0.001 | 0.48 | 9.71 | 1.21 | 0.08 | 1302 | 201.1 | 7.52 | 4.13 | 0 | 0 |
| 6 | 82 1 17 | 101.1 | 67.9 | 9.3 | 0.11 | 0.0002 | 5.61 | 77.09 | 6.81 | 0.74 | 2179 | 421.0 | 8.30 | 13.0 | 23.4 | - |
| 6 | 10.3.82 | 130.1 | 82.1 | 11.9 | 0.14 | 0.001 | 22.7 | 99.9 | 8.2 | 0.97 | 2094 | 162.4 | 9.5 | 6.5 | 19.5 | 0.0 |
| 7 | 26.3.82 | 133.8 | 105.3 | 20.1 | 0.15 | 0.005 | 6.0 | 185.1 | 10.7 | 1.3 | 1386 | 268 | 6.3 | 4.4 | 14.3 | 0.0 |
| 10 | 17.1.82 | 89.8 | 89.6 | 17.0 | 0.10 | 0.003 | 4.51 | 126.7 | 7.41 | 0.93 | 1683 | 1443 | 6.0 | 6.81 | 35.6 | - |
| 10 | 21,3,82 | 91.8 | 92.1 | 19.7 | 0.13 | 0.004 | 27.9 | 157.5 | 6.6 | 1.1 | 1275 | 135.8 | 7.03 | 4.1 | 26.3 | 0.0 |
| 11 | 17.1.82 | 267 | 148.5 | 27.1 | 0.23 | 0.006 | 11 | 210 | 21.7 | 1.53 | 1067 | 32 | 5.55 | 4.41 | 39.5 | - |
| 11 | 31.182 | 251 | 164.1 | 28 | 0.34 | 0.009 | 6.9 | 204.3 | 22.2 | 1.8 | 853 | 78.6 | 13.8 | 23 | 40.2 | 0.0 |
| 12 | 19.1.82 | 167.4 | 86.1 | 13.0 | 0.12 | 0.003 | 10.38 | 118.1 | 12.33 | 1.13 | 1366 | 105.1 | 6.21 | 37.03 | 21.6 | - |
| 12 | 12.3.82 | 180.9 | 102.9 | 15.7 | 0.13 | 0.004 | 6.8 | 13.16 | 14.5 | 1.42 | 1121 | 149.4 | 9 | 3.3 | 18.5 | 0.0 |
| 20 | 82 1 16 | 81.3 | 70.6 | 12.7 | 0.09 | 0.002 | 7.4 | 94.7 | 9.3 | 0.68 | 112.2 | 130.2 | 5.1 | 2.01 | 8.3 | - |
| 21 | 18.3.82 | 2.7 | 1.7 | 0.30 | 0.01 | 0.001 | 0.34 | 2.04 | 0.14 | 0.002 | 1444 | 265.4 | 8.6 | 5.23 | 0 | 0 |

Table 3. Total discharge composition of wells in the Olkaria Field. Concentrations in ppm.

4 MINERAL EQUILIBRIA AND GEOTHERMOMETRY

The chemistry of the fluids discharged from the wells at Olkaria has been evaluated quantitatively in two ways. Firstly by relating computed activities of cation/proton ratios and undissociated weak acid concentrations to empirical curves for equilibrated waters (Arnorsson et al., 1982b) and secondly by studying the state of saturation with respect to selected minerals. Examination of the alteration mineralogy at Olkaria (Browne 1981, and Odongo, 1982) and in Icelandic geothermal systems (Arnorsson et al., 1982b) reveals that the alteration minerals are the same, for similar temperatures, with the exception that fluorite is present in the intermediate and acidic rocks in Olkaria but not in the altered basaltic rocks in Iceland.

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4.1 Empirical evaluation of equilibrium compositions

The thermodynamic criterion for equilibrium in open systems is described by Gibb's phase rule:

$$F + P = M + C + 2$$
,

where F is the number of degrees of freedom, i.e. the minimum number of independent variables whose values must be fixed to determine the state of system: P is the number of phases (in this case, minerals, water and steam). M and C are the numbers of mobile and compatible components, respectively. It has been shown (Arnorsson et al., 1982b) that in a chemical system, with a general composition, at equilibrium, the number of phases will be equal to the number of compatible components. From the phase rule it follows that F = M + 2. The number of variables needed to define a multiphase system at equilibrium will hence be equal to the number of mobile components plus two (temperature and pressure). In geothermal systems pressure variations are generally within 1-200 bars. In this range Arnorsson et al., (1982b)

pointed out that the effect of pressure variations upon mineral equilibria is insignificant.

In geothermal waters there is only one mobile component, chloride. It follows therefore that the major element chemistry of geothermal waters at an overall equilibrium is defined by two variables; chloride and temperature. However, the actual activities of the various aqueous species are determined by the minerals with which the water equilibrates. The temperature dependence is the basis of chemical geothermometry which has proved its reliability by the close correlation with directly measured temperatures.

The dependence on temperature for cation/proton ratios and undissociated weak acid concentrations in Iceland geothermal waters is shown in Appendix I. Mean and standard deviations of the Icelandic data are incorporated in that Appendix.

Downhole chemistry of the analyses from Olkaria was calculated for the two models discussed in chapter 3 and the results are shown in Fig. 1 (A - J). It can be seen from Fig. 1 that the calculated enthalpy values based on the model which assumes excess enthalpy due to evaporation of pore-water give a better fit than the measured enthalpy values with the empirical "equilibrium curves" which are based on Icelandic waters. The same pattern is observed all cation/proton ratios and acid for molecule concentrations except for fluoride. This is due to the control of fluoride mobility by the fluorite solubility at Olkaria but the Iceland waters used to derive the empirical curves are fluorite undersaturated. The calcium/ proton activity ratio tends to be lower than that of other cations relative to the equilibrium curve. This could be due to low calcium in the well discharges compared with calcium concentrations in the reservoir fluid as a result of calcite precipitation which is caused by the flashing of the water entering the wells. Some data points have low cation/proton ratios, for example three points in Fig. 2



(C), which assume measured enthalpy. These data represent water from OW-5 and OW-21. These wells have a very high and somewhat variable discharge enthalpy (almost dry steam). For such wells calculated concentrations of ions in the deep water is very sensitive to the enthalpy values selected. Therefore little weight can be given to these data in the interpretation.

The results represented in Fig. 1 (A - J) may be used to evaluate boiling processes in the reservoir around discharging wells. They indicate that evaporation of pore water is more important in producing high enthalpy wells than the relative permeability effects to steam and water flow. It is, however, apparent that both processes are operative.

4.2 Mineral solubility

When sparingly soluble compounds dissolve in water an equilibrium between the compound and the dissolved species may be established. A solubility product is defined as the product of the activities of the dissociated species raised to appropriate powers equal to the number of particles of the respective species, that one "molecule" of the solid breaks into. The solubility products of some common minerals occurring in geothermal environments are given in Appendix II. If physical constraints are exerted on the solubility equilibria they will respond according to Le Chartelier's principle. Such constraints on the equilibria could be temperature changes and addition or depletion of species from the system. The response will therefore mean dissociation of the solid or formation of more solid Examples of the formation of more particles. solid particles are the well known menaces of calcite and silica deposits inherent to geothermal utilisations.

The solubilities of calcite, anhydrite, and fluorite were studied in respect to the two models under discussion in



Fig. 2. Solubility products of selected minerals from the Olkaria Field.

this report. It was found that for both models the aquifer significantly undersaturated with respect to anhydrite was and apparently also with fluorite and calcite (Fig. 2 A-C). The apparent undersaturation may be due to loss of calcium through precipitation in the formation. It is well known that deep geothermal waters equilibrate with calcite. Upon boiling, which occurs around producing wells these deep waters become calcite supersaturated and this mineral tends to precipitate and a substantial part of the originally dissolved calcium may be removed. The overall low calcium/proton activity ratio compared to that of other cations is indicative of "low" calcium in well discharges.

4.3 Feldspars, quartz and geothermometry

Potassium and sodium feldspars and quartz are abundant as alteration minerals in the Olkaria geothermal reservoir (Browne 1981, Odongo, 1982). Chemical equilibria of these minerals with the geothermal water are dependent on temperature. Theoretically any temperature dependent variable can be calibrated to measure the aquifer temperature as long as the dependence is known. Many calibrations have been made, some only suitable in certain fields and temperature ranges and others suitable for universal application. The Na-K and guartz geothermometry curves that were selected to calculate the aquifer temperatures are from Arnorsson et al. (1982c), Fournier (1977), and a new quartz geothermometer of Ragnarsdottir and Walther (1982). The Na-K curve of Arnorsson et al. (1982c)and that of Ragnarsdottir and Walther (1982) compare well, but the other geothermometer gave systematically lower values.

If one assumes that equilibrium is attained between quartz and solution and the feldspars and solution, the geothermometry temperatures can in conjunction with measured temperatures be used to evaluate the levels of dominant aquifers in wells. More weight is put on the Na-K

geothermometer because the absolute concentration levels of elements are sensitive to modeling that must always be assumed in the calculations of aquifer water chemistry whereas element ratios are not. The Na-K temperatures were thus used to figure out which aquifers are dominant where two or more inflow zones are feeding wells. The results are given in Table 4. A correlation of temperatures obtained from Na-K and quartz (Ragnarsdottir and Walther 1982) geothermometers is shown in Fig 3. It is observed that where significant discrepancies occur, then the Na-K temperature is higher than the quartz temperature. There is a crude correlation between discharge enthalpy and the difference of the two geothermometers, as shown in Fig. 5. Therefore boiling processes can be expected to be partly responsible for the discrepancy, particularly when the discharge is almost dry steam.

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| Well no. | Date of sampling | Geoth | ermomet (°C) | ters | Fluid inflow (depth m) | Temperature fluid inflow | of ("C) |
|-------------|---------------------|-------|-----------------|----------|---------------------------|-----------------------------|------------|
| | | Na-K | Quar | rtz | | | |
| 2 | 17.1.82 | 263 | A 258 | B 267 | 725, <u>990,</u> 1100 | 232,264,274 | |
| 2 | 10.3.82 | 245 | 242 | 254 | | | |
| 5 | 17.1.82 | 233 | 157 | 160 | <u>700,</u> 800 | 242,255 | |
| 5 | 20.3.82 | 231 | 146 | 148 | | | |
| 6 | 17.1.82 | 236 | 228 | 238 | 800,830 | 242,247 | |
| 6 | 10.3.82 | 238 | 236 | 238 | | | |
| 7 | 26.3.82 | 278 | 233 | 243 | 795, <u>*</u> | 242-245 | |
| 10 | 17.1.82 | 277 | 225 | 234 | 663, <u>900,</u> 1100 | 231,261,277 | |
| 10 | 21.3.82 | 298 | 217 | 226 | | | |
| 11 | 17.1.82 | 271 | 248 | 261 | 728, <u>1025,</u> 1100 | 238,271,277 | |
| 11 | 31.3.82 | 263 | 243 | 256 | | | |
| 12 | 19.1.82 | 246 | 249 | 262 | 575,750, 850,888 | 209,238, 251,256 | |
| 12 | 19.1.82 | 248 | 247 | 256 | | | |
| 20 | 16.1.82 | 268 | 217 | 226 | 756,1050 | 252,279 | |
| 21 | 18.3.82 | 246 | 80 | | | | |

| Table 4. | Comparison | of quart | z and Na-K | geothermometry | tempera- |
|----------|------------|----------|------------|----------------|----------|
| | tures with | measured | temperatur | es in Olkaria | wells. |

Footnotes:

- A: Assuming the calibration curve recommended by Fournier (1977) and Arnorsson et al., (1982c).
- B: Based on the quartz solubility curve of Ragnarsdottir and Walther (1982).

 $t(^{\circ}C) = 771 + (336 + 0.017P) \text{ LogSi0}_{2} + 38.8 \text{ LogSi0}_{2}^{2}$

P: Pressure in the aquifer in bars.

SiO₂: Molal conentration of unionised silica at 100 °C.

990: The dominant aquifer in the well.

*: Additional inflow suspected.



Fig. 3. Correlation of Na-K and quartz geothermometry temperatures in the Olkaria Field (based on quartz solubility curve of Ragnarsdottir and Walther, 1982).



Fig. 4. Correlation of discharge enthalpy with the difference between two geothermometry temperatures. Na-K (Arnorsson et al. 1982c) and quartz (Ragnarsdottir, Walther, 1982).

5 VARIATION IN FLUID COMPOSITION BETWEEN WELLS

Distribution of chemical components in the discharges of individual wells in the field can be used to visualise the water movement and to locate upflow zone(s) and evaluate mixing, if any, of the geothermal water with fresh water. The Na/K ratios and undissociated silica concentrations in the well discharges when substituted into the respective geothermometry equations, can be used to to map variations in aquifer temperature within a particular field and to evaluate mixing processes. The tendency of silica to equilibrate faster with quartz than sodium and potassium with feldspars, at least for relatively saline waters, means that the Na/K ratios would be more reliable relative to silica in mapping the lateral movement and in locating upflow zone(s) in the geothermal system.

There is an overall increase in Na-K temperature from the southeast to northwest across the Olkaria bore field (Fig. 5), although quartz temperatures do not reveal such a variation. The two geothermometers yield similar results for wells in the southeastern part of the field, and wells in the northwestern part show greatest discrepancy. This is taken to mean that an upflow zone is located to the north west of the borefield.

There is a crude correlation between Na-K temperatures and salinity (Fig. 6), suggesting that the upflowing hotter water is more saline and that mixing occurs during lateral flow to the southeast, presumably by either mixing with down percolating fresh water or with condensed steam.

Carbon dioxide, hydrogen sulpide and hydrogen distribution in the Olkaria field is shown in Fig. 7. The gas distribution in the field does not show any significant regular variation (Fig. 7). If an upflow of boiling water in the northwest is assumed and a lateral flow to the southeast, the constant gas concentrations imply flow of two phases in a confined aquifer. This is indeed supported by the lack of thermal manifestations in the drilled area. Surface activity, such as fumaroles, would otherwise have meant steam separation and strong degassing of the reservoir fluid during its lateral movement, i.e. one would expect well discharges in the southeast to be depleted in gas.



Fig. 5. Chloride and Na-K geothermometry temperature isolines in the Olkaria Field.



Fig. 6. Correlation of salinity with reservoir temperature in the Olkaria Field.



Fig. 7. Distribution of gases in the Olkaria Field.

6 RECOMMENDATIONS

The recommendations on sampling and analysis of well discharges given in Appendix II of the Status Report on Steam Production (KPC 1982b) are supported by the author of this report. Specifically it would be of interest to analyse for iron and aluminium in selected samples from each well with the aim of evaluating further mineral solution equilibria in the Olkaria reservoir and to see if data from additional wells strengthen the model presented here.

It is recommended to carry out detailed study of changes in enthalpy and the gas content of selected wells when discharged for the first time in order to evaluate further boiling processes within the reservoir.

Substantial amount of analytical data will be produced in the future. For effective compilation and assessment of these data it is necessary to adopt filing computer programmes such as used at the National Energy Authority of Iceland (copies of these programmes were made available to the author; thanks to Dr. Jon Orn Bjarnason).

The author had an opportunity to work and observe appliances in two well equipped geochemical laboratories, at the University and National Energy Authority of Iceland. The suggestions below take into consideration the existing facilities at the Olkaria Geochemistry Laboratory. Since the bulk of the work to be done in the laboratory, involve routine monitoring studies and therefore analyses of many the use of the recommended equipment samples, and instruments will greatly facilitate analyses and collection of samples, both with respect to speed and precision. These recommendationds are based on discussions on modern laboratory instrumentation and equipment, between the author and Dr. S. Arnorsson, of the University of Iceland and Dr. H. Armansson of the National Energy Authority of Iceland.

Recommended additional equipment at Olkaria Laboratory:

- (1) Automatic dilutor. With this instrument, 50-100 analyses of silica, sodium and potassium, each, can be carried out in one day by one person. Using conventional dilution methods, such as by volumetric flasks one can hardly handle more than 20 such analyses per day.
- (2) Automatic chloride titrator a similar speed margin as in (1) above and a higher precision than silver nitrate titration.
- (3) An effective cooling system for collection of samples from wells. A system using a motor vehicle radiator has been fabricated at the National Energy Authority of Iceland and a design plan was made available to the author, thanks to Dr. Halldor Armannsson.
- (4) Glass gas sampling bulbs with septum and pressure check valves.
- (5) Automatic pipettes with tip ejectors, and fixed volume micropipettes.
- (6) Silicone tubing suitable in high temperature fluid sampling as they have excellent heat and solvent resistances and good release characteristics.

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APPENDIX I Equations describing the temperature dependence of cation/proton ratios and undissociated weak acid concentrations in geothermal well discharge (From Arnorsson et al., (1982b)).

*

| Weak acid/ ion ratio (moles/kg) | | Temper | ion | mean deviation | standard deviation | |
|---------------------------------------|--------|-----------|-------------|-------------------|-----------------------|------|
| logH4SiO4 | -0.588 | -0.00441T | -1515.21/T | +1.3470logT | 0.06 | 0.05 |
| logH ₂ CO ₃ | -1.794 | -0.00510T | -4469.63/T | +4.1414logT | 0.30 | 0.26 |
| logH ₂ S | -1.678 | -0.00355T | -5071.05/T | +3.88891ogT | 0.36 | 0.33 |
| 10gH2504 | -6.436 | -0.03906T | -13335.68/T | +14.7958logT | 0.57 | 0.48 |
| logHF | -5.262 | -0.3511T | -7964.11/T | +12.1022logT | 0.32 | 0.28 |
| logNa ⁺ /H ⁺ | 2.694 | +0.02023T | +4243.47/T | -6.2069logT | 0.14 | 0.12 |
| logK ⁺ /H ⁺ | 2.505 | +0.0197T | +3325.71/T | -5.7814logT | 0.12 | 0.09 |
| log√Ca++/H | 1.733 | +0.01117T | +3890.51/T | -3.9977logT | 0.17 | 0.12 |
| log√Mg++/H | 1.816 | +0.01078T | +3727.48/T | +4.16401ogT | 0.34 | 0.27 |

APPENDIX II Equations describing the temperature dependence of mineral solubilities and equilibrium constants. (from Arnorsson et al. 1982a)

MINERAL. REACTION TEMPERATURE FUNCTION (°K) $KAlsi_{3}O_{R} + 8H_{2}O = K^{+} + Al(OH)_{4}^{-} + 3H_{4}SiO_{4}^{\circ}$ 401 ADULARIAC +38.85 -0.0458T -17260/T +1012722/T² $NaAlSi_{3}O_{8} + 8H_{2}O = Na^{+} + Al(OH)_{4}^{-} + 3H_{4}SiO_{4}^{\circ}$ 402 LOW-ALBITE +36.83 -0.0439T -16474/T +1004631/T² $NaAlSi_2O_6 \cdot H_2O + 5H_2O = Na^+ + Al(OH)_4^- + 2H_4SiO_4^\circ$ 403 ANALCIME +34.08 -0.0407T -14577/T +970981/T² $CaSO_4 = Ca^{+2} + SO_4^{-2}$ 404 ANHYDRITE +6.20 -0.0229T -1217/T $CaCO_3 = Ca^{+2} + CO_2^{-2}$ 405 CALCITE^d +10.22 -0.0349T -2476/T $SiO_2 + 2H_2O = H_4SiO_4^\circ$ 406 CHALCEDONY^e +0.11 -1101/T $Mg_{5}Al_{2}Si_{3}O_{10}(OH)_{8} + 10H_{2}O = 5Mg^{+2} + Al(OH)_{4}^{-} + 3H_{4}SiO_{4}^{0} + 8OH^{-}$ 407 Mg-CHLORITE -1022.12 -0.3861T +9363/T +412.461ogT $CaF_2 = Ca^{+2} + 2F$ 408 FLUORITE^f +66.54 -4318/T -25.47logT $FeOOH + H_0 O + OH = Fe(OH)_4$ 409 GOETHITE⁹ -80.34 +0.099T +20290/T -2179296/T² $CaAl_2Si_4O_{12} \cdot 4H_2O + 8H_2O = Ca^{+2} + 2Al(OH)_4^- + 4H_4SiO_4^\circ$ 410 LAUMONTITE +65.95 -0.0828T -28358/T +1916098/T² $KAlSi_3O_8 + 8H_2O = K^+ + Al(OH)_4^- + 3H_4SiO_4^\circ$ +44.55 -0.0498T -19883/T +1214019/T² 411 MICROCLINE $Fe_{3}O_{4} + 4H_{2}O = 2Fe(OH)_{4}^{-} + Fe^{+2}$ 412 MAGNETITE -155.58 +0.1658T +35298/T -4258774/T2 413 Ca-MONTMOR +30499.49 +3.5109T -1954295/T +125536640/T² -10715.661ogT 414 K-MONTMOR 3K0.33A12.33S13.67O10(OH)2 + 30H2O + 60H $= K^{+} + 7Al(OH)_{4} + 11H_{4}SiO_{4}^{\circ}$ +15075.11 +1.7346T -967127/T +61985927/T² -5294.72logT 415 Mg-MONTMOR. +30514.87 +3.5188T -1953843/T +125538830/T² -10723.711ogT $3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 30H_2O + 60H^{-}$ = Na⁺ + 7AL(OH)⁻₄ + 11H₄SiO^o₄ 416 Na-MONIMOR +15273.90 +1.7623T -978782/T +62805036/T² -5366.18logT $Kal_{3}si_{3}O_{10}(OH)_{2} + 10H_{2}O + 2OH^{-} = K^{+} + 3Al(OH)_{4}^{-} + 3H_{4}siO_{4}^{\circ}$ 417 MUSCOVITE +6113.68 +0.6914T -394755/T +25226323/T² -2144.77logT $Ca_{2}Al_{2}Si_{3}O_{10}(OH)_{2} + 10H_{2}O = 2Ca^{+2} + 2Al(OH)_{4}^{-} + 2OH^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 20H^{-} + 3H_{4}SiO_{4}^{\circ} + 90.53 - 0.1298T - 36162/T + 2511432/T^{2} + 300/T^{2} + 300/T^{2}$ 418 PREHNITE 419 PYRRHOTITE $8Fes + so_4^{-2} + 22H_2O + 6OH^{-} = 8Fe(OH)_4^{-} + 9H_2s$ +3014.68 +1.2522T -103450/T -1284.861ogT $8Fes_2 + 26H_2O + 100H = 8Fe(OH)_4 + SO_4^2 + 15H_2S$ 420 PYRITE +4523.89 +1.6002T -180405/T -1860.33logr 421 QUARTZh $SiO_2 + 2H_2O = H_A SiO_A^\circ$ +0.41 -1309/T (0-250°C); +0.12 -1164/T (180-300°C) 422 WAIRAKITE $CaAl_{2}Si_{4}O_{12} \cdot 2H_{2}O + 10H_{2}O = Ca^{+2} + 2Al(OH)_{4}^{-} + 4H_{4}SiO_{4}^{\circ}$ +61.00 -0.0847T -25018/T +1801911/T² 423 WOLLASTONITE Casio₃ + $2H^+$ + $H_2O = Ca^{+2} + H_ASio_A^\circ$ -222.85 -0.0337T +16258/T -671106/T² +80.68logT $Ca_2Al_3Si_3O_{12}(OH) + 12H_2O = 2Ca^{+2} + 3Al(OH)_4^- + 3H_4SiO_4^\circ + OH^-$ 424 ZOISITE +106.61 -0.1497T -40448/T +3028977/T² $Ca_2FeAl_2Si_3O_{12}(OH) + 12H_2O = 2Ca^{+2} + Fe(OH)_4$ 425 EPIDOTE + 2AL (OH) + 3H4SIO + OH -27399.84 -3.8749T +1542767/T -92778364/T² +9850.38logT $8Fes_2 + 26H_2O + 10OH = 8Fe(OH)_4 + 8O_4^{-2} + 15H_2S$ 426 MARCASITE +4467.61+1.5879T-169944/T -1838.451ogT

aif not otherwise specified data for minerals and aqueous species are from HELGESON et al. (1978) and HELGESON (1969). ^bData on $Al(OE)_4^{-}$ and $Fe(OH)_4^{-}$ are from ARNÓRSSON et al. (1982a) and GUNNLAUGSSON and ARNÓRSSON (1982) respectively. ^CThermodynamic data on adularia are from HELGESON (1969). ^dData on the enthalpy and entropy of calcium ion at 25°C are from ROBLE et al. (1978). ^eARNÓRSSON et al. (1982b). Their empirical solubility function is very similar to the experimental solubility data of FOURNIER (1977). ^fNORDSTROM and JENNE (1977). ^GLANGMUIR (1971). ^hMOREY et al. (1962), KENNEDY (1950). ¹NAUMOV et al. (1971).

for these references see Arnorsson etal. 1982a.

| 8 | | | | | | | | | | | | | | | 1 | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|-------------------------------------|-------------------|-----------------|------------------------|----------------|-------------------|------------------|------------|-----------------|-----------------|-------------------------|-----------------|-----------------|--------------|-----------------|-----------|-------------|---------|---------|--------|-----------|----------------|--------|-----------|------------------|------------|----------|------------------|------------|---------------|-------------|-----------|------------------|-----------|-------------|---------|----------------|------------------|-----------------|-----------|---------------------------|-------------|------------|---------------------------|
| | 4SHA | | | 0.0 (MAK) | 0 0 | 2.015 (MEASURED) | 6.0 | 0.0 | 0.0/ 0.0 | 0*0 /000*0 | | CUID INFLOW | | 0.0 | 0.0 | 0.0 | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | | | | | JRES (BARS ABS.) | 0.5526-01 | 0.1595-01 | 0.111E-01 | 0.1116-02 | 0.165E-02 | 0.000E+00 | 0.492E+02 | | | | | | | | | |
| | HAIN | | | DEGREES C | DADC ADC | PY NJOUL/KG | K6/SEC. | T PROPERTY N | . OHMM/DEG.C | W/ JED.L | | HOLE TEMP. F | | 0.0 | 0.0 | 0.0 | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | | | | | GAS PRESSI | CIII | H2S | 앞응 | CHA | N2 | UCH UCH | TOTAL | 0 70 | 0.40 | | | | | | | |
| | OLKARIA DU-2 | | | EFERENCE TEMP. | ANDI TUC PECCIIDI | ISCHARGE ENTHAL | ISCHARGE | CACHDET TEMPEDA | ESISTIVITY/TEMP | H/16/1. | | HEASURED DOWN | הבטתבבס ניוו | 0.0 | 0.0 | 0.0 | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | | EB.)0.02963755 | (Z) 8.50 | | EAN (PPN) | 10.8470 | 613,00 | 25.33 | 20.17 | 52.41 | 0.00 | | | PORTION | | | | | | | |
| | | | | 8 | 65.36 | 13.07 B | 0.00 | 1.31 1.05 M | | | 5 | 1.73/20.0 | | | 0.00/ 0.0 | 0.00 | 00.0 | | | | (ADH (PPK) | 0.00 | | CATTONS (HOL | DIFFFRENCE | | DEEP STI | CUJ | H2S | 도 | CHA | N2 | EHN | | 147 007 | BOILING | | | | | | | đ |
| OLK. | EY | | TEAN SAMPLE | AS (VOL.Z) | 02 | 00 | 5 | H4 | 4 | | ITERS GAS PER K | DNDENSATE/DEB.C | | ONDENSATE (PPM) | H/DEG.C | 22 | 5P | £ | | | ONDENSATE WITH | 20 | 3 | IONIC BALANCE : | | | | 75. 87 | 33.00 | 0.05 | 10.0 | 0.09 | 00.0 | | | | OR : 1.00 | | | | | | |
| W | 002 RIFT VALL | | s (| 8.38/20.0 6 | 00.88.00 | H 00.50 | 0.52 0 | 0.011 0 | 42.90 | 0.51 | 58.40 L | 0*00 C | .3000 | .0000 C | .0000 P | 0: | E 2 | E | | | 0. | 3 3 | 5 | 0.02891 | | | | COL N | 9 H2S | 8 | CHA | V6 N2 | EHM II | | 0.0 | 2 0 | LTIPLYING FACT | | | | | | |
| ORKUSTOFNUN JHI 1982-09-10 WANBI | 99999001028201170 | PROGRAM WATCH1. | VATER SAMPLE (PP) | PH/DEG.C | S102 | NA X | 4 53 | 11G | 504 S04 | H2S CI | 1 m | DISS.SOLIDS | B | H |) EHN | | | | | | | | | IONIC STRENGTH = | | | DEEP WATER (PPH) | - 103 CU10 | HA 375. | K 64. | MG 0.00 | S04 25. | CL 453.2 | DISS.S. 0.0 | AL 0.00 | FE 0.000 | GAS SOLUBILITY N | | | | | | |
| 1 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 6 | | • 6 | 4 | o- o- | 5 | | 6 |
| | 1 | 0.148 | 0.784 | 111.0 | 0.179 | 0.784 | 111.0 | 0.104 | 101-0 | 000*0 | 0000*0 | 00000 | 0.000 | 0000*0 | 00000 | 000.0 | 0.000 | 0.000 | 0.000 | 0.000 | 00000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0000 | 0.000 | | | | | | | | 3= 99,99 | | 59.99 | -2.07 | 66.99 | 66.99 | -2.07 | 66*66 |
| | | ALTH+ | AL (0H)2+ AL (0H)4- | AL 504+ | AL (504)2- | ALF24 | ALF4- | ALF3 | HLO | 00 | 0.00 | 00.0 | 0.00 | 0.00 | 0.00 | 0.0 | 0.00 | 00.0 | 00.0 | 0.00 | 00.0 | 0.00 | 00.00 | 00*0 | 0.00 | 00.00 | 0.0 | 00.0 | | | | | | | | 813 EH NH | | -11.551 | Y -1.944 | -15.687 | R74.088 | -3/./6- | -38.546 |
| | | 0.781 | 0.781 | 0.373 | 0.784 | 182.0 | 0.373 | 18/*0 | 0//*0 | FE(0H)3 | FE(0H)4- | FECL + | FECLH | FECL24 | FECL3 | FEUL4- | FFS041 | ALTH | ALOHH | AL (DH)24 | AL (OH) 3 | ALS044 | AL (S04)2 | ALF H | ALF3 | ALF4- | ALFS | ALFS | 01759458 | V3.0 | AC. 1 | 78.1 = MIN | | | | EH H2= -0. | | ANALCINE | CHALCEDON | GOE THITE MAGNETITE | NG-MONTHO | QUARTZ | ZOISITE |
| | 1 | . ± ≠ | H)3 | ŧ | H)2+ | 1 | ‡ ; | 4 | ŧ | 1.097 | 3.568 | 1.773 | 4.472 | 2.919 | 7,435 | 20/10 | 808.2 | 8.904 | 6.590 | 6.814 | 0.000 | 0.000 | 0.000 | 0000 | 0.000 | 0.000 | 0.000 | 000.0 | MOL. 50. 10 | MUL.EU. 19 | 3 | BREES KEL | | | | 4= -0.724 | | CALC. 99.999 | -13.297 | 66.999 | 666'66 | 666.66 | 7.048 |
| | i | | FELL | E S | PEC | FESC | FEDI | 1034 | 192 | 0.00 - | 15.79 | 1.26 | 4.56 | 0.16 | 0.0 | 20.0 | 51.0 | 0.00 | - 10.0 | 0.01 | 0.0 | 00.00 | 0.00 | 0.0 | 0.00 | 0.00 | 0.00 | 0.00 | CATIONS (| DIFFFRUNC (| | 1000/T DE | | | | EN CH | 1000 | -13.939 | -13.104 | -11.027 | -33.895 | -1/.85/ | 7.273 |
| | 55 | 0.769 | 0.773 | 0.388 | 0.415 | £77.0 + | 0.788 | 0.742 | 10/10 miles | NG++ | NACL | NCL NASR4- | -504- | CASO4 | HGS04 | MOLUS WORDS | COHCU3+ | MGHC03+ | CAOH | HOGH+ | NH40H | 1133 | HEH | FEOH12 | FE(OH)3- | FE(0H)-1 | FE (OH) #+ | FE(UN)21 | ITC BALANCE : | | | 0 | | | | EH H2S= -0.688 | S IN DEEP WATER | ALBITE LOW | CALCITE | FLUUKITE MICROCLINE | K-MONTMOR. | PYRITE | WOLLASTONITE MARCASITE |
| | TS IN DEEP HAT | -nev -13 | ten tx | CAH | RIGHT CAHENT | MGHCO3 | CAOH | HIDH | TTON NATE IN | 11 JEEF WRIEN -7,422 | -3,491 | -2,074 | -7.521 | -4,446 | 11917- | 11710- | CH2.2- | -7.138 | E0E*E- | -3,327 | -10.467 | -5.001 | -3.720 | -4,728 | -1,903 | -1.797 | -2,794 | 616+6- | 01699 10 | | | TERS DEGREES | | | | (VOLTS) : | CTS OF MINERAL | 5 99.999 | 1 -9,887 | 666.66 | 666"66 1 | 666*66 5 | 666°66 1 |
| | REFLICIEN | 0.775 | 0.379 | 6.773 | 0.749 | E/E.0 | 0.777 | 855.0 APT 0 | 01/01 | 0,00 | 5,50 | B11,54 | 0.00 | 4.23 | 14.39 | 22.02 | 17.11 | 0.00 | 16.95 | 15.58 | 0.00 | 0.10 | 18.32 | 12.4 | 143.13 | 367,30 | 52.81 A 26 | 1210 | STE = 0. | | | JTHERMONE | 5.7.50 | 5.999 | 01707 | DTENTIAL | TTY PRODU | -14.37 | -8.34 | -24.666 | -72.58 | -13.77. | -24.80 |
| | ACTIVITY CO | 64- 132104- | H25104 | -500H | 500 | 1 | H504- | | TOOR | THE MILLIAL CO | 吉 | H4SID4 | H25104 | MAH3SID4 | 17803 | -20121 | HC03- | 203 | SZH | HS- | S | HS04- | +68 | te d | с. | NA4 | K4 Call | 1111 | IONIC STREM | | | CHENICAL BEI | 084877 | CHALCEDOWY | dHu | OXIDATION PI | 1180105 201 | ADULARIA | ANHYDRITE | MU-UHLUKITE LAUMONTITE | CA-HONTMOR. | PYSRHOTITE | WAIRAKITE EPIDOTE |

Typical deep calculations computer in- and output. APPENDIX III

APPENBIX IV Geothermometry calibration curves.

| | CHALCEDONY | Range °C | |
|------------------|-------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|------------------------------------------------|
| (1) | $t^{\circ}C = \frac{1112}{4.91 - \log SiO_2} - 273.15$ | 25 - 180 | |
| (2) | $t^{\circ}C = \frac{1264}{5.31 - \log SiO_2} - 273.15$ | 100 - 180 | after adiabatic steam loss to 100°C |
| (3) | $t^{\circ}C = \frac{1021}{4.69 - \log SiO_2} - 273.15$ | 25 - 180 | |
| | Na-K (LOW ALBITE MICROLINE) | | |
| (4) | t°C = <u>933</u> - 273.15 0.993 + logNa/K | 25 - 250 | |
| (5) | t°C = <u>1319</u> - 273.15 1.699 + logNa/K | 250 - 350 | |
| (6) | LogNa/K = - 1.782 - 2775.5/T + 55878 + 4.104logT (T °K) Rang | 30/T ² - 0.0 je 25 - 350 | 00969T) |
| (7) | $t^{C} = \frac{1164}{4.90 - \log Si0_2} - 273.15$ | 180 - 300 | |
| (8) | $t^{\circ}C = \frac{1498}{5.70 - \log Si0_2} - 273.15$ | 180 - 300 | after adiabatic steam loss to 100 °C |
| (9) | t°C = 771 + (336 + 10 ⁻² p)logSi0 ₂ + 38.8log2Si0 ₂ | after ac (Ragnars | diabatic steam loss sdottir, Walther, 1981) |
| | CO2 IN STEAM FLASHED TO 100°C | | |
| (10) | LogCO ₂ = 37.43 + 73192/T - 11829·10 ³ - 86.187logT (t °K), mole | ³ /T ² + 0.18 es CO ₂ per | 8923T kg steam. |
| (11) | $LogKH_4SiO_4 = -2549/T - 15.36 \cdot 10^{-6}T^2$ | 0 - 3 | 50 |
| (12) | Log(mNa/aH ⁺) = 2306/T - 0.426 | 25 - 20 | 00 |
| T: ter logSi(| mperature in degrees Kelvin, m: mola 0 ₂ : concentration of SiO ₂ is in ppm. | ality, a: a | activity, |