

Report 7, 1992

**INTERPRETATION OF HYDROGEOCHEMICAL RESULTS  
FROM THE ZUNIL I GEOTHERMAL FIELD, GUATEMALA**

Carolina Grajeda,  
UNU Geothermal Training Programme,  
Orkustofnun - National Energy Authority,  
Grensasvegur 9,  
108 Reykjavik,  
ICELAND

Permanent address:  
Instituto Nacional de Electrificación (INDE),  
Unidad de Desarrollo Geotérmico,  
7a Av. 2-29 Zona 9,  
Guatemala City,  
GUATEMALA

**ABSTRACT**

In Guatemala the first geothermoelectric plant of 15 MW is being scheduled for June 1993 in Zunil I, a geothermal field located approximately 200 km west of Guatemala city. The fluids of the springs in the Zunil I geothermal field are of different chemical compositions but they clearly define a deep fluid of high temperature. The chemistry of the fluid from well ZD-1, the first production well in the granodiorite basement is undersaturated with respect to calcite and quartz and the chemical geothermometer temperature calculated on the basis of its deep water composition is 290°C. This high temperature fluid has a high chloride content (1490 ppm) and a calculated enthalpy of 1291 kJ/kg.

Thermal manifestations along the Samalá River are evaluated and their deep water composition is derived from the analyzed surface chemical composition using the WATCH3 programme. The temperature evaluated by geothermometers is about 280°C. There are three types of springs along the Samalá River, chloride, bicarbonate and sulphate springs. The first type is presumably derived from the mixing of geothermal fluid (probably boiled) with local groundwater, whereas the latter two derive from condensation of steam and mixing with surface water.

## TABLE OF CONTENTS

	Page
ABSTRACT .....	3
TABLE OF CONTENTS .....	4
LIST OF FIGURES .....	5
LIST OF TABLES .....	5
1. INTRODUCTION .....	6
2. GEOLOGY AND AREA OF STUDY .....	7
3. SAMPLING AND ANALYSIS .....	9
3.1 Field sampling .....	9
3.2 Laboratory analysis .....	9
3.3 Analytical results .....	13
4. CHEMISTRY OF THE GEOTHERMAL WATERS .....	17
4.1 Water chemistry and mineral solubilities .....	17
4.2 Equilibrium calculations .....	17
4.3 Geothermometers .....	18
4.4 Comparison of thermal waters from springs and wells using chloride-enthalpy diagrams .....	18
4.5 Silica solubility in hydrothermal solutions .....	21
4.6 The silica-mixing model .....	21
4.7 Calcite solubility in hydrothermal solutions .....	22
5. CHEMISTRY OF THE FLUID OF WELL ZD-1 .....	23
6. DISCUSSION .....	27
6.1 Summary of results .....	27
6.2 Conclusions and recommendations .....	28
ACKNOWLEDGEMENTS .....	29
REFERENCES .....	30
APPENDIX: Printouts from the programme WATCH1 .....	33

## LIST OF FIGURES

	Page
1. Plate boundaries in the Central American-Caribbean region .....	7
2. The structural provinces of Guatemala and location of five geothermal areas .....	8
3. Location of geochemical sampling sites in Zunil geothermal field .....	10
4. Distribution of dissolved carbonate species as a function of pH at 20°C .....	12
5. Classification of Zunil geothermal waters .....	15
6. Enthalpy-chloride relations for waters from Upper Basin Yellowstone Park .....	20
7. Enthalpy-chloride relations for waters from Zunil at measured temperatures .....	20
8. Relation of waters from springs in Zunil to the silica solubility curve .....	21
9. Enthalpy-silica graph illustrating calculations of silica mixing model temperatures ..	21
10. Enthalpy-silica graph for springs in the Zunil geothermal area for calculating silica-mixing model temperatures .....	22
11. Enthalpy-chloride relationships for fluids from production and thermal gradient wells in the Zunil geothermal system .....	23
12. Calcite solubility, deep water cooling from well ZD-1 .....	26
13. Calcite solubility, deep water boiling from well ZD-1 .....	26

## LIST OF TABLES

1. Geochemical laboratory of INDE, Guatemala, methods of chemical analyses .....	11
2. Chemical composition of the fluid from ZD-1, derived from averages .....	12
3. Geochemical analyses of water samples from the Zunil geothermal field, January 1991 .....	13
4. Chemical composition of discharges from wells and springs in the Zunil geothermal field .....	14
5. Ionic balances and log solubilities for calcite and quartz selected Zunil fluids .....	16
6. Geothermometry calculations for selected springs in Zunil .....	19
7. Analytical results for deep water composition of well ZD-1 fluids .....	25

## 1. INTRODUCTION

Since 1976 geoscientific surveys have been carried out in Guatemala to locate and evaluate the geothermal resources in the country. OLADE in cooperation with the United Nations located 13 areas as geothermal prospects in 1981. INDE (Instituto Nacional de Electrificación) has been in charge of the geothermal project centering the activities on five areas: Amatitlán, Moyuta, San Marcos, Tecumburro and Zunil. According to the 1979 prefeasibility studies, Zunil has been divided into Zunil I and II. Zunil I is the most promising area and is regarded as a high priority target for geothermal exploration and is actually in the developing and production stage. ZD-1, the first production well, has been completed and the first production test carried out and is reported on here. Three more production wells are planned.

Thermal manifestations in the Zunil geothermal field have been sampled and the fluids analyzed and a lot of data from these analyzes has been available for many years. Giggenbach et al. (1988) carried out geochemical investigations in the area within the framework of the IAEA Coordinated Research Program on the "Application of Isotopic and Chemical Techniques to Geothermal Exploration in Latin America". They quantified the degree of chemical equilibrium reached by thermal waters through the application of geothermometers based on Na-, K-, and Mg-bearing minerals. Adams et al. (1990) reported the chemical and isotopic relationships of fluids from wells and springs in the region of the Zunil geothermal field and defined a high temperature water originating in the western part of the existing well field flowing to the south and east, boiling and mixing with shallow steam-heated waters and suggested that the deep fluid may have a temperature as high as 335°C. The conceptual model of the Zunil geothermal field defines it as an "exploitation block", which receives hydrothermal fluids by lateral migration from the Cerro Quemado zone.

During the exploration stage the chemistry of the fluids can be used to infer the subsurface temperature of the geothermal system and its exploitation potential. Monitoring the chemistry of the fluids during the exploitation stage is important for the prediction of scaling, corrosion and changes in the system. Analytical results for selected springs in the Zunil geothermal field and well fluids obtained during the flow test of well ZD-1 are interpreted using the WATCH computer programme of Arnorsson et al. (1982) which takes into account the attainment of overall chemical equilibrium between the geothermal fluid and possible mineral phases (Reed and Spycher, 1984).

This report describes work done on spring samples from the Zunil geothermal field and well samples from the first flow test on well ZD-1. Chloride-enthalpy diagrams and silica mixing models are used to evaluate the temperature in the reservoir and the result compared with calculated quartz geothermometer results.

## 2. GEOLOGY AND AREA OF STUDY

Geographically the Republic of Guatemala can be divided into four main structurally and physiographically different regions. They are from north to south: The Petén Lowland including the Chapayal Basin, the Central Cordillera, the Volcanic Belt and the Pacific Coastal Plain. According to the concept of plate tectonics the regions belong to the following plates (Figure 1):

- The North American Plate including the area of Mesozoic folds and the Petén Lowland.
- The Caribbean Plate; its northwestern end is composed of metamorphic rocks, igneous rocks and sediments and makes up the Central Cordillera.
- The Cocos Plate, which has subducted into the the mantle below the Middle America Trench and is thus responsible for the belt of Tertiary and Quaternary volcanoes and the young sediments derived from them.

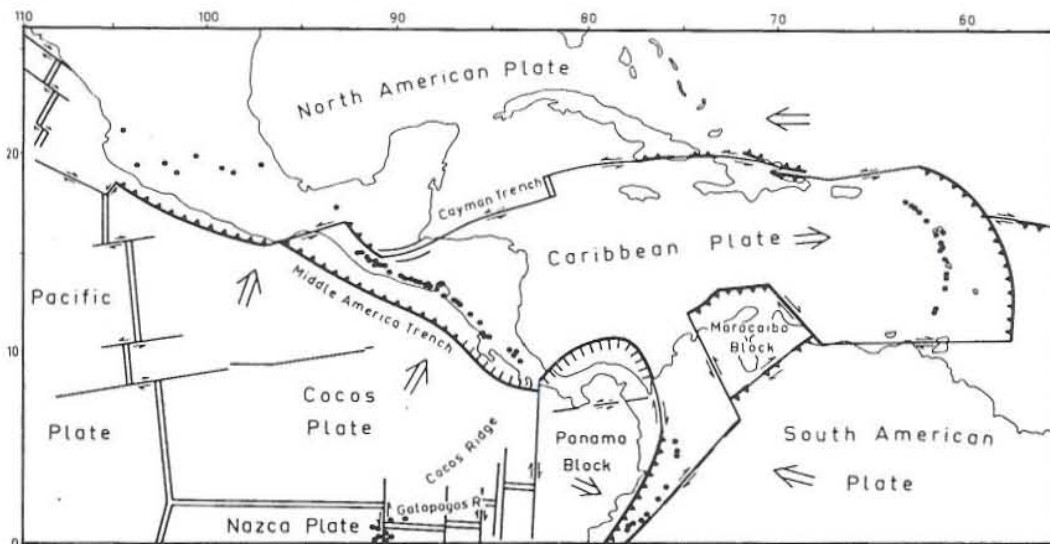


FIGURE 1: Plate boundaries and tectonics in the Central American-Caribbean region (Weyl, 1980)

In the north the Tertiary volcanism has resulted in the pumice-filled basins and grabens. The different regions in Guatemala are shown in Figure 2. Inside the volcanic belt there are several hydrothermal systems. One of them is closely associated with the Cerro Zunil-Domo el Azufra volcanic complex. The Zunil geothermal area is located within this complex (Figure 2). The volcanic belt rises steeply from the coastal plain in the south.

The Zunil area consists of a Cretaceous granitic basement covered by Tertiary and Quaternary lavas and pyroclastic deposits. The tectonic influence is apparent in a series of alternating grabens and horsts with a general tendency to deepen to the west. In addition there are many circular features and curved faults in the Zunil area (García and Estrada, 1991). There are three predominant fault systems, NE-SW trending, W-E trending, and NW-SE and/or WNW-ESE trending.

In the Zunil region (Figure 3), volcanic activity started during the Miocene and continued throughout the Quaternary. The Tertiary lavas were extruded from fissure eruptions and formed a large plateau. The Quetzaltenango caldera is located in this zone. In the depression zone there is a thick pile of ash-flow tuff and tuffaceous sediments.

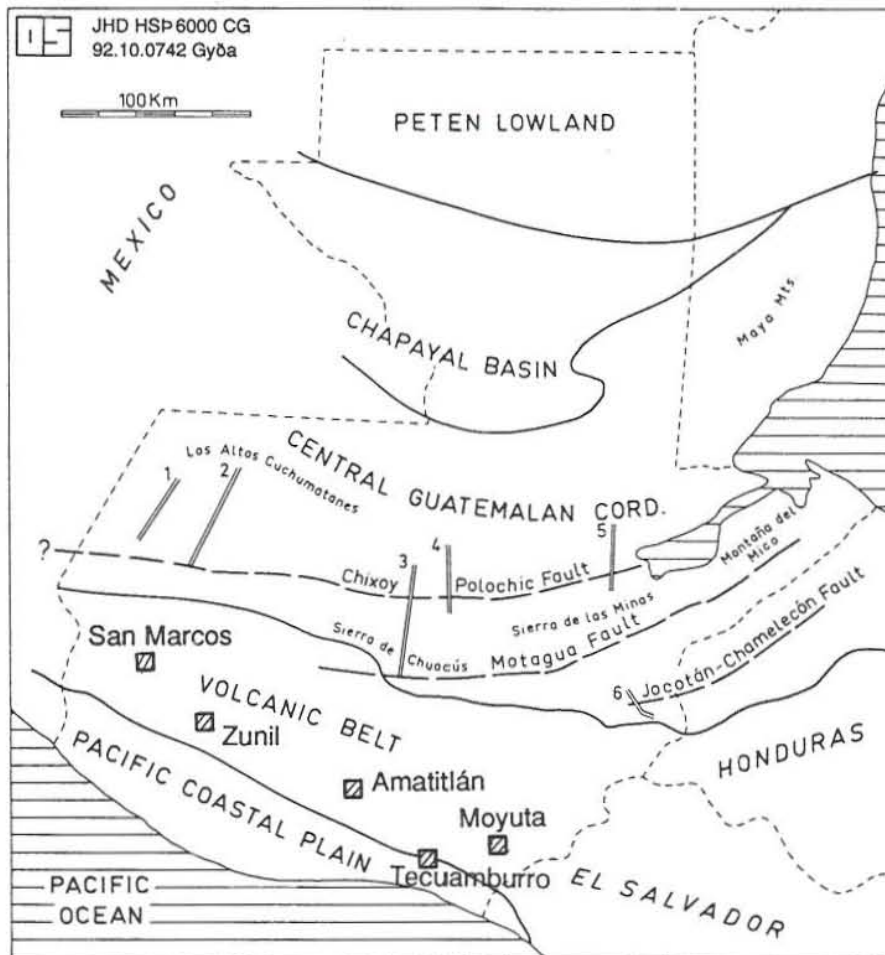


FIGURE 2: The structural regions of Guatemala and the location of the 5 geothermal areas under exploration (after Weyl, 1980)

Thermal manifestations are concentrated along the Samalá River where the chloride type hot springs discharge. Adams et al. (1990) evaluated the geochemistry and hydrology of the Zunil field and suggested that the high temperature water originates in the western part of the existing well field and flows south and east to mix with shallow steam-heated water.

### 3. SAMPLING AND ANALYSIS

#### 3.1 Field sampling

Water samples were collected from springs and the Samalá river in January 1991. The water was filtered through  $0.45\mu$  millipore filters with the help of a hand-held vacuum pump. Two sampling bottles were filled at each site and one of the samples acidified with 1 N HCl (10 drops). The acidified sample was used for the determination of silica while the untreated one was used for the analysis of major anions and cations.

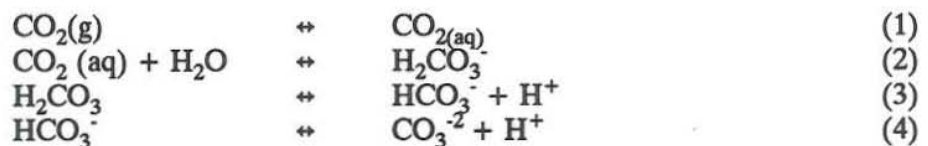
Carbon dioxide and hydrogen sulphide were not determined in the field. The water temperature was measured on site and pH in the laboratory using a glass electrode pH meter. The general sampling sites in the Zunil geothermal area are shown in Figure 3. They are sampled three times per year. The locations of the springs encircle the area, including the Samalá River.

For sampling during the flow test on well ZD-1 the flow was split into two lines at the wellhead. Samples were taken from both lines to ensure that the chemistry of the well could be correctly reconstructed. The samples were taken from 45 degree one-inch ports using a cyclone miniseparator. The miniseparator was mounted horizontally on two one-inch pipes joined by an elbow. The entire length of the pipe was insulated to preserve identical pressure and temperature conditions in the flow line and in the miniseparator (UURI, 1992b).

The liquid samples were filtered with a 0.45 micron in line filter. Aliquots for ICP and ammonia determinations were furthermore filtered through a 0.45 micron syringe filter. ICP aliquots were preserved with 20% nitric acid, ammonia ones with 0.5 ml nitric acid per 30 ml, Hg aliquots with 50 ml  $K_2CrO_7$  saturated nitric acid per 250 ml. Samples for TDS, bicarbonate and anion determinations were filtered only. The pH was measured on site and in the laboratory. A sample record was taken for each line and the data recorded are date, time, sample location, sample type, operator, critical lip pressure, separator pressure before sampling, separator pressure after sampling, sample fraction and comments (weather, flowrate, etc.).

#### 3.2 Laboratory analysis

All the methods used in the INDE Laboratory are listed in Table 1. Some components like F and  $H_2S$  are not reported and  $CO_2$  is analyzed as  $HCO_3^-$ , but reported as total alkalinity after computation. Relative bicarbonate, carbonate and dissolved  $CO_2$  contents of geothermal waters are a function of solution pH and  $P_{CO_2}$  as illustrated by the reactions:



Dissolved  $CO_2$  and  $H_2CO_3$  contents depend strongly on  $P_{CO_2}$  and are therefore only representative if samples are taken in a way preserving the original pressure. This is generally impossible, because when most hot water samples are collected at least some vapor separation from the original deep fluid occurs. This loss of vapor and therefore  $CO_2$  is accompanied by a rise in pH and a general increase in the ionization of all weak acids present in solution such as  $HCO_3^-$ ,  $NH_4^+$ ,  $H_3BO_3$  and  $H_4SiO_4$ . Loss of carbon dioxide from the sample before, during or after sampling leads to a redistribution of the ions  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $H_2BO_3^-$ ,  $H_3SiO_4^-$  and  $NH_4^+$ . True



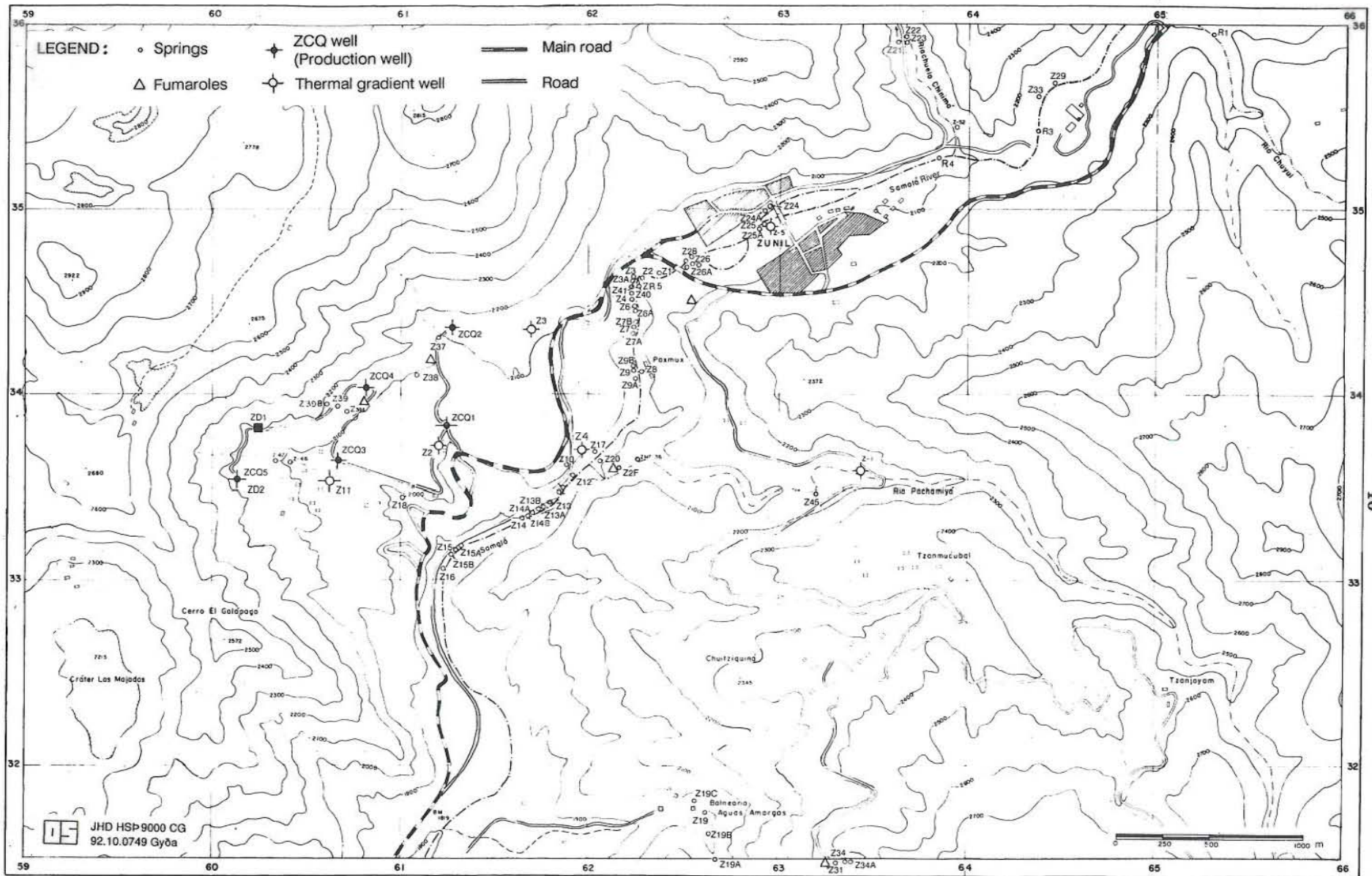


FIGURE 3: The Zunil geothermal field and locations of geochemical sampling sites

TABLE 1: Geochemical laboratory of INDE, Guatemala; methods of chemical analysis

Constituent	Methodology	Precision	Reference
pH	Glass electrode pH meter	+/- 0.01	Orion, 1990
SiO <sub>2</sub>	UV/VIS silico-molybdate complex	1.6%	Giggenbach and Goguel, 1989
Na	Atomic absorption spectrometry with lithium as inhibitor	1.5%	Perkin Elmer, 1990
K	Atomic absorption spectrometry with lithium as inhibitor	1.5%	Perkin Elmer, 1990
Li	Atomic absorption spectrometry	1.5%	Perkin Elmer, 1990
Ca	Atomic absorption spectrometry with La as inhibitor	4.3%	Perkin Elmer, 1990
Mg	Atomic absorption spectrometry with La as inhibitor	4.3%	Perkin Elmer, 1990
HCO <sub>3</sub>	Alkalinity titration	1.5%	Giggenbach and Goguel, 1989
SO <sub>4</sub>	UV/VIS reaction of sulfate with barium chromate suspension	2.5%	Giggenbach and Goguel, 1989
Cl	Mohr, titration method	0.5%	Franson, 1980
TDS	Evaporation	3.2%	Franson, 1980

presampling HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>-2</sup> contents can be obtained by recalculating the distribution of solute species in the original deep fluid by use of one of the computer programmes available. In this recalculation of the deep composition accurate information on both bicarbonate and carbonate contents of the sample is required.

The analytical method consists essentially of an alkalinity titration corrected for the effects of other weak acids, mainly boric and silicic acid and ammonium ion, by back titration. The distribution of dissolved carbonate species is given in Figure 4 as a function of pH at 20°C, a chloride concentration of up to 2000 mg/kg, with B at 25 mg/kg and SiO<sub>2</sub> at 600 mg/kg.

For samples with a laboratory pH >8.3 the amount of carbonate, CO<sub>3</sub><sup>-2</sup>, is obtained by titration with 0.02N HCl to pH 8.3 or 8.0. This reaction converts all CO<sub>3</sub><sup>-2</sup> to HCO<sub>3</sub><sup>-</sup>. Subsequent titration with 0.02N HCl to pH 3.8 converts all HCO<sub>3</sub><sup>-</sup> to H<sub>2</sub>CO<sub>3</sub> which is removed as CO<sub>2</sub> by bubbling with N<sub>2</sub> or CO<sub>2</sub>-free air. By titrating the now CO<sub>2</sub>-free solution with 0.02 N NaOH back to the original pH, all interfering species are converted back to their original state of ionization. CO<sub>2</sub> was computed stoichiometrically for this report.

The samples from well ZD-1 were analyzed by UURI (1992a and b). The data computed by UURI is based on the chemical composition of the water fraction. The steam fraction is derived from the separation temperature and the enthalpy obtained by the James method (1962). Two lines were split at the wellhead to accommodate more easily the high production of this well. From each line, 14 sample records were taken for the liquid and the steam. The analyses from the flow lines are reported for each line but an average result is used for calculations. Table 2

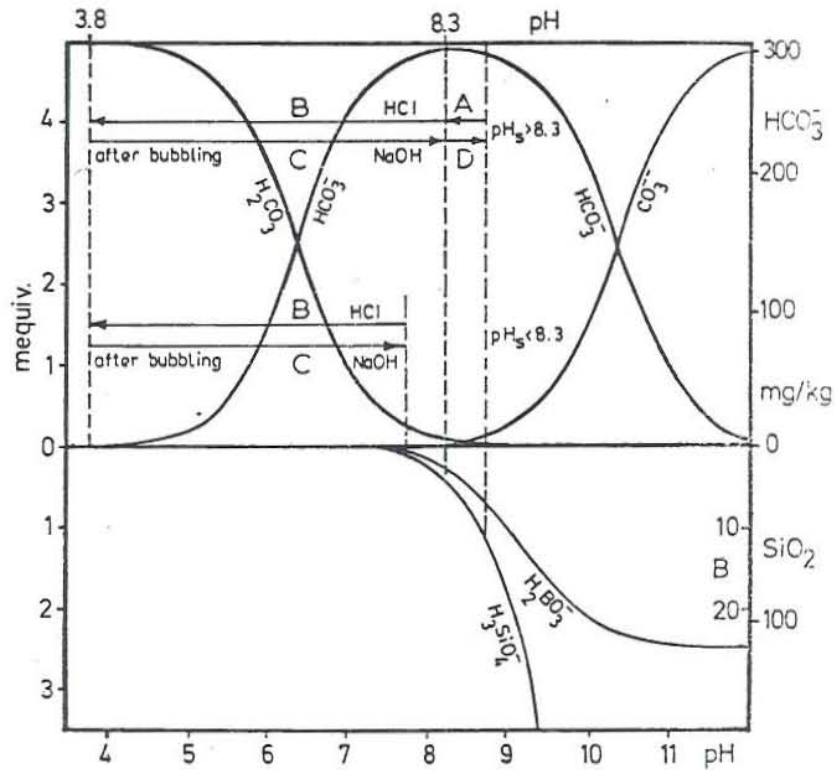


FIGURE 4: Distribution of dissolved carbonate species as a function of pH at 20°C

TABLE 2: Chemical composition of the fluid from ZD-1 in ppm, derived from averages

Constituent	Av. concentration	Stand. dev.
Na	623.00	11.0
K	157.00	3.0
Ca	2.95	0.07
SiO <sub>2</sub>	638.00	11.00
B	24.70	0.80
Li	6.29	0.13
Sr	0.014	0.00
As	5.79	0.11
Cl	1073.00	23.33
F	3.52	0.09
SO <sub>4</sub>	18.60	1.00
pH (mea.)	5.80	0.1
TDS	2667.00	47.0
CO <sub>2</sub>	2308.00	137.0
H <sub>2</sub> S	57.20	1.8
NH <sub>3</sub>	2.20	0.12
Ar	0.04	0.002
N <sub>2</sub>	12.80	1.2
CH <sub>4</sub>	0.48	0.049
H <sub>2</sub>	0.141	0.007

TABLE 3: Results of geochemical analyses of water samples from the Zunil field, January 1991 (ppm) (INDE, 1991)

Sample	pH lab	T (°C)	Na	K	Ca	Mg	Li	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	B	SiO <sub>2</sub>	TDS
Z-3	8.3	58	127	12.5	15.25	4.75	0.27	99.26	106.1	203.8	3.78	359.7	851
Z-3a	8.3	50	129.5	12	13.5	4.5	0.26	99.17	90.86	197.7	2.38	368.6	810
Z-4 (B-3)	8.09	62	150.5	12	15	5	0.3	102.8	122.3	236	3.53	363	863
Z-6	8.23	60	149	12	14	4.75	0.29	99.26	122.3	228.2	4.3	352.1	858
Z-7	7.9	60	145	12.5	18.5	6	0.29	95.71	110.1	252.6	3.78	346.8	578
Z-7a	8.21	60	148	12.5	15.75	6.25	0.29	99.26	116.6	238	4.66	371.9	668
Z-7b	7.81	61	155.5	13.5	15.75	7	0.3	102.8	115	264.8	3.28	326	600
Z-7c	8.63	60	151	13.5	15.5	7	0.31	106.4	125.2	224.5	3.7	328	616
Z-9 (B-4)	8.26	60	185.5	18.5	21.25	14.25	0.38	113.4	146.2	346.6	7.85	401	782
Z-10(B-6)	8.43	62	260	36.5	28	38.75	0.59	191.4	430.7	639.4	7.37	517.5	1175
Z-12	2.96	89	17	8	25	13.25	0.10	7.09	358.9	0	0.02	403.4	754
Z-13(B-7)	7.62	65	202.5	29	39.25	41.25	0.48	134.7	259.9	485.7	5.04	382.2	1110
Z-13a	7.88	65	237	37	44.25	46.25	0.6	173.7	228.2	580.9	5.79	397.4	1143
Z-13b	7.67	65	232.5	34	44.75	44.75	0.58	163.1	237.5	610.2	5.67	441	1171
Z-14	8.01	70	139.5	30.5	33.5	24.50	0.77	138.3	203.2	262.4	4.21	439.7	837
Z-14a	7.9	64	140.5	35	35.75	25.50	0.78	148.9	227.1	251.4	4.89	368.6	921
Z-15(B-8)	7.58	62	145.5	19.5	76.75	26.75	0.88	81.53	198.7	356.3	3.61	357.5	803
Z-16	6.92	20	41	7.5	18.25	7.25	0.09	35.45	53.76	114.7	1.5	211.2	248
Z-17(B-5)	7.92	70	268	34.5	28.5	34.25	0.58	187.9	238.1	606.5	6.68	507	1198
Z-18	6.44	34	42.5	14	43.5	24.75	0.1	38.99	86.89	261.2	0.7	326	458
Z-19(S-3)	2.36	51	740	28	35.5	10.75	0.02	10.63	1284	0	1.09	517.5	2301
Z-20(C-1)	9.15	92	946	92	8.75	0.25	2.83	694.8	202.1	3.67	26	820	1910
Z-22	8.02	40	88	5.5	14	5.00	0.2	60.26	102.8	131.8	0.31	328	419
Z-23(B-1)	7.57	35	64.5	9.5	40.5	11	0.11	31.9	77.36	225.8	0.81	371.9	450
Z-24a	8.11	50	104.5	13	19	7.75	0.26	85.08	83.29	207.5	4.11	391.5	489
Z-25	7.78	50	98.5	15	14	6.50	0.28	106.4	67.05	189.2	3.12	428.1	484
Z-26	6.81	51	89	12.5	16.75	8.75	0.26	63.81	77.7	194	3.7	403.4	473
Z-28	7.78	55	115	12.5	15.5	5.00	0.26	85.08	90.86	187.9	4.94	360.8	526
Z-28a	8.17	56	113	13	16	6.25	0.27	85.08	95.22	189.2	3.16	355.4	300
Z-29(B-2)	7.93	44	63	10.5	8.75	4.00	0.17	53.17	36.61	130.6	3.05	693.5	393
Z-31(S-4)	2.16	70	129.5	32.5	61.5	22.75	0.07	63.81	2552	0	2.66	326	1594
Z-33	7.41	50	71.5	11	8.75	4.00	0.21	63.81	36.07	149.4	2.24	517.5	33
Z-R1	7.4	18	23.25	4.88	13.38	5.63	0.02	14.18	0	102.5	0	128.4	506
Z-R2	7.35	18	29.13	5.63	13.75	5.88	0.02	21.27	15	106.2	0.76	185.8	432
Z-R3	7.43	20	43.88	7.88	14.5	7.25	0.1	35.45	42.66	109.8	0.81	164.9	489
Z-R4	7.52	18	41	7.75	14.25	7.25	0.09	31.9	39.38	111.1	0.37	254.4	497
Z-R5	7.43	18	41.38	7.75	16.88	7.88	0.08	31.9	48.43	108.6	0.61	213.3	513
Z-R6	7.65	18	44.13	8.38	16.25	9.88	0.08	35.45	51.47	126.9	1.01	198.4	523
Z-R7	7.86	18	33.88	6.75	13.88	8.75	0.06	28.36	39.38	108.6	0	228.4	488
Z-R8	7.43	18	31.88	6.38	13.63	8.50	0.06	24.81	36.73	82.98	0.09	182	473

shows the analytical results obtained during the flow test as averages of the flow line fluid compositions. Previous analytical results for fluids from the Zunil geothermal area are presented in Tables 3 and 4 and analytical results from INDE are reported in addition for comparison.

### 3.3 Analytical results

The analytical results are presented in Tables 3 and 4. Table 3 shows the results from the INDE laboratory for the water samples from the Zunil geothermal area. The springs were selected according to a previous classification of Zunil geothermal waters (Figure 5) as sodium chloride, sodium bicarbonate, sulfate and surface waters (Giggenbach et al., 1988).

TABLE 4: Chemical composition of discharges from wells and springs in the Zunil geothermal field (ppm)

Sample	pH lab	T (°C)	Na	K	Ca	Mg	Li	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	CO <sub>2</sub>	SiO <sub>2</sub>	TDS	B
<b>Wells</b>														
Z3 a	8.1		933	231	15	0.01	8.70	1810	31	51	36.78	951		40.0
Z6 a	8.4		1028	212	11	0.04	8.10	1700	61	157	113.24	889		45
Z11a	7.8		1092	101	30	0.07	6.31	1740	105	41	29.57	580		50.8
<b>Cl</b>														
C1 c	9.0		545	51.1	7	0.3	2.70	728	404	96	69.24	404		26.2
C1 c*	9.15	92	946	92.0	8.75	0.25	2.83	694.8	202.1	3.67	2.64	820	1910	26.0
<b>HCO<sub>3</sub></b>														
B1 a	9.2		79	7.4	22	11.6	0.13	31	64	79	56.98	160		0.7
B1 c*	7.57	35	64.5	9.5	40.5	11.0	0.11	31.9	77.36	225.8	162.84	371.9	450	0.81
B2 b	7.0		65	10.0	11	5.4	0.18	57	22	140	100.98	132		1.3
B2 c*	7.93	44	63	10.5	8.75	4.0	0.17	53.17	36.61	130.6	94.18	643.5		3.05
B3 b	7.0		166	12.2	17	5.9	0.28	101	103	259	186.82	138		2.8
B3 c*	8.09	62	150.5	12	15	5.0	0.3	102.8	122.3	236	170.24	363	863	3.53
B4 a	8.4		199	18.6	25	18.1	0.37	114	129	340	245.24	161		3.4
B4 c*	8.26	60	185.5	18.5	21.25	14.25	0.38	113.4	146.2	346.6	249.98	401	782	7.85
B5 a	7.8		286	37.2	42	36.2	0.56	180	210	463	333.97	194		4.7
B5 c*	7.92	70	268	34.5	28.5	34.25	0.58	187.9	238.1	606.5	437.47	507	1198	6.68
B6 a	8.7		372	36.6	41	40.5	0.56	163	194	491	354.16	196		4.7
B6 c*	8.43	62	260	36.5	28	38.75	0.59	191.4	430.7	639.4	461.23	517.5	1175	7.37
B7 a	8.7		258	27.3	43	45.2	0.57	168	193	501	361.38	200		4.6
B7 c*	7.62	65	202.5	29	39.25	41.25	0.48	134.7	259.9	485.7	350.33	382.2	1110	5.04
B8 b	6.1		157	19	18	30.8	0.91	71	235	503	362.82	146		2.5
B8 c*	7.58	62	145.5	19.5	76.75	26.75	0.88	81.53	198.7	356.3	257.02	357.5	803	3.61
<b>SO<sub>4</sub></b>														
S3 a	2.1		89	30.9	43	14.6	0.05	7	1600	0	0	209		1.8
S3 c*	2.36	51	740	28	35.5	10.75	0.02	10.63	1284	0	0	517.5	2301	1.09
S4 a	2.0		134	32.3	72	28.3	0.07	8	2060	0	0	287		1.7
S4 c*	2.16	70	129.5	32.5	61.5	22.75	0.07	63.81	2552	0	0	326	1594	2.66
<b>Surface</b>														
R1 b	7.0		9	4.4	9	5.6	<.01	15	-	74	53.38	28		0.3
R1 c*	7.4	18	23.25	4.88	13.38	5.63	0.02	14.18	-	102.5	73.94	128.4	506	0
R2 b	7.1		8	3.3	8	3.8	<.01	15	56	69	27.41	56		<0.1
R2 c*	7.35	18	29.13	5.63	13.75	5.88	0.02	21.27	15	106.2	76.58	185.8	432	0.76

a: Giggenbach et al., 1988;  
c: INDE, 1984;

b: Giggenbach et al., 1988; INDE, 1988;  
c\*: INDE, 1991.

In Table 4 a comparison is made between the analytical results obtained by Giggenbach et al. (1988) and the ones reported by the INDE laboratory (1984; 1988; 1991) for these springs. In both cases total alkalinity is reported as HCO<sub>3</sub><sup>-</sup>, which needs to be converted to CO<sub>2</sub> for use in the WATCH computer programme. The data reported by Giggenbach et al. (1988) are referred to as a and b; with pH, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup> having been analysed by INDE (1988) in those labelled b. The data reported by INDE (1984) are referred to as c and by INDE (1991) as c\*.

The values for some of the components like pH, Na, K, Mg, Li, Cl and B are in the same range but for SiO<sub>2</sub> the concentration found in this study is three times the value reported by

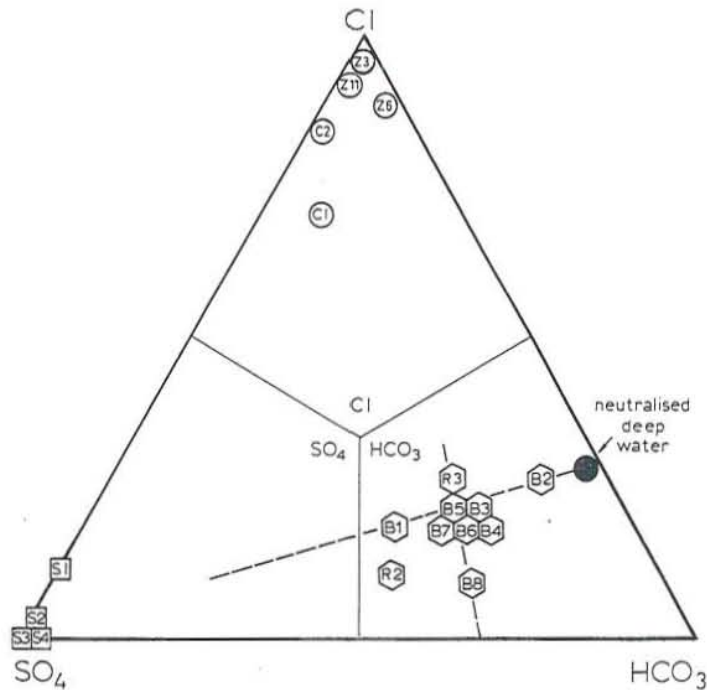


FIGURE 5: Classification of Zunil geothermal waters (Giggenbach et al., 1988)

Giggenbach et al. (1988). The value for  $\text{HCO}_3^-$  in the chloride water reported by INDE (1984) is higher (96 ppm) than the one reported by INDE (1991). The difference has been checked with recent reports (Nov. 1991, 16.96 ppm). The result remains doubtful and special care must be taken at this site during sampling and analysis to obtain reliable data.

The group of waters from the total discharge wells (Z3, Z6, Z11) are chloride waters but no recent data is available for comparison. Well Z11 is a thermal gradient well and wells Z3 and Z6 are the productive ones, named ZCQ, with an average depth of 1000 m, temperature range of 270-290°C and a production enthalpy of 1000 kJ/kg (Caicedo and Palma, 1990).

Ionic balances for the two sets of data were calculated. The results obtained by both laboratories are variable but very poor for the sulphate waters and the surface river waters probably due to contamination during sampling. Therefore the procedures and the equipment have to be checked and attempts made to improve them. The results for the ionic balance calculations and those for the solubility products of silica and calcite are shown in Table 5.

TABLE 5. Ionic balances and log solubilities for calcite and quartz from selected fluids in Zunil; \* refers to data from INDE (1991)

Sample	Ionic balance	Log Q SiO <sub>2</sub>	Log K SiO <sub>2</sub>	Log Q/K SiO <sub>2</sub>	Log Q CaCO <sub>3</sub>	Log K CaCO <sub>3</sub>	Log Q/K CaCO <sub>3</sub>
C1*	46.20	-1.972	-3.175	1.203	-10.227	-9.305	-0.922
C1	-10.84	-2.234	-3.195	0.961	-9.272	-9.096	-0.176
B1*	-1.26	-2.234	-2.261	0.027	-9.678	-11.908	2.230
B1	34.14	-2.637	-2.682	0.045	-9.043	-10.403	1.360
B2*	-17.77	-1.954	-1.954	0	-11.528	-13.779	2.251
B2	3.61	-2.669	-2.715	0.046	-9.855	-10.310	0.455
B3*	-16.18	-2.255	-2.280	0.025	-9.990	-11.812	1.822
B3	4.99	-2.652	-2.698	0.046	-9.554	-10.359	0.805
B4*	-12.62	-2.220	-2.248	0.028	-9.784	-11.975	2.191
B4	1.96	-2.619	-2.665	0.046	-8.812	-10.454	1.642
B5*	-2.19	-2.125	-2.155	0.030	-9.855	-12.478	2.623
B5	9.47	-2.531	-2.574	0.043	-8.820	-10.733	1.913
B6*	-43.18	-2.127	-2.156	0.029	-9.845	-12.469	2.624
B6	27.13	-2.557	-2.601	0.044	-8.554	-10.648	2.094
B7*	-12.93	-2.238	-2.264	0.026	-9.491	-11.891	2.400
B7	0.91	-2.546	-2.590	0.044	-8.539	-10.684	2.145
B8*	7.05	-2.256	-2.281	0.025	-9.299	-11.805	2.506
B8	10.06	-2.617	-2.662	0.045	-10.458	-10.463	0.005
S3*	50.40	-2.065	-2.065	0	-24.482	-13.021	-11.461
S3	194.72	-2.459	-2.500	0.041	-22.481	-10.984	-11.497
S4*	-121.22	-2.266	-2.290	0.024	-23.454	-11.762	-11.692
S4	-102.09	-2.321	-2.341	0.02	-24.863	-11.521	-13.342
R1*	15.13	-2.686	-2.733	0.047	-9.584	-10.261	0.677
R1	36.75	-3.334	-3.377	0.043	-13.652	-9.007	-4.645
R2*	3.08	-2.527	-2.570	0.043	-9.801	-10.747	0.946
R2	-77.19	-3.068	-3.114	0.046	-10.038	-9.410	-0.628
Wells							
Z3	-11.73	-2.330	-3.098	0.768	-7.938	-9.438	1.500
Z6	-4.40	-2.014	-2.014	0	-13.443	-13.358	-0.085
Z11	-3.59	-2.147	-2.176	0.029	-13.543	-12.356	-1.187

## 4. CHEMISTRY OF THE GEOTHERMAL WATERS

### 4.1 Water chemistry and mineral solubilities

The chemical composition of geothermal fluids is controlled by temperature-dependent reactions between minerals and fluids. High temperature geothermal systems are often connected to volcanic rock. The volcanic minerals have formed from melting at high temperature, i.e. in a "high energy" environment and are therefore "energy rich", i.e. unstable. What is observed is that the geothermal waters are undersaturated with primary igneous minerals but close to saturation (close to equilibrium) with hydrothermal minerals. The reactivity of the water-rock system is controlled by the chemical potential of the species in solution which depends on the temperature and pressure at the prevailing conditions. To evaluate the chemical equilibrium between minerals and solutions in a geothermal system the determination of the activities of aqueous species and knowledge of the solubilities of the minerals found in the altered rocks is required. Many complex reactions take place in the hydrothermal systems; the alkali carbonates, those of Na, K and Li, are relatively soluble at all temperatures and generally precipitate only in conditions of extreme evaporation. In contrast, the alkaline earth carbonates, those of Ca, Mg, Sr, and Ba, are moderately to sparingly soluble and commonly precipitate. Calcite is the most abundant and important carbonate found in hydrothermal systems, and more solubility data are available for it than for any other carbonate. Its solubility is strongly influenced by pH, the partial pressure of carbon dioxide, temperature and the presence of other dissolved salts. The solubilities of the most common silica minerals have been determined experimentally as functions of temperature at the vapor pressure of the solution. Pressure and added salt have little effect on the solubilities of quartz and amorphous silica below about 300°C. Above 300°C both pressure and added salts become very important. This independence from effects other than temperature allows the dissolved silica concentration in a hydrothermal solution to be used as a chemical geothermometer.

### 4.2 Equilibrium calculations

The complex reactions that take place in hydrothermal systems are handled by computer programmes, such as the WATCH programme. The types of geothermal fluids for which analytical data can be obtained can be divided into three groups:

1. Wet steam well discharges;
2. Boiling hot springs;
3. Waters from springs and drillholes that have not boiled.

All the chemical components that occur in major concentrations in geothermal waters and/or rocks commonly found in geothermal systems were included in the programme as well as 65 reactions describing equilibria between 73 aqueous species and 7 gases. Solubility data for 26 commonly occurring geothermal minerals are also incorporated to facilitate comparison between water chemistry and mineral solubilities with the aim of predicting particular mineral/solution equilibria. The programme can be used to calculate speciation in water and steam water mixtures which have

1. Boiled adiabatically in one stage to specified sets of temperatures;
2. Cooled without steam loss to specified sets of temperatures.

All the calculations can be carried out at any specified temperature in the interval 0-370°C. The selected parameters are



1. Reference temperature that is
  - a) measured,
  - b) chalcedony equilibrium,
  - c) quartz equilibrium,
  - d) Na-K feldspar equilibrium or
  - e) arbitrary;
2. Degassing factor used for wet-steam well discharges and boiling hot springs;
3. Discharge enthalpy (only for wet steam wells).

The computed parameters are

1. Deep water composition (water present in the geothermal reservoir);
2. Species concentrations;
3. Activity coefficients;
4. H<sup>+</sup> activity;
5. Redox potential;
6. Gas partial pressure;
7. Mineral solubilities;
8. Results of special computations of speciation of variably boiled and cooled water.

### 4.3 Geothermometers

The calculation of geothermal reservoir temperatures with the aid of chemical geothermometers using data on springs, fumaroles and shallow drillholes involves various assumptions. Chemical geothermometry when applied to specific sites can be expected to reveal the temperature of the aquifer feeding the respective spring or site. Thus, it is used to evaluate the temperature in the geothermal reservoir at depth below the cooling zone using data on the chemical composition of waters from hot springs and shallow drillholes. In the same way the composition of steam in fumaroles can be used to estimate reservoir temperatures below the zone of extensive boiling. One of the basic assumptions is that a temperature-dependent equilibrium is attained in the geothermal reservoir between specific solutes and minerals. It is further assumed that the respective solutes are not affected by chemical reactions in the upflow where the cooling occurs. Several geothermometers have been developed to predict reservoir temperatures in geothermal systems (Fournier, 1989).

The results of chemical analysis of selected springs in Zunil were used to calculate temperatures based on these geothermometers using the WATCH3 aqueous speciation programme of Arnorsson et al. (1982). The results of these computations have also been compared to those obtained using the geothermometer of Fournier and Potter (1982). The results of the geothermometry calculations for selected springs in Zunil are shown in Table 6.

### 4.4 Comparison of thermal waters from springs and wells using chloride-enthalpy diagrams

Chloride is the main anion in alkali chloride waters (Ellis and Mahon, 1977). In hot springs with high chloride content where a hot water system is indicated, the chloride concentration is not related in a simple way to subsurface temperatures and its use as a geothermometer is not common. Truesdell and Fournier (1976) have suggested a method to calculate the subsurface temperature from chloride content and enthalpies of the fluids from thermal, cold and mixed springs. The range of chloride concentrations can give information about the minimum

temperature of the reservoir that feeds the springs. When this range appears to result mainly from different extents of boiling such data is used to estimate the temperature of the reservoir. The chloride range in two chemically distinct types of hot springs in Upper Basin, Yellowstone Park in the U.S.A., plotted for the enthalpies corresponding to liquid water at the measured temperature of each spring is shown in Figure 6. The minimum temperature of the water in the reservoir feeding the hot springs can be determined by first drawing a straight line from point A, representing the spring with maximum chloride, to the point representing zero chloride and enthalpy of steam at 100°C, and then extending a vertical line from point B, representing the spring with least chloride. The intersection of that vertical line with the previous line, point C, gives the minimum enthalpy of the water in the reservoir as 936 joules, equivalent to 218°C. The silica (quartz) geothermometer applied to this water (assuming maximum steam loss) gives a calculated reservoir temperature of 216°C. The agreement between the calculated reservoir temperature using this chloride-enthalpy diagram and the quartz geothermometer is evident in this case but too high temperatures are often predicted by wrongly assuming that mixing of waters takes place.

TABLE 6: Geothermometry calculations for selected springs in Zunil

Sample	Quartz				Na/K	Chalcedony	
	1	2	3	4	5	6	7
C1*	283.2	268	266	288	199.4	----	238
C1	215.9	214	211	224	194.3	196.6	188
B1*	215.8	210	205	217	242.3	196.5	182
B1	150.2	158	152	155	194.8	127.7	130
B2*	288.1	249	246	266	250.4	----	221
B2	145.7	149	139	144	249.1	123.1	120
B3*	211.9	207	205	215	174.4	192.4	181
B3	148.1	150	143	145	168.9	125.5	122
B4*	218.5	215	212	222	197.3	199.3	187
B4	152.6	158	152	154	193.5	130.3	131
B5*	238.6	230	228	244	220.7	----	204
B5	165.5	170	162	166	228.2	143.7	141
B6*	238.3	233	231	246	223.4	----	205
B6	161.6	171	164	168	198.4	139.7	142
B7*	215.1	212	207	218	235.3	195.8	184
B7	163.3	172	164	168	206.3	141.4	143
B8*	211.6	206	204	212	229.7	192.1	180
B8	153.0	153	145	148	219.8	130.7	125
S3*	259.6	233	231	246	111.8	----	205
S3	176.7	173	168	171	336.4	176.7	146
S4*	209.8	200	196	206	301.7	190.3	173
S4	199.8	192	187	196	297.7	179.8	165
R1*	143.4	146	139	141	283.6	120.6	118
R1	72.5	80	65	85	37.1	46.5	49
R2*	166.1	168	161	163	274.3	144.4	139
R2	98.3	108	95	106	353.6	73.3	78
<u>Wells</u>							
Z3	198	283	277	303	298.0	178	249
Z6	272.4	275	272	296	279.8	----	244
Z11	233.8	241	238	255	191.6	----	

- References:
1. Fournier, 1977, WATCH programme;
  2. Fournier and Potter, 1982;
  3. Arnorsson et al., 1983;
  4. Ragnarsdottir and Walther, 1982;
  5. Arnorsson et al., 1983, WATCH programme.

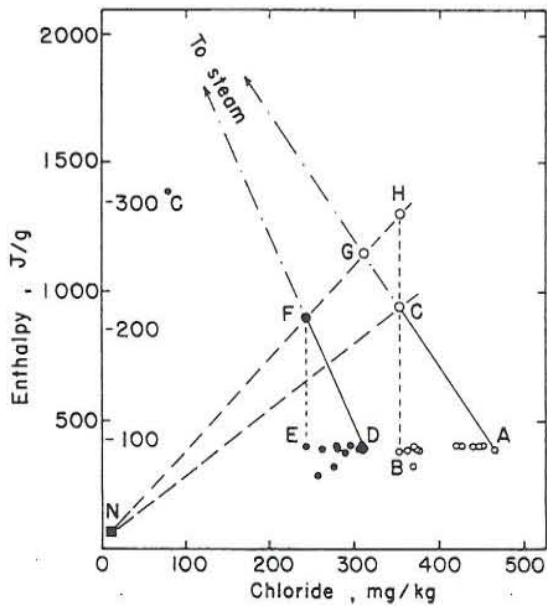


FIGURE 6: Enthalpy-chloride relationships for waters from Upper Basin Yellowstone Park; circles indicate Geyser Hill-type waters, dots Black Sand-type(Fournier,1981)

Figure 7 shows the chloride range in four chemically distinct types of springs from the Zunil geothermal field, plotted at the enthalpies corresponding to liquid water at the measured temperature of each spring. The chloride concentrations of the springs range from 15 to 695 ppm. The lowest concentration represents the coolest water in the field, which is a surface water from the Samalá River, point R. The bicarbonate waters are plotted as group B waters, the sulphate waters as S, and that with the highest chloride content as C (694.8 ppm). The chloride concentration of ZD-1 is plotted as W (1500 ppm). The assumption that water R is related to water C is valid because the changes in chloride concentration correspond to those resulting from adiabatic boiling with single-stage separation and the same assumption is made to connect RC with water W, R-C-W. The intersection of RCW with the enthalpy axis gives

1100 kJ/kg equivalent to 253°C. The enthalpy calculated in the diagram should be the same as the one calculated by the Watch programme for the well but the values are slightly different, 1100 kJ/kg from the diagram and 1291 kJ/kg computed by WATCH.

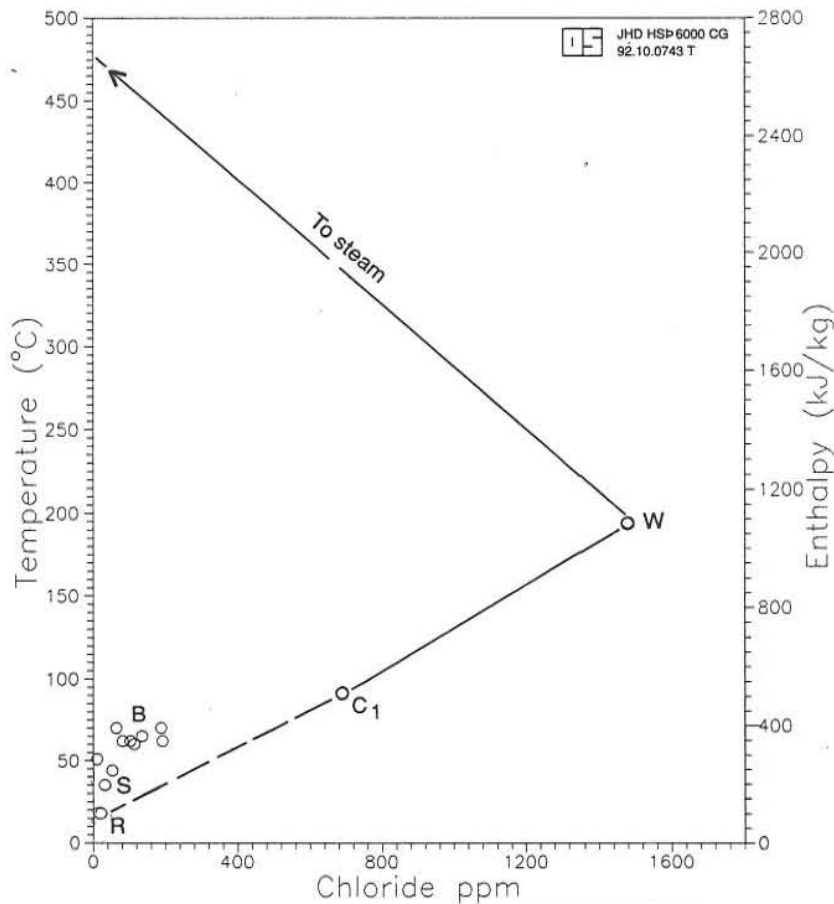


FIGURE 7: Enthalpy-chloride relationships for waters from Zunil at measured temperatures

The silica (quartz) geothermometer applied to water C gives a temperature of 283°C assuming maximum steam loss. The minimum temperature of the water in the reservoir that feeds this zone evaluated from water C is, thus, 30°C lower than that evaluated by the quartz geothermometer.

#### 4.5 Silica solubility in hydrothermal solutions

In the reservoir water silica concentrations are controlled by quartz solubility. Silica scaling can be a major problem during production and disposal of geothermal fluids. The predictions of conditions at which silica polymerization and scaling will occur are of great importance in all geothermal operations. The enthalpy-silica diagrams are very useful in predicting the effects of boiling and mixing of different waters and in calculating scaling potentials.

A temperature-silica graph is shown in Figure 8 and the calculated quartz solubilities in liquid water and steam at the vapor pressure of the solution are plotted at 10°C temperature intervals up to the critical point. Data on temperature, enthalpy and silica solubility (Fournier, 1989) in liquid and gaseous water (steam) at the vapor pressure of the solution are shown. Also shown as points above the solubility curve are data for waters from springs in the Zunil geothermal field.

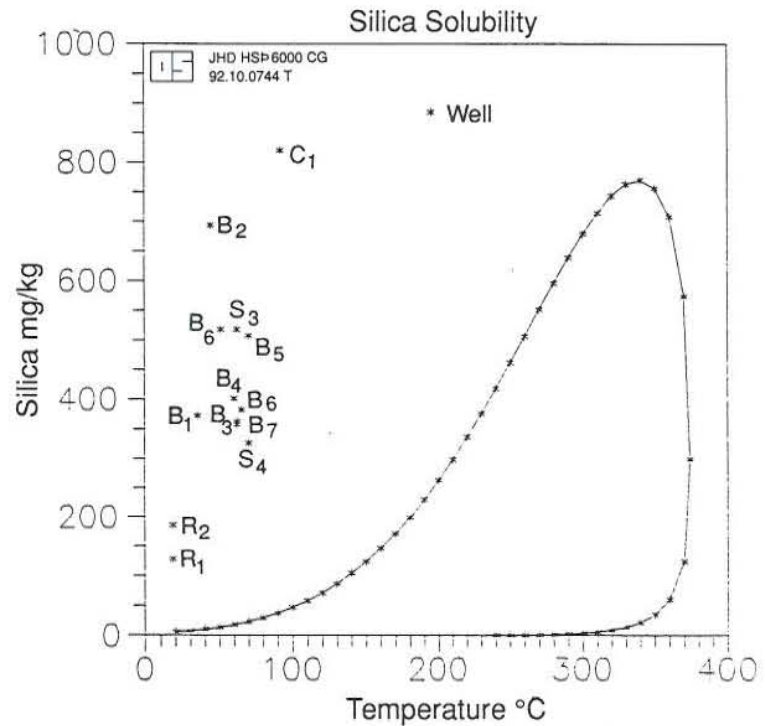


FIGURE 8: Relationships of waters from springs in the Zunil geothermal area to the quartz solubility curve

#### 4.6 The silica mixing model

Mixing models are used on geothermal waters in addition to geothermometers as an aid in the evaluation of underground temperatures. The silica mixing model proposed by Fournier (1977) may be used to determine the source temperature of the hot water component. In Figure 9 the following procedure is used: A straight line is drawn from point A through point B representing the enthalpy and the silica concentration of the mixed warm water to the solubility curve, the intersection with which gives the initial silica concentration and enthalpy of the hot water component (point C). The assumption is that no adiabatically formed steam separated from the residual liquid water before it mixed with the cold water component. If steam was lost at atmospheric pressure prior to mixing (point

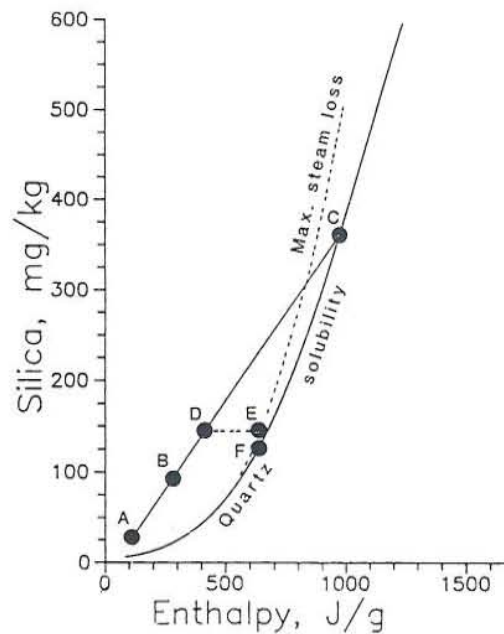


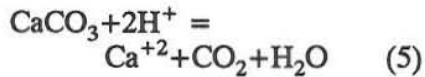
FIGURE 9: Enthalpy-silica graph illustrating calculations of silica mixing model temperatures

D) a horizontal line is drawn from point D to intersect with the maximum steam loss curve at point E which gives the initial enthalpy of the hot water component.

Data from thermal springs in the Zunil geothermal area is plotted on the enthalpy-silica graph of Fournier to calculate the silica mixing model for waters from Zunil (Figure 10). Three points of steam loss, I, II, III representing enthalpies of 950, 1100 and 1200 kJ/kg, are defined by the dashed lines intersecting the maximum steam loss lines. Underground temperatures calculated using the silica mixing model are 221.5°C for group I, 253°C for group II and 273°C for group III assuming steam loss at atmospheric pressure.

#### 4.7 Calcite solubility in hydrothermal solutions

The solubility of calcite and other calcium carbonate minerals may be expressed by the reaction:



The equilibrium constant K is

$$\frac{(\text{Ca}^{2+})}{(\text{H}^+)^2} P_{\text{CO}_2} = K_s \quad (6)$$

The solubility of calcite decreases with increasing temperature but there are various minerals that act as buffers controlling the  $(\text{Ca}^{2+})/(\text{H}^+)^2$  ratio of geothermal waters depending on the temperature and the composition of the rocks in the system. The solubility of calcium carbonate minerals in aqueous solution at any particular temperature increases with increasing partial pressure of  $\text{CO}_2$ . Boiling causes drastic decreases in  $\text{CO}_2$  partial pressures and thus leads to calcite supersaturation and deposition. The supersaturation reaches maximum soon after boiling sets in. At this maximum the liquid fraction has been almost quantitatively degassed with respect to  $\text{CO}_2$ . The degassing of  $\text{CO}_2$  leads to an increase in pH and a strong increase in the carbonate ion concentration and this causes calcite deposition. Deposition is most intense at the lowest temperatures, the highest salinity and the highest  $\text{CO}_2$  partial pressure. The calcite solubilities for springs in the Zunil geothermal field are shown in Table 5.

The chloride waters are undersaturated, the bicarbonate waters are supersaturated and the sulphate waters are undersaturated, the river waters are undersaturated and the well waters saturated with respect to calcite.

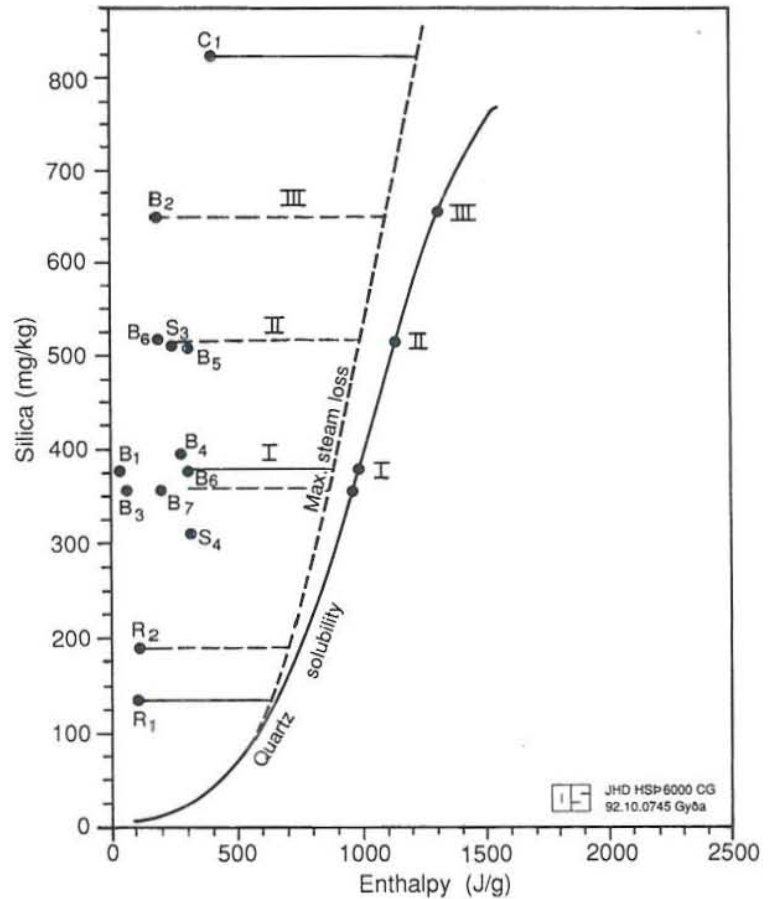


FIGURE 10: Enthalpy-silica graph for springs from the Zunil geothermal area for calculating silica mixing model temperatures

## 5. CHEMISTRY OF THE FLUID OF WELL ZD-1

The fluid was analyzed and the restored chemical composition of the fluid reported by UURI (1992a). Fluid/mineral equilibria for the fluid were calculated using the WATCH1 programme. The CO<sub>2</sub> and H<sub>2</sub>S concentrations in the total fluid are calculated from the analysed concentrations in the liquid and vapour samples collected, and the steam fraction obtained from the measured separator temperature which varied from 150 to 191°C in the different flow lines and the enthalpy is derived from the enthalpy-chloride relationships for fluids from production and thermal gradient wells in the Zunil geothermal system (1400 kJ/kg). The enthalpy-chloride relationships for fluids from production and thermal gradient wells in the Zunil geothermal system are shown in Figure 11 (UURI, 1992a).

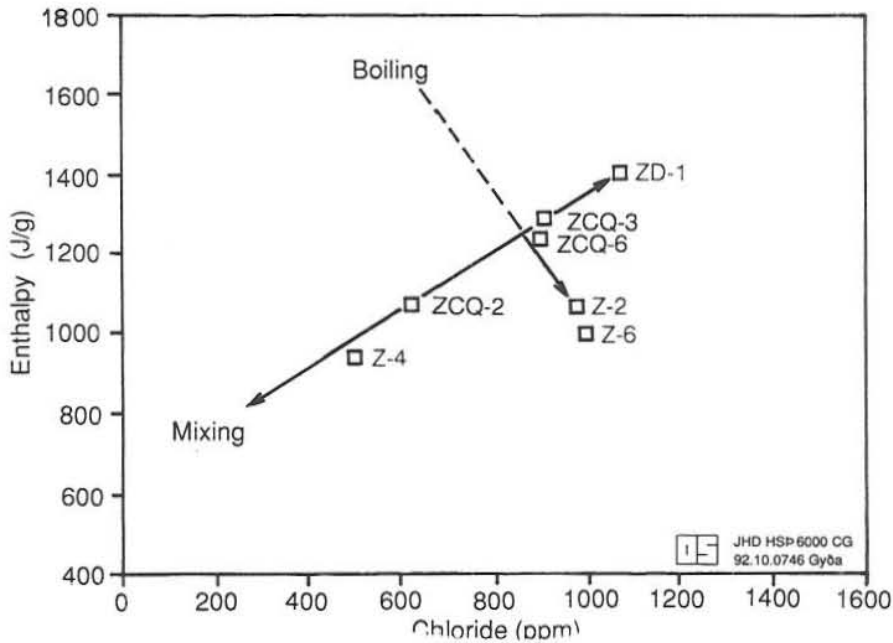


FIGURE 11: Enthalpy-chloride relationships for fluids from production and thermal gradient wells in the Zunil geothermal area

By using the relationship of steam fraction to enthalpy

$$y = (H - H_p) / L_p$$

where

- $H$  = measured enthalpy of fluid;
- $H_p$  = enthalpy corresponding to the sampling pressure;
- $L_p$  = latent heat of evaporation corresponding to the sampling pressure;

a pressure of 14.596 bar is obtained for the total flow using the tables of Schmidt (1979). The pressure actually reported for the separator is below the computed one.

The following equation describes the relationships between the concentrations of a constituent in the various sample fractions and the total sample:

$$(1-y)C_w + yC_s = C_{tot} \quad (8)$$

where

$y$	= steam fraction;
$C_w$	= concentration in water (liquid) phase;
$C_s$	= concentration in steam (vapour) phase;
$C_{tot}$	= concentration in total sample.

For a gas the following equation is derived:

$$(1-y)G_w + y\left(C_c + \frac{G\%gas}{100} \frac{GLKT}{GC} MW\right) = C_{tot}^{gas} \quad (9)$$

where

$G\%gas$	= volume % in non-condensable gas;
$GLKT$	= liters gas per kg steam;
$GC$	= liters gas per mole gas;
$MW$	= molecular mass (g gas per mole gas)
$C_{tot}^{gas}$	= concentration of gas in total sample g/kg

For all the line samples, the WATCH1 programme was used to calculate the deep water composition and speciation using analytical results for all the sample fractions obtained from the well fluid (water, gas and condensate). The enthalpy used as a reference in the calculations is calculated from the reference temperature. The ionic balance for the calculated composition in the lines is between -0.26 to 5.15%. The analytical results and the calculated deep water composition are tabulated in Table 7.

The chemical geothermometer temperatures calculated for ZD-1 are

<b>Quartz:</b>	Fournier and Potter (1982)	298°C
	Arnorsson et al. (1983)	287°C
	Ragnarsdottir and Walther (1982)	320°C
<b>Chalcedony:</b>	Arnorsson et al. (1983)	260°C

A printout of results obtained with the WATCH1 computer programme is included in the Appendix. The quartz temperature there was obtained by Arnorsson's et al. (1983) geothermometer in a slightly different way from the one employed above but the difference between the results is not significant.

Calcite is undersaturated according to the log solubility product at the quartz temperature assumed. The chemical composition after assumed boiling and cooling were calculated and the resulting calcite solubility products are shown in Figures 12 and 13.

TABLE 7: Analytical results and deep water composition for well ZD-1  
(average for the samples)

Water sample	Concentr. (ppm)	Steam sample	Gas vol. (%)	Condensate with NaOH	Concentr. (ppm)
pH/25°C	5.80	CO <sub>2</sub>	0.00	CO <sub>2</sub>	8828.08
SiO <sub>2</sub>	886.11	H <sub>2</sub> S	0.00	H <sub>2</sub> S	216.22
Na	865.28	H <sub>2</sub>	12.53		
K	218.05	O <sub>2</sub>	0.17		
Ca	4.09	CH <sub>4</sub>	5.34		
Mg	0.10	N <sub>2</sub>	81.94		
CO <sub>2</sub>	17.16				
SO <sub>4</sub>	25.83				
H <sub>2</sub> S	1.36				
Cl	1490.28				
F	4.88				
TDS	3704.17				
Al	0.00				
B	34.30				
Fe	0.00				
NH <sub>3</sub>	0.00				
As	8.04				
Sr	0.01				
Li	8.74				
<u>Deep water</u>					
SiO <sub>2</sub>	683.48				
Na	667.36				
K	168.16				
Ca	3.15				
Mg	0.07				
SO <sub>4</sub>	19.92				
Cl	1149.30				
F	3.76				
TDS	2856.88				
B	26.45				
CO <sub>2</sub>	2032.56				
H <sub>2</sub> S	50.51				
Ionic strength = 0.04349			Ionic balance: Cations (mol.eq.) = 0.04337861 Anions (mol.eq.) = 0.04286892 Difference (%) = 1.18		



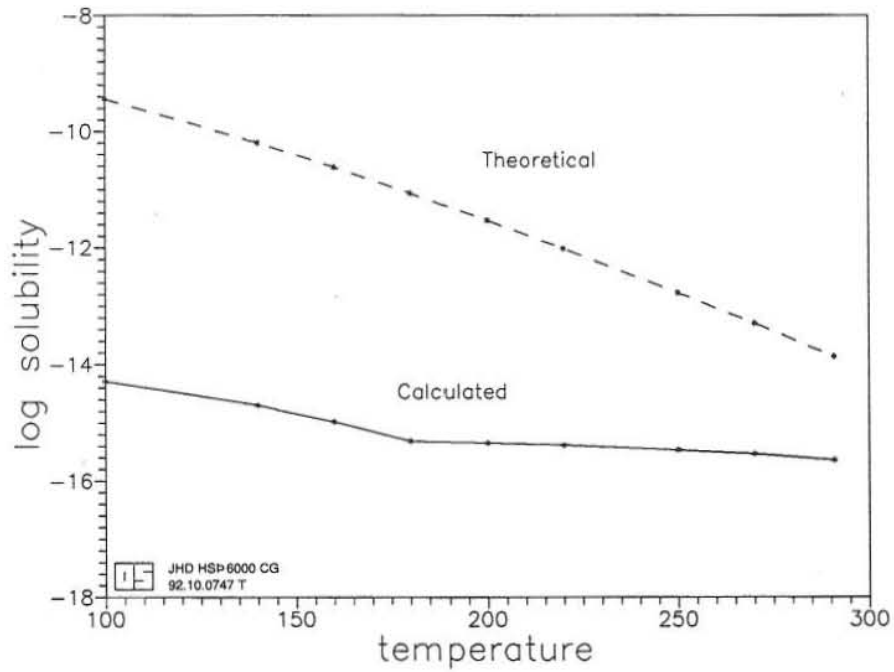


FIGURE 12: Calcite solubility, deep water cooling from well ZD-1

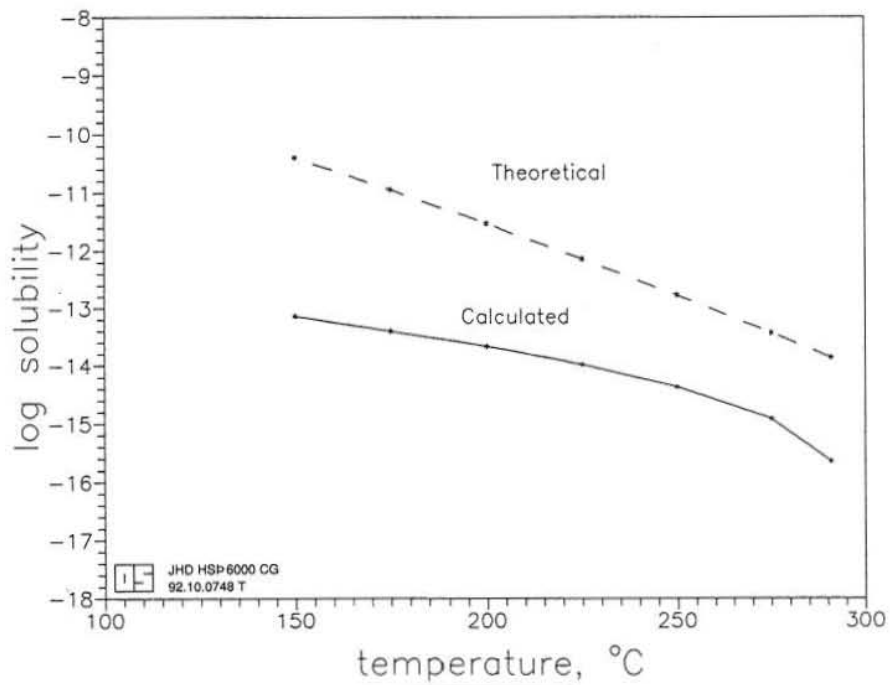


FIGURE 13: Calcite solubility, deep water boiling from well ZD-1

## 6. DISCUSSION

### 6.1 Summary of results

A reliable method for the collection of samples from thermal manifestations is of prime importance for obtaining good geochemical data. "The credibility and usefulness of a geochemical data depend on the methods used and care taken in the collection of samples." (Ellis and Mahon, 1977). From this point of view many remarks and discussions may be made regarding the methods of sampling but in the present case the sampling methods used are acceptable. The methods used for analysis are similar to the ones used at the Orkustofnun Laboratory and most of the equipment is of the same type. The analytical results presented show a large variation in the ionic balances in the laboratories (DSIR and INDE), but in the same range except for sulphate, river waters. The results of the chemical analyses of the waters are similar to those reported by DSIR (Giggenbach et al., 1988) suggesting no major changes in the chemistry of all components, except  $\text{SiO}_2$ .

The existence of three different types of water is likely to reflect three different environments of water-rock interaction and consequently three distinct degrees of attainment of water-rock equilibrium. Thermodynamics are used to approach the speciation of geothermal water using the WATCH programme. The computations assume an equilibrium situation and for each spring the deep water composition in equilibrium with quartz is calculated. Different deep water temperatures suggest local boiling during the movement of the waters. The river waters represent the coldest point in the field, the sulphate content is relatively high for samples S3 and S4 and the temperature is below boiling. The sulphate waters seem to be depleted in  $\text{CO}_2$ , probably because gaseous  $\text{CO}_2$  is formed at their low pH (see reactions in Chapter 3.2).

The chemical geothermometer temperatures calculated are in good agreement. The lowest temperature is obtained by the chalcedony geothermometer. The log solubility products of minerals in deep water calculated for calcite and quartz are shown in Table 5 and show that the scaling potential of the fluid is small.

Use of the enthalpy chloride diagram to calculate the reservoir temperature for the springs in the Zunil geothermal area gives a 10-20°C higher value than the one computed with the quartz geothermometer. A better diagram might be constructed if more data with high chloride content were available. The chloride spring represents a mixed water of groundwater of the same origin as the river water and deep geothermal water.

The silica mixing model for the same groups of spring data, clearly defines three groups of points with steam loss and different temperatures for each group. The results are in agreement with those suggested by the geothermometer temperatures, in the range, 221-273°C.

A good ionic balance is obtained from the calculations done on the basis of the analytical results for the fluid from ZD-1. This is the first flow test on this well. The well fluid is undersaturated with respect to calcite and quartz. Cooling and boiling do not cause calcite supersaturation in the range 300-100°C. Good thermodynamic data, especially on aluminum and iron, is not available and solid solutions and interlayered clay minerals have not been taken into consideration. Analytical data on these metals are not presented in this report.

## 6.2 Conclusions and recommendations

The WATCH programme was used to calculate chemical speciation on the basis of analytical results obtained in the INDE laboratory. Special care must be taken in the sampling procedure to avoid contamination of samples, especially when sampling for  $\text{SiO}_2$ .

The chloride water C1 (Z-20) is a mixed water between the deep water and groundwater of the same origin as the river waters. It is difficult to determine how much cooling occurs when the water travels but upon considering the silica solubility diagram, it is obvious that steam is lost from most of them.

To predict and describe equilibrium with other minerals, analysis for iron and aluminum is needed and the monitoring of the chemical changes in the wells needs more frequent sampling, especially in the early stages.

More data is needed for a complete geochemical interpretation, e.g. gas content, the composition of fumarole fluids and isotope ratios in the fluids of the area. Updated maps of the area showing thermal manifestations are also needed.

**ACKNOWLEDGEMENTS**

In the name of my country, Guatemala, and myself, I wish to thank the government of Iceland for the opportunity to participate for the first time in the United Nations University, Geothermal Training Programme. I am especially grateful to Dr. Ingvar B. Fridleifsson and Ludvik S. Georgsson for all their support and understanding that made this course a successful one, to Dr. Halldor Armannsson and Dr. Jon Orn Bjarnason for their guidance and advice in writing this report, to Dr. Einar Gunnlaugsson for his assistance and generosity, and further help and cooperation provided by Orkustofnun and Unidad de Desarrollo Geotérmico (INDE) staff.

## REFERENCES

- Adams, M., Mink, L., Moore, J., White, L., and Caicedo, A., 1990: Geochemistry and hydrology of the Zunil geothermal system, Guatemala. *Geothermal Resources Council Transactions*, vol. 14, 837-844.
- Arnorsson, S., Sigurdsson, S., and Svavarsson, H., 1982: The chemistry of geothermal waters in Iceland I. Calculation of aqueous speciation from 0° to 370°C. *Geochim. Cosmochim. Acta*, 46, 1513-1532.
- Arnorsson, S., Gunnlaugsson E., and Svavarsson, H., 1983: The chemistry of geothermal waters in Iceland III. Chemical geothermometry in geothermal investigations. *Geochim. Cosmochim. Acta*, 47, 567-577.
- Caicedo, A., and Palma, J., 1990: Present status of exploration and development of the geothermal resources of Guatemala. *Geothermal Resources Council Transactions*, 14-I, 97-105.
- Ellis, A.J., and Mahon, A.J., 1977: Chemistry and geothermal systems. Academic Press, N.Y., 392 pp.
- Fournier, R.O., 1977: Chemical geothermometers and mixing models for geothermal systems. *Geothermics*, 5, 299-335.
- Fournier, R.O., 1981: Application of water geochemistry to geothermal exploration and reservoir engineering. In: Rybach, L., and Muffler, L.J.P., (editors.): *Geothermal Systems. Principles and Case Histories*. John Wiley and Sons, N.Y., 109-143.
- Fournier, R.O., and Potter, R.W.II, 1982: A revised and expanded silica (quartz) geothermometer. *Geothermal Resources Council Bulletin*, 11, 3-12.
- Fournier, R.O., 1989: Lectures on geochemical interpretation of hydrothermal waters. UNU G.T.P., Iceland, report 10, 66 pp.
- Franson, M.A.H., 1980: Standard methods for examination of water and waste-water. American Public Health Association, American Waste Water Association, Water Pollution Control Federation, Washington, 15th. edition, 1134 pp.
- García, O., and Estrada, L., 1991: Well ZD-1, the first production well in granodiorite basement at the Zunil I field, Guatemala. *Proceedings of the 13th New Zealand Geothermal Workshop*, 297-301.
- Giggenbach, W., de Gudiol, D.P., and Manzo, A.R., 1988: The isotopic and chemical composition of water and gas discharges from the Zunil geothermal system, Guatemala. IAEA Coordinated Research Program on the Application of Isotopic and Chemical Techniques to Geothermal Exploration in Latin America, 46 pp.
- Giggenbach, W., and Goguel, R.K., 1989: Collection and analysis of geothermal and volcanic water and gas discharges. DSIR, chemistry report CD 2401, Petone, New Zealand, 82 pp.
- INDE, 1984: Analysis for Zunil geothermal field. Geochemical Laboratory, Unidad de Desarrollo Geotérmico, internal report.

INDE, 1988: Analysis for Zunil geothermal field. Geochemical Laboratory, Unidad de Desarrollo Geotérmico, internal report.

INDE, 1991: Analysis for Zunil geothermal field. Geochemical Laboratory, Unidad de Desarrollo Geotérmico, internal report.

James, R., 1962: Steam-water critical flow through pipes. Proc. Inst. Mech. Eng., London, 176, 741-745.

Orion, 1990: Orion ionalyzer instruction manual, pH electrodes. Orion Research Inc., U.S.A., 32 pp.

Perkin Elmer, 1990: Analytical methods for atomic absorption spectrophotometry. Norwalk, Connecticut, U.S.A.

Ragnarsdottir, K.V., and Walther, J.W., 1983: Pressure sensitive "silica geothermometer" determined from quartz solubility experiments at 250°C. Geochim. Cosmochim. Acta, 47, 941-946.

Reed, M.H., and Spycher, N., 1984: Calculation of pH and mineral equilibria in hydrothermal waters with application to geothermometry and studies of boiling and dilution. Geochim. Cosmochim. Acta, 48, 1429-1492.

Schmidt, E., 1979: Properties of water and steam in SI units. Second revised and updated printing edited by Girgull, U., Springer, Berlin, 189 pp.

Truesdell, A.H., and Fournier, R.O., 1976: Conditions in the deeper parts of the hot spring systems of the Yellowstone National Park, Wyoming. U.S. Geological Survey, open-file report 76-428, 22 pp.

UURI, 1992a: Sample records flowlines, well ZD-1. University of Utah Research Institute, report to Cordón and Mérida, 16 pp.

UURI, 1992b: Chemistry of the fluid from March 1992, flow test of well ZD-1, Zunil geothermal field, Guatemala. University of Utah Research Institute, report to Cordón and Mérida, 12 pp.

\*Weyl, R., 1980: Geology of Central America. Second completely revised edition, Gebruder Borntraeger, Berlin-Stuttgart, 371 pp.



APPENDIX: Printouts from the computer programme WATCH1

ORZUSTOFNUM

Zunil

March, 1992

wl-aver

PROGRAM WATCH1.

WATER SAMPLE (PPM)

STEAM SAMPLE

PH/DEG.C	5.80/25.0	GAS (VOL.%)		REFERENCE TEMP.	DEGREES C	.0 (QTZ)
SI02	886.11	CO2	.00			
NA	865.28	H2S	.00	SAMPLING PRESSURE	BARS ABS.	15.6
K	218.05	H2	12.53	DISCHARGE ENTHALPY	MJ/OL/EG	1.291 (CALCULATED)
CA	4.09	O2	.17	DISCHARGE	EG/SEC.	.0
MG	.100	CH4	5.34			
CO2	17.16	N2	81.94	MEASURED TEMPERATURE	DEGREES C	195.0
SO4	25.83			RESISTIVITY/TEMP.	OHM/DEG.C	.0/ .0
H2S	1.36			EH/TEMP.	MV/DEG.C	.000/ .0
CL	1490.28					
F	4.88	LITERS GAS PER KG				
DISS.SOLIDS	3704.17	CONDENSATE/DEG.C	.00/ .0	MEASURED DOWNHOLE TEMP.	DEGREES C/METERS	FLUID INFLOW
AL	.0000					DEPTH (METERS)
B	34.3000					
FE	.0000	CONDENSATE (PPM)		.0	.0	.0
NH3	.0000	PH/DEG.C	.00/ .0	.0	.0	.0
As	8.04	CO2	.00	.0	.0	.0
Sr	0.019	H2S	.00	.0	.0	.0
Li	8.74	NA	.00	.0	.0	.0
				.0	.0	.0
				.0	.0	.0
				.0	.0	.0
				.0	.0	.0
		CONDENSATE WITH NAOH (PPM)		.0	.0	.0
		CO2	8828.08	.0	.0	.0
		H2S	216.22	.0	.0	.0

IONIC STRENGTH = .04349

IONIC BALANCE : CATIONS (MOL.EQ.) .04337861  
 ANIONS (MOL.EQ.) .04286892  
 DIFFERENCE (%) 1.18

DEEP WATER (PPM)

DEEP STEAM (PPM)

GAS PRESSURES (BARS ABS.)

SI02	683.48	CO2	2032.56	CO2	.00	CO2	.393E+01
NA	667.36	H2S	50.51	H2S	.00	H2S	.382E-01
K	168.16	H2	.00	H2	.00	H2	.000E+00
CA	3.15	O2	.00	O2	.00	O2	.000E+00
MG	.077	CH4	.00	CH4	.00	CH4	.000E+00
SO4	19.92	N2	.00	N2	.00	N2	.000E+00
CL	1149.30	NH3	.00	NH3	.00	NH3	.000E+00
F	3.76					H2O	.757E+02
DISS.S.	2856.88					TOTAL	.796E+02
AL	.0000						
B	26.4518			H2O (%)	.00		
FE	.0000			BOILING PORTION	.00		



SAMPLE = March, 1992

## ACTIVITY COEFFICIENTS IN DEEP WATER

H+	.743	KSO4-	.704	FE++	.256	FECL+	.686
OH-	.679	F-	.679	FE+++	.069	AL+++	.069
H3SIO4-	.686	CL-	.671	FEOH+	.699	ALOH++	.246
H2SIO4--	.246	NA+	.686	FE(OH)3-	.699	AL(OH)2+	.704
H2BO3-	.663	K+	.671	FE(OH)4--	.239	AL(OH)4-	.693
HCO3-	.686	CA++	.256	FEOH++	.239	ALSO4+	.693
CO3--	.230	MG++	.289	FE(OH)2+	.704	AL(SO4)2-	.693
HS-	.679	CAHCO3+	.712	FE(OH)4-	.704	ALF++	.246
S--	.239	MGHCO3+	.686	FESO4+	.699	ALF2+	.704
HSO4-	.693	CAOH+	.712	FECL++	.239	ALF4-	.693
SO4--	.221	MGOH+	.717	FECL2+	.699	ALF5--	.230
NASO4-	.704	NH4+	.663	FECL4-	.686	ALF6---	.037

## CHEMICAL COMPONENTS IN DEEP WATER (PPM AND LOG MOLE)

H+ (ACT.)	.01	-5.128	MG++	.07	-5.540	FE(OH)3	.00	.000
OH-	.03	-5.725	NACL	133.65	-2.641	FE(OH)4-	.00	.000
H4SIO4	1093.19	-1.944	KCL	12.56	-3.773	FECL+	.00	.000
H3SIO4-	.08	-6.061	NASO4-	2.05	-4.764	FECL2	.00	.000
H2SIO4--	.00	-12.287	ESO4-	4.24	-4.504	FECL++	.00	.000
NAH3SIO4	.03	-6.620	CASO4	.50	-5.435	FECL2+	.00	.000
H3BO3	151.28	-2.611	MGSO4	.03	-6.673	FECL3	.00	.000
H2BO3-	.02	-6.516	CACCO3	.00	-8.571	FECL4-	.00	.000
H2CO3	2860.54	-1.336	MCCO3	.00	-11.447	FESO4	.00	.000
HCO3-	3.92	-4.192	CAHCO3+	.44	-5.360	FESO4+	.00	.000
CO3--	.00	-10.263	MGHCO3+	.00	-7.979	AL+++	.00	.000
H2S	50.39	-2.830	CAOH+	.00	-7.632	ALOH++	.00	.000
HS-	.12	-5.453	MGOH+	.00	-7.173	AL(OH)2+	.00	.000
S--	.00	-14.609	NH4OH	.00	.000	AL(OH)3	.00	.000
H2SO4	.00	-9.742	NH4+	.00	.000	AL(OH)4-	.00	.000
HSO4-	10.11	-3.983	FE++	.00	.000	ALSO4+	.00	.000
SO4--	4.88	-4.294	FE+++	.00	.000	AL(SO4)2-	.00	.000
HF	3.12	-3.807	FEOH+	.00	.000	ALF++	.00	.000
F-	.80	-4.375	FE(OH)2	.00	.000	ALF2+	.00	.000
CL-	1062.25	-1.523	FE(OH)3-	.00	.000	ALF3	.00	.000
NA+	614.38	-1.573	FE(OH)4--	.00	.000	ALF4-	.00	.000
E+	160.35	-2.387	FE(OH)++	.00	.000	ALF5--	.00	.000
CA++	2.83	-4.151	FE(OH)2+	.00	.000	ALF6---	.00	.000

IONIC STRENGTH = .03070    IONIC BALANCE :    CATIONS (MOL.EQ.) .03097622  
 ANIONS (MOL.EQ.) .03017942  
 DIFFERENCE (%) 2.61

CHEMICAL GEOTHERMOMETERS DEGREES C

1000/T DEGREES KELVIN = 1.77

QUARTZ 290.8  
 CHALCEDONY 999.9  
 NAE 304.7

OXIDATION POTENTIAL (VOLTS) :    EH H2S= - .428    EH CH4= 99.999    EH H2= 99.999    EH NH3= 99.999

## LOG SOLUBILITY PRODUCTS OF MINERALS IN DEEP WATER

	TEOR.	CALC.		TEOR.	CALC.		TEOR.	CALC.
ADULARIA	-14.401	99.999	ALBITE LOW	-13.982	99.999	ANALCINE	-11.670	99.999
ANHYDRITE	-8.879	-9.691	CALCITE	-13.862	-15.643	CHALCEDONY	-1.841	-1.944
MG-CHLORITE	-88.515	99.999	FLUORITE	-11.193	-13.828	GORRHITE	4.637	99.999
LAUMONTITE	-25.010	99.999	MICROCLINE	-14.974	99.999	MAGNETITE	-12.842	99.999
CA-MONTMOR.	-72.544	99.999	K-MONTMOR.	-33.725	99.999	MG-MONTMOR.	-74.048	99.999
NA-MONTMOR.	-34.008	99.999	MUSCOVITE	-17.847	99.999	PREHNITE	-38.912	99.999
PYRRHOTITE	2.661	99.999	PYRITE	-11.538	99.999	QUARTZ	-1.943	-1.944
WAIRAKITE	-25.472	99.999	WOLLASTONITE	6.828	3.570	ZOISITE	-40.031	99.999
EPIDOTE	-40.436	99.999	MARCASITE	3.982	99.999			