PUBLIC POWER CORPORATION

ATHENS, GREECE

MILOS GEOTHERMAL DEVELOPMENT

MILOS M-2

Production Test - December 1984

Consultants' Report





MILOS GEOTHERMAL DEVELOPMENT MILOS M-2 Production Test - December 1984 Consultants' Report

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1 INTRODUCTION

1. INTRODUCTION

A contract between the Public Power Corporation (PPC) and Virkir Consulting Group Ltd. and the National Energy Authority (Virkir/NEA) regarding the Milos geothermal development (especially brine studies, brine treatment and reinjection) was signed on November 14 1984. The Consultants' work however started earlier upon reciept of the Clients' tester dated ...

A short report was presented on November 11, containing comments and recommendations on MHI/GEOSPAC document 9700-2737A, followed by telexes on more specific points. This report and the telexes are presented in Appendix 1.

Mr. S. Thorhallsson and Dr. H. Ármannsson witnessed the production test during December 1984. Their interim field reports constitute appendices 2 and 3, but their memos and observations are more fully presented in the main text of this report.

The results presented in the following chapters are based on data obtained from the production test and results of the Consultants` own studies and analysis, since the Contractors` report (Mitsubishi/Geospac) has not yet been received.

The main findings and recommendations are incorporated in chapter 2. All results obtained so far are described in chapters 5-9.

2 MAIN FINDINGS AND RECOMMENDATIONS

2. MAIN FINDINGS AND RECOMMENDATIONS

2.1 Logging data

Findings. The most important finding is that the maximum temperature in well M-2 when not flowing is 318°C, at 1150-1200 m depth. There is a small inversion below this depth supporting previous interpretation that the main inflow is at 1150-1200 m and that incomplete heating up has taken place in the bottom part of the well since the last flow test of September 1984. Inspection of temperature logs made during previous production tests suggest boiling to the well bottom during flow since then the maximum temperature was 214°C.

The maximum temperature in the non-flowing well (318 $^{\circ}$ C) deviates greatly from previous published data of about 280 $^{\circ}$ C.

Recommendations. All previous data on temperature and pressure in well M-2 and other Milos wells should be carefully inspected and reinterpreted with these findings in mind.

2.2 Flow parameters

<u>Findings.</u> As had been anticipated the production test was much too short to obtain meaningful data on the long term flow characteristics of the well. However, some important conclusions can be drawn from this test. The enthalpy fluctuated from day to day (from 1500 to above 1700 kJ/kg), but it increased in the whole. During long term production the enthalpy is expected to become still higher.

<u>Recommendations.</u> The enthalpy of the well fluid after initial stabilization can only be obtained from a test lasting at least about 6 months. It is recommended to define the flowing parameters accurately as the chemical properties of the fluid depend on them.

2.3 Chemistry

Findings. It was established that the silica concentration in the brine at 8 bar a (the proposed production pressure) and discharge enthalpy of $1600~\rm kJ/kg$ (which may become higher) was about $900~\rm mg/kg$, which is not unexpected considering the high temperature of inflow. At $318\,^\circ\text{C}$ the solubility of quartz is $762~\rm ppm$ giving a concentration of $1184~\rm ppm$ after flashing to 8 bars. The value of $900~\rm ppm$ is much higher than the $400~\rm ppm$ quoted in the PPC-Mitsubishi contract. Bench scale studies on

silica deposition indicate that it occurs very rapidly and already in the 8 bar abs. line.

Recommendations.

- a) More information needs to be obtained on scaling and deposition rates under different conditions. From the information obtained so far it appears that the only acceptable solution to the problem of brine disposal would involve silica removal from solution followed by reinjection.
- b) In tests on Icelandic brines, however, it was observed that no precipitaion of silica occurred at pH=3. If this is the case for the Milos fluid, acidification is a possibility to inhibit silica deposition. The titration curve for the brine shows that relatively little hydrochloric acid needs to be added to bring its pH to 3, and this would not be costly.
- c) The fact that deposition is already occurring in the 8 bar abs. line shows that the wellhead pressure and steam separator pressure during production needs be considerably higher to avoid deposition.
- d) The fluid reaches saturation with respect to amorphous silica at about 20 bar abs. and it is recommended if possible to keep production wellhead pressure above this. Pressure rating of production equipment to be supplied by MHI should exceed this figure.

It is recommended that PPC show great caution in accepting other methods than the above for the problem of brine treatment, especially regarding unproven technology such as a magnet hydraulic system, which in any case would only prevent scaling, and the brine will still have to be injected as a suspension containing a large amount of silica particles.

2.4 Injectivity test

<u>Findings.</u> The injectivity test was not started as scheduled, as it was demonstrated by the Consultants that the use of sea water for the test involved a danger of clogging the reinjection well M-l, by anhydrite precipitate.

Recommendations. Until further brine treatment tests have been made no other fluid than fresh water should be injected.

2.5 Tracer test during reinjection.

<u>Findings</u>. The literature on similar tests show that positive indications of connection between wells which are spaced as far appart as M-1 and M-2 (1200 m) are very rarely found by adding tracers. The tracer

suggested (131 I) would cease to be detected after about 3 weeks and no examples could be found in the literature where a connection between wells spaced further appart than 500 m, was clearly established by this method.

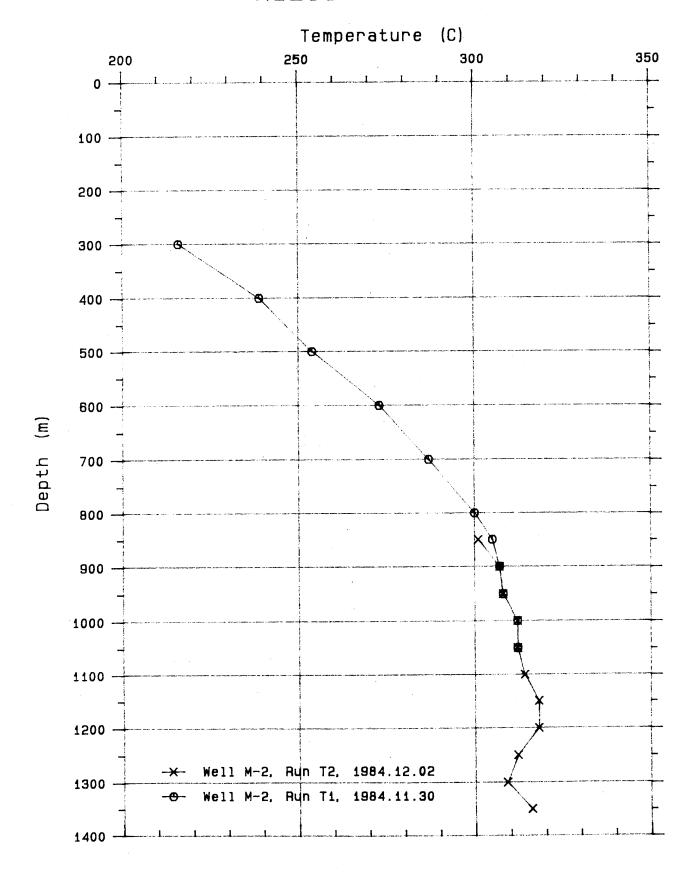
Reccommendations. The choice of tracer should be reconsidered, and tracers which are easier to handle and have a longer lifetime should be considered.

3 TEMPERATURE AND PRESSURE LOGS

JHD-VT-9000. SP 85.02. 0288. T

Fig. 1

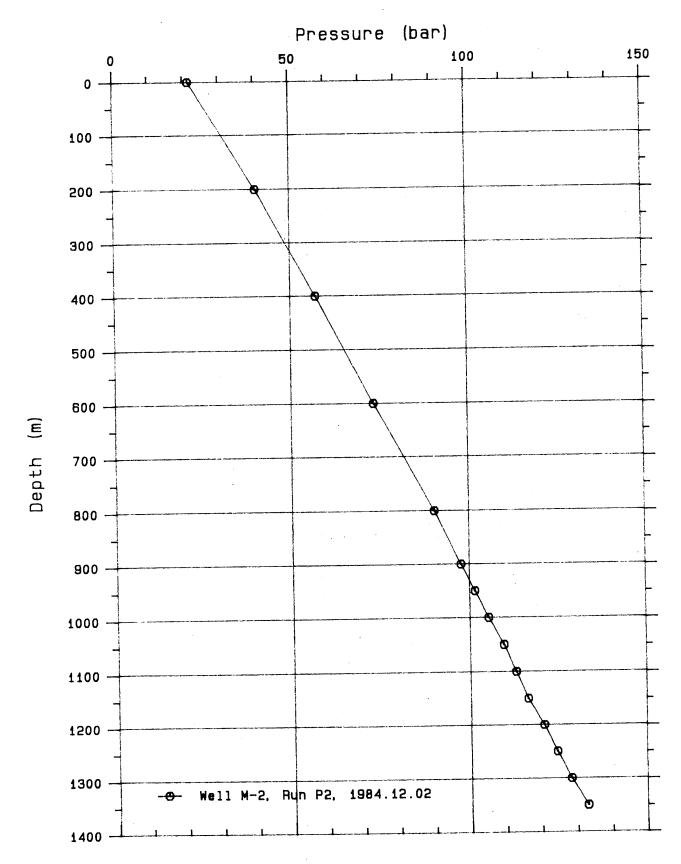
MILOS WELL M-2



JHD-VT-9000.Sp 85.02. 0289. T

Fig. 2

MILOS WELL M-2



4 RESULTS OF FLOW TESTS

4. RESULTS OF FLOW TESTS

Calculated output and enthalpy values using the reported data are listed in Table 11. Calculations are based on the Russel-James formula and the density and enthalpy of the liquid are assumed to be the same as for the pure water phase at 100°C . No correction was thus made for salinity.

The change in pressure, output and enthalpy, over the test period of 12 days are shown in Fig. 3. The enthalpy increases gradually from about $1500~\rm kJ/kg$ on the first day to about $1700~\rm kJ/kg$ on the last day. This is an indication of boiling in the reservoir and phase separation in the aquifer and/or enhanced boiling by heat transfer from the rock.

Total massflow decreased from about 12 kg/s to 10 kg/s over the test period mainly as a result of decreasing liquid flow. The steam output was almost constant during the period. Average steam production is close to 6 kg/s fluctuating between 5.1 and 6.9 kg/s over the test period. By adjusting the throttle valve it was attempted to hold the critical pressure at constant level. Pressure (WHP) declined from 57 barg to 47 barg which is the result of increasing pressure drop in the reservoir as a result of adjustments of throttle valve and flashing farther from the well.

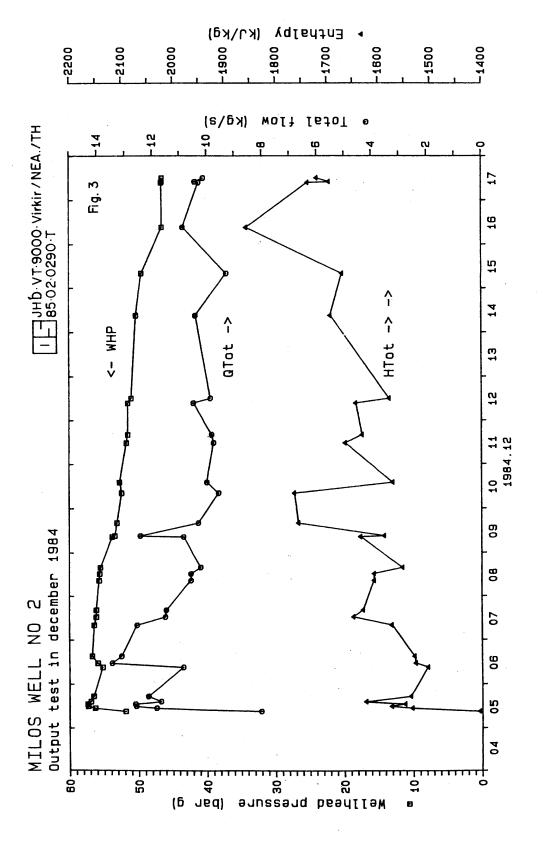
From this test it is inferred that liquid flow will continue to decrease under prolonged production but steam flow will probably change less and the well can be expected to produce about 5-6 kg/s of steam for some time. It is possible that the liquid flow will eventually decrease to zero and the well produce dry steam only but whether and when this happens cannot be predicted from the present short term test.

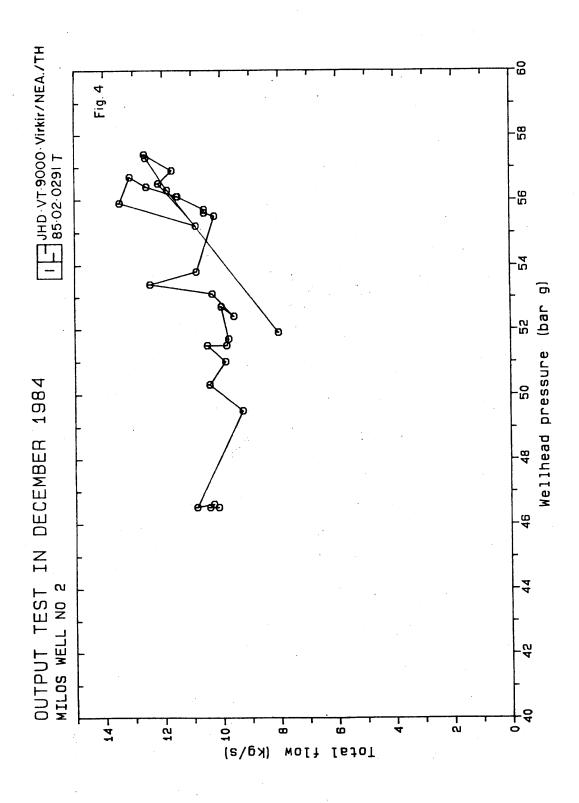
Different behavior was observed during the flow test in September 1983. Then the enthalpy reached a stable value of about $1600~\rm kJ/kg$ in 21 days and the WHP rose from 20 barg to 50 barg. Total output on the other hand decreased from approx. 12 kg/s to 10 kg/s as in the December 1984 test.

The production curve (total flow versus wellhead pressure) (Fig. 4) is flat which is characteristic for wells withdrawing fluid from two phase reservoir. The flow from such wells is controlled by a restriction in the reservoir and a change in wellhead pressure does not significantly affect the flow over a certain WHP range.

TABLE 1 MILOS M-2. Results of production test.

Date	Time	WH- press. (barg)	Total flow (kg/s)	En- thalpy (kJ/kg)	Steam at O barg (kg/s)	Liq. at O barg (kg/s)	Remarks
84.12.05	09:00	51.90	8.0	1405	3 . 5	4.5	Opened 84.12.04 13:0
84.12.05	10:45	56.30	11.8	1535	5 . 9	6.0	+ 25-30 turns 09:00
84.12.05	11:50	57 . 30	12.6	1575	6.4	6.1	+ 25-50 turns 05:00
84.12.05	13:00	57 . 40	12.6	1549	6.3	6.3	
84.12.05	14:20	56.90	11.7		6.2	5.4	
84.12.05	17:12	56.50	12.1	1538	6.0	6.1	
84.12.06	09:00	55.20	10.9	1504	5.2	5.6	
84.12.06	11:15	55.90	13.5	1528	6.6	6.8	
84.12.06	15:00 4	56.70	13.1	1531	6.5	6.7	+ 1.5 turn at 10:55
84.12.07	08:00	56.40	12.6	1575	6.4	6.1	Bore cycling
84.12.07	12:30	56.10	11.5	1649	6.3	5.2	Cycle period 3-5 min
84.12.07	16:18	56.10	11.5	1630	6.2	5.3	Cycling
84.12.08	08:30	55.70	10.6	1609	5.6	5.0	Appears stable
84.12.08	12:15	55.60	10.6	1609	5.6	5.0	
84.12.08	15:46	55.50	10.2	1553	5.1	5.1	
84.12.09	08:30	53.80	10.8	1635	5.8	5.0	+ 1/4 turn .08 16:50
84.12.09	09:00	53.40	12.4	1589	6.4	6.0	+ 1/4 turn 08:44
84.12.09	16:00	53.10	10.3	1755	6.1	4.2	
84.12.10	08:15	52.40	9.6	1763	5.7	3.9	
84.12.10	14:05	52.70	10.0	1572	5.1	4.9	
84.12.11	11:30	51.70	9.7	1664	5.4	4.4	+ 1/4 turn .10 15:26
84.12.11	16:00	51.50	9.8	1631	5.3	4.5	
84.12.12	09:23	51.50	10.5	1643	5.7	4.8	+ 1 turn .11 16:30
84.12.12	12:00	51.00	9.9	1578	5.1	4.8	
84.12.14	09:00	50.30	10.4	1693	5.9	4.5	Thr. opened 84.12.13
84.12.15	08:00	49.50	9.3	1670	5.1	4.1	•
84.12.16	09:15	46.50	10.9	1857	6.9	3.9	+ 2-3 turns .15 09:0
84.12.17	09:30	46.60	10.3	1737	6.0	4.3	
84.12.17	10:00	46.50	10.4	1695	5.9	4.5	
84.12.17	12:00	46.50	10.1	1719	5.8	4.3	Closed at 13:30





5 BRINE TREATMENT

5. BRINE TREATMENT. BENCH SCALE STUDIES PERFORMED DURING M-2 PRODUCTION TEST, DECEMBER 1984.

5.1 Introduction

During the production test of well M-2, Milos, in December 1984, the following bench scale tests regarding brine treatment were performed by Virkir/NEA:

- a) Titration curve for 50 ml 0,1 N NaOH and 0,1 N HCl.
- b) Monomer decrease of silica in brine at different temperatures and pH.
- c) Rate of colloid settling.
- d) Rate of precipitation as determined by filtration at different times.
- e) Scaling rate in the 8 bar abs. line by coupon test.
- f) Characterization of scales, deposits and precipitates by X-ray diffraction, X-ray fluorescence and electron microprobe analysis.

The results of these tests are reported here.

5.2 Titration curve.

The results are presented in Table 2. and Fig. 5. Buffering effect of silica is apparent at pH $^{\circ}10$, but the effect of bicarbonate appears negligible due to its low concentrations. It can be seen that about 6 mequiv/l NaOH are needed to raise the pH to 8 and about 2 meq/l HCl to lower it to 2.

5.3 Monomer decrease.

Brine samples were collected at the silencer outlet, and cooled by passage through a coil inserted in a bucket containing cooling water at The titration curve (Fig. 5) was used to detervarying temperatures. mine the amount of sodium hydroxide needed to adjust the pH (5 ml $1,2\,$ N NaOH per liter give pH=8). The Hach colorimeter kit owned by PPC was used for determination of silica and for some pH determinations In the first experiments the silica determination involved the use of preweighed vials containing sodium molybdate, acid mixture and citric acid. In later tests ammonium molybdate (10%), hydrochloric acid (5N) and oxalic acid (0,1N) were substituted as the vials were used up. good comparison was obtained between the two methods. The samples were diluted 50 times before analysis. The results of the tests are given in Tables 3 - 5 and in Fig. 6.

As is to be expected at such high salinity the rate of monomer decrease is relatively fast, and even at the initial pH (5,2) the solubility value for amorphous silica (AS) has been reached after 1 day. The effect of temperature is apparently negligible in the range tested, but the rate becomes much faster if the pH is raised to approximately 8, and then values close to the AS saturation are obtained after 20-30 minutes.

5.4 Settling rate.

An untreated sample was added to a 500 ml glass measuring cylinder. The sample became cloudy, but no apparent settling was observed. A very obvious flocculate was observed in a sample whose pH had previously been raised to approximately eight. The observed rate of settling in the cylinder is shown in Fig. 7. and is seen to be very fast under these conditions. In fact the bulk of the flocculate has settled in 5 minutes.

5.5 Rate of precipitate formation.

Four hundred ml of brine sample from the silencer outlet were filtered through a preweighed filter paper (Whatman No. 41) immediately after sampling. The filtrate was left overnight and the precipitate now formed filtered off in the same way. The filter papers and precipitates were dried at 105°C and weighed. A portion of each precipitate (about 0,25 g) was subjected to X-ray diffraction analysis, but the rest was washed with 0,5 - 1 l distilled water, dried at 105°C , reweighed and subjected to X-ray diffraction analysis again.

The results of the X-ray diffraction analysis are described in 5.7, but the results of the weighings are presented in Table 6. These reveal, although there is considerable monomer decrease on the first day (Chapter 3) at pH 5-6 that there is no significant precipitation of silica, whereas on the next day most of the silica has precipitated in these conditions.

5.6 Scaling rate test with coupon

A scaling coupon was inserted in the 8 bar abs. pipeline on 1984-12-05 and removed on 1984-12-12. Measurement of the scale thickness showed 0,75 mm at the wall end, but 2 mm in the main flow where the turbulence is greater. The average scaling rate is probably about 1,5 mm which suggests 80-100 mm of scale formation per year which is very high.

5.7 XRD examination of scales and deposits

Prior to the flow test two samples were collected, one of scale from the pipeline just behind the throttle, and a sample of deposit from the silencer. A sample was also obtained from the pipe which had been used for pumping brine from the receiving pond to the sea in previous flow tests after a mean settling time of about 5 days. These samples, along with the precipitates obtained in the precipitate formation test (5.5) and the deposits from the coupon (5.6) were subjected to X-ray diffraction analysis. All the results are shown in Table 7. The deposit from the coupon was furthermore subjected to electron microprobe analysis by Dr. K. Grönvold of the Nordic Volcanological Institute in Iceland. His assistance is duly appreciated.

The silencer sample was subjected to X-ray fluorescence analysis, but due to the unusual matrix, reference standards were not available for accurate quantitative estimates. However it can be stated that silica and calcium are the major constituents, and that fair quantities of chlorine, potassium and iron are present along with traces of zinc. Thus silica deposition is observed, calcium apparently precipitated, but the lack of crystallisation probably suggests a calcium silicate rather than calcite, aragonite or anhydrite. Apart from that some metal precipitates, possibly sulphides (Fe, Cu, As, Zn) are inferred.

The electron microprobe analysis reveal that the scale on the coupon consists mainly of silica with a small iron component. In summary the deposits consist mainly of amorphous silica as was to be expected.

TABLE 2. Milos M-2. Water from silencer outlet. Results of acid and base titrations at t = 18° C.

0.1N NaOH		0.1N HC1	
ml titrated	рН	ml titrated	рН
0,00	5,18	0,00	5,18
0,05	5 , 48	0,09	4,52
0,10	5 ,7 0	0,12	4,00
0,15	5,82	0,19	3,62
0,21	5 , 93	0,28	3,40
0,24	6,01	0,31	3,28
0,26	6,08	0,35	3,21
0,30	6,12	0,40	3,12
0,34	6,20	0,45	3 , 05
0,42	6,30	0,51	2,99
0,44	6,31	0,57	2,92
0,50	6,33	0,92	2,65
0,54	6,38	1,25	2,48
0 , 59	6,40	1,93	2,27
0,60	6,40	3 , 00	2,05
0,64	6,41	4,00	1,91
0,71	6,45	4,97	1,82
0,79	6,52	6,01	1,73
0,86	6,55	7 , 01 .	1,66
1,00	6,61	8,10	1,60
1,14	6,68	8,99	1,56
1,25	6 , 73	9,97	1,51
1,42	6,83	15,10	1,39
1,57	6,91	20,00	1,30
1,76	7,01	25,00	1,21
1,92	7,08	29,97	1,15
2,05	7,12	35,02	1,11
2,15	7,19	40,00	1,09
2,25	7,20	45,10	1,06
2,46	7,22	50,01	1,02
2,56	7,30		
2,71	7,34		
3,04	7,44		
3,18	7,51		
3,41	7,58		
3,65	7,63		
4,04	7 , 70		
4,22	7,76		
4,42	7,80		

TABLE 2 continued

O.lN NaOH		
ml titrated	рН	
4,66	7,83	
•	· .	
5,06	7,92	
5,56	8,01	
5,81	8,04	
6,04	8,10	
6,74	8,20	
7,36	8,29	
8,17	8,38	
8,86	8,48	
9,14	8,50	
10,04	8,62	
11,02	8,73	
12,07	8,84	
13,04	8,99	
14,04	9,10	
14,77	9,22	
19,86	10,20	
24,84	11,09	
29,86	11,40	
34,94	11,58	
39 , 86	11,70	
44,98	11,80	
49,86	11,85	
77,00	11,00	

TABLE 3 Milos M-2. Water from silencer outlet. Molybdate reactive SiO2 at 19°C pH 5-6.

Time of analysis Min after sampling	Molybdate reaction SiO2 mg/kg	Amorphous silica Saturation value in pure water mg/kg	Notes
0	700		Average value
26	650		from W.A.J. Mahon
36	575		
49	500		
58	490		•
68	450		
78	400		
90	375		
99	350		
109	375	•	
121	365	•	
196	220		
1443	110		
2971	106	106	AS saturation at 2 (Weres et al. 1980

TABLE 4 Milos M-2. Water from silencer outlet.

Molybdate reactive SiO2 at 56 +- 3°C pH 5-6.

Time of analysis			Molybdate	Amorphous silica satura	ation
Min after colletion	Flask No.	Temperature °C	reactive SiO2 mg/kg	value in puro water mg/ko	
0		60,7	700		SiO2 Average
17	1	62,3			Value from
17	2	58 , 3			W.A.J. Mahon
17	3	58,3	675		
33	3	57 , 9	575		
48	3	57 , 7	500		
62	3	57 , 2	430		
75	3	56 , 9	425		
90	3	56,5	385		
103	3	55 , 9	375		
119	3	55,3	330		
135	3	54,3	310		
148	1	56,4	250		
163	3	53,4	27 5		
195	1	55,8	230		S saturation at 60°C Weres et al. 1980)
1520	2	37,3	165		S saturation at 40°C Weres et al. 1980)

TABLE 5 Milos M-2. Water from silencer outlet. Molybdate reactive SiO2 at 47 +-5 $^{\circ}$ pH 8

Time of analysis	•		Molybdate	Amorphou silica satur	
Min after colletion	Flask No.	Temperature °C	reactive SiO2 mg/kg	value in pur water mg/kg	
0		- 4 widefal	700		Average value
20	1	51,7	175		from W.A.J. Mahon
20	2	48,8			
34	1	48,5	165		
52	1	46,3	160		
75	1	41,8	150	153	AS saturation at 40° (Weres et al. 1980)

TABLE 6 Milos M-2. Water from silencer outlet. Rate of precipitate formation.

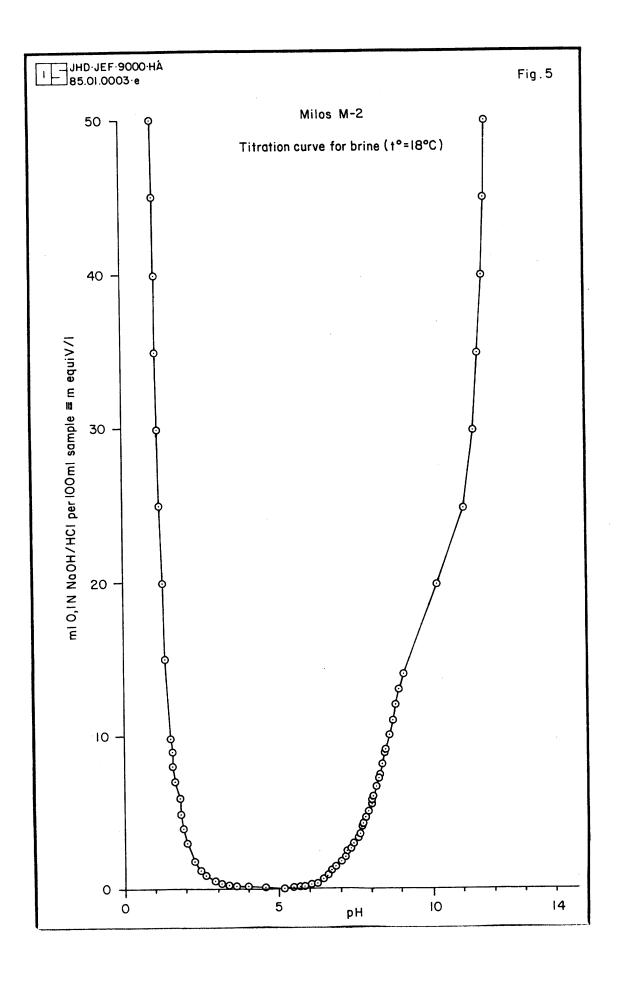
Filtration time Days after collection	Total precipitate mg/l	Washed precipitate mg/l		
0	1875	0		
1	4050	1094		

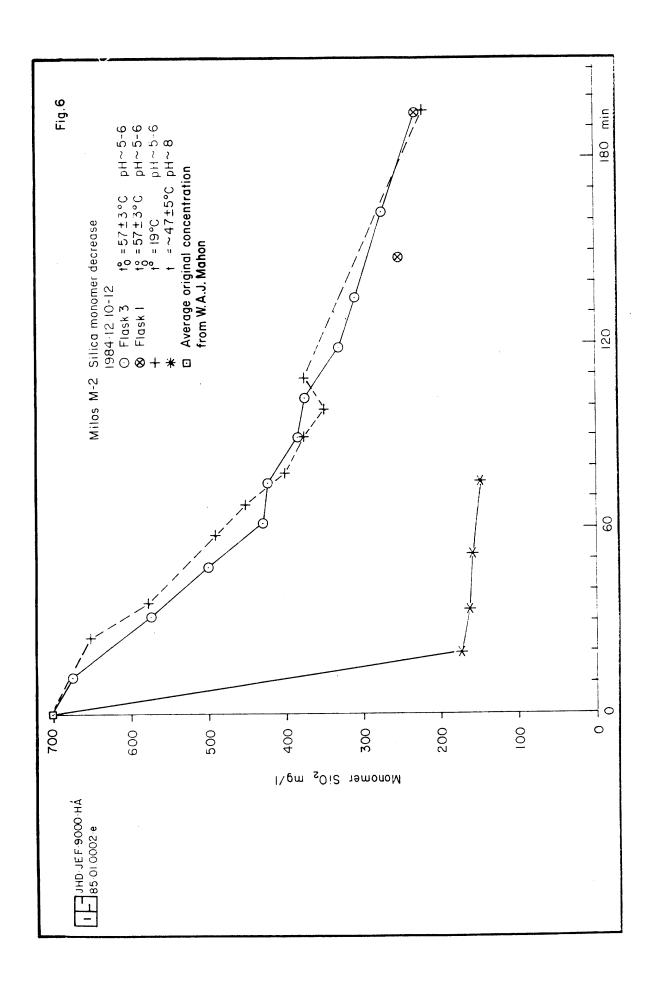
TABLE 7 Milos M-1 and M-2. Scales and deposits.

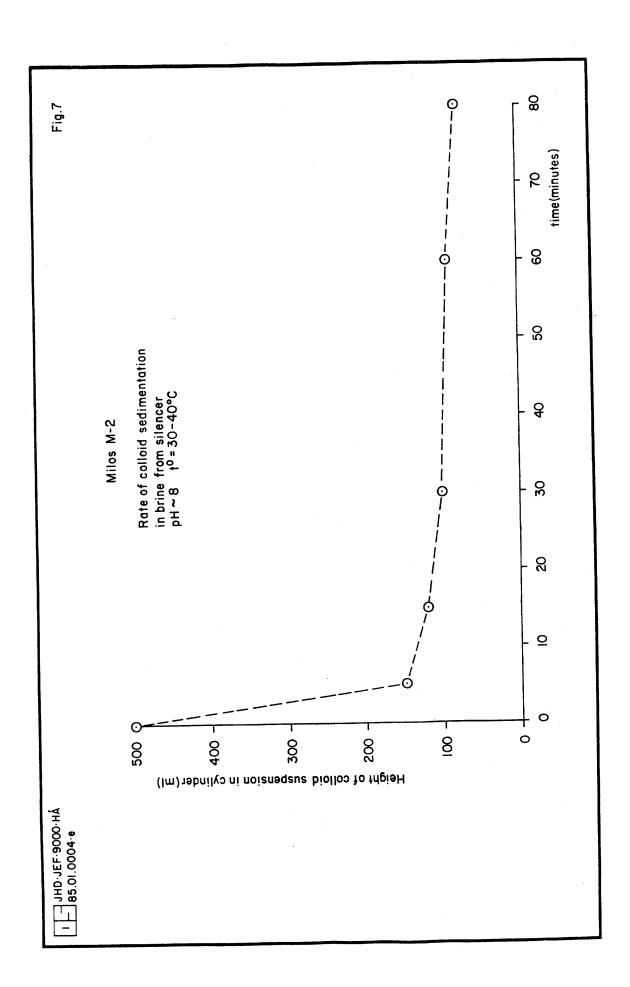
Sampling	Sampling	Sample	Sample	R	Results	
Date	Location	Туре	Treatment	XRD	XRF	EPM
84-12-01	Low pressure pipe	Scale accumu- lated during previous tests		Probably Fe, Cu, A		
84-12-12	Coupon inserted in 8 bara line	l Scale	_ " _	_ " _		SiO2:95-98% Fe: 0,5-1,8%
84-12-01	Silencer	Deposit accumu lated during previous tests		Salt, amophous silica	Ca,Si: la quantity Fe,K,Cl: quantity Zn: trace	fair
84-12-11	Silencer outlet	Precipitate filtered from fluid	_ # _	Salt		
84-12-11	_ #	_ " _	Washed with distilled water	None		
84-12-11	Brineline to seashore close to M-l	Scale	None	Salt, amophous silica		

XRD = X-ray diffraction
XRF = X-ray fluorescence

EPM = Electron microprobe analysis (Tested for Si,Ti,Al,Fe,Mn,Mg,Ca,Na,K,P)







6 CHEMICAL COMPOSITION OF THE BRINE

6. CHEMICAL COMPOSITION OF THE BRINE

6.1 Sampling and analysis

6.1.1 Sampling programme and available results.

During the PPC Consultants` stay in Milos the Contractors` Consultants (Geospac) took between 60 ant 70 samples for analysis. Analysis for volatile constituents (CO2, H2S and O2) and for pH, chloride and silica were performed in a field laboratory in the Milos PPC office, but the rest of the analyses were carried out on samples which were transported to the IGME laboratory in Athens.

The PPC Consultants took one brine sample which was analysed for non-volatile constituents in the NEA laboratory, Reykjavík. They also performed some analyses in connection with brine treatment studies (Chapter 5). So far, the results of the analyses performed by IGME in Athens, which include a series of analyses for total silica, have not been obtained by Virkir/NEA, nor have detailed descriptions of analytical techniques been received.

The proposed scope of chemical work with suggestions on analytical methods, submitted by Geospac prior to the test are presented in Appendix 4, and summary of sampling and analytical methods preferred by Virkir/NEA in Appendix 5.

6.1.2 Sampling separator.

The sampling separator employed could not withstand the relatively high well head pressure (about 57 bar) and therefore no samples were drawn before the 8 bar abs. line. There were indications that silica was already polymerzing at this stage and thus other compositional changes might be occurring. Therefore, it is not certain that a representative downhole fluid composition can be obtained from the analytical results.

6.1.3 Filtering of samples

Membrane filters were not employed for the filtering of samples on the island. Very inefficient filter papers were used for the few samples which were filtered there.

6.1.4 Sampling and analytical methods for pH, CO2 and H2S in brine.

The brine fraction in which the volatile constituents were to be determined was drawn into a plastic sampling bottle, which then was trans-

ported to the field laboratory often after hours of waiting. During this time losses and reactions might have occurred thus severely limiting the reliability of analytical results. It is common practice to use gas sampling tubes made of glass for such sampling The hydrogen sulphide determination was made by an iodine titration which is good practice for dilute waters, but in very concentrated brines such as the ones handled here the danger arises that more reducing substances than the hydrogen sulphide react with the iodine thus causing the result for the hydrogen sulphide to be too high. Furthermore our observation was that the total carbon dioxide concentration was obtained from a pH titration after subtracting the contribution from other weak acids, of which hydrogen sulphide is the most important. The carbon dioxide values might therefore be too low.

6.2 Results and discussion.

The present comments on the chemistry of the Milos, M-2 well fluid are based on the results of the field laboratory analyses (Tables 8 and 9), the results of the analyses of the NEA sample (Table 10) and previous information (Mitsubishi Heavy Industries, Nagasaki Shipyard & Engine Works 1984, Public Power Corporation, ENEL 1981, PPC unpublished results).

Some idea of the results obtained in the Athens laboratory may also be gleaned from Table 11 which appeared in the brine treatment proposal just recieved from Mitsubishi (Mitsubishi Heavy Industries, Nagasaki Shipyard & Engine Works 1985).

From solubility considerations more carbon dioxide could be expected to be present (Patterson et al 1982) than is observed and the hydrogen sulphide values appear high. In our experience brines from Reykjanes and Svartsengi contain 30-120 mg/kg CO2 and 1-5 mg/kg H2S, and a brine from Salton Sea is listed as containing 7100 mg/kg CO2 and 16 mg/kg H2S by Ellis & Mahon (1977) citing Muffler & White (1969). Thus a review of the results presented to us for CO2 and H2S in brine and condensate is suggested. Earlier analyses of gas from well M-3 suggest substantial carbon dioxide concentrations (Mitsubishi Heavy Industries, Nagasaki Shipyard & Engine Works 1984).

A look at the field laboratory results suggests a remarkable variation in the results for chloride and silica in the brine. As the enthalpy fluctuated during the test an attempt was made at relating these parameters (Fig. 8), but a relationship was not found. A relationship is likely to exist between enthalpy and chloride but since their determinations were not made at exactly the same time the fluctuations were too

fast to give comparable results. The chloride values vary from 55.656 to 81.180 mg/kg for the samples from the 8 bar abs. line. The NEA chloride result was similar to the lower field results, whereas previously results higher than any of the present ones have been obtained (PPC, reported results).

It therefore raises questions that in the design condition an even higher chloride value is listed. This could be due to a higher design enthalpy being assumed for the fluids, but this is not stated.

The reported decrease in silica concentration with time is high and cannot be explained by quartz re-equilibration in the aquifer Several determinations on the NEA sample under flowing conditions. 1984-12-12 all showed concentrations in excess of 800 mg/kg. Boiling that sample with sodium hydroxide did not produce significant increases, so the total silica concentration in the 8 bar abs. line is considered to be between 800 and 900 mg/kg. This value however, somewhat low if it is assumed that the main inflow is at 1150 m depth with a temperature of 317-318°C as temperature measurements have In view of this the design condition value of 400 mg/kg seems too low, especially if, as suggested by the chloride value the design, enthalpy is higher than that obtained during the present produc-Another feature which regards the silica concentration is the rate of monomer decrease (Table 2) which appears relatively slow in the samples taken on 1984-12-05, but much faster in the one sample collected a day later, and this is the only result which resembles those found in the brine treatment beneath scale studies (chapter 6). it seems possible that the rate of monomer decrease was not as fast in the brine flowing on the first day of sampling as later, and that therfore it was easier to obtain a representative sample for total silica determination in the field in the beginning. This could explain the apparent silica decrease with time. The results of the total silica determinations form IGME should clarify this.

There are apparently two notable differences between the NEA results and the design condition concentrations (Tables 14 and 15) i.e. for magnesium and sulphate. As far as is known the same method of determination was used for magnesium in both cases, so that the values should be reconsidered.

In the case of sulphate, however, different analytical methods were used, i.e. a gravimetric method at IGME, but ion chromatography at NEA. The former method is liable to give high results for concentrated brines, but on the other hand earlier results are high, and calculation of solubility products (Table 5) employing the WATCH1 computer programme (Arnorsson et al 1982) assuming 318°C as inflow temperature shows that

the deep water is slightly undersaturated with respect to anhydrite if the lower value for sulphate is used but supersaturated if the higher ones are employed.

TABLE 8 Milos M-2. Production test. December 1984. Results of analyses performed in the Milos field laboratory.

Date	Sa	ample no.	Po bara	pH/oc	CO2 mg/kg	H2S mg/kg	02 mg/kg	Cl mg/kg	SiO2 mg/kg	Notes
84-12	-05	1	8				•	68773	950	
_		2	-					65228	887	
_		3	-					70235	825	
	06	12	_				,	65937	725	
_		13	-			•		63810	750	
-		14						60619	525	SiO2 after boiling
-		15	-	5,5/						with 4N NaOH
_		16	-						500	
-		17	-					60974		
	07	29	-					56277	465	
_		30	-	4,2/	4,4	138	8,5	69482		
	08	39	_					55656	450	
_		41	_	5,5/				58493	290	
	10	50	-			•		56720	560	
_		51			4,4	67,2		55656		
	11	60		4,7/20				81180	575	
		61	-	4,4/20				71609	590	
	05	5	2,5					75736	875	
-		6	_					72672	787	
_		7	_					73559	719	
-		10B	-		8,3	385		07077		Condensate
	07	35	-	4,4/14,7	13,2	150	5	93233		W.4N NaOH
	80	36	-					102000	440	
-		41A	-	4,6/17				63810	490	
_		45	-	5,1/17				68773	715	
	10	54	-	5,1/18				68773	360	C : 3
	05	9	1,0					83308	750	Silencer "
		10	-					84194	662	11
	06	18				•		88662	700	11
-		19	-					86853		
-		20	-					85080	450	" -10 ml 4N NaoH
	07	27	-	4,6/	2,2	170	6	99960	775	" t =86,5°C
-		28	-					87916		"
	08	38	-	4,9/17				85434		"
-		43	-	4,9/17				84371		
	09	46	-	5,1/				86498		" t =86°C "
-		47	-	5,0/27	,5			87207		"
	10	57	-					85435		11
_	•	58	_	4,9/	8,8	94,	4	85789		11
	12		-					84725		" "
. –		64	-					84371		
	06		-	6,9/18			,	85080		Pond '' + =35°C
	07		-	5,0/4,	7 30,8	53	6 4,5	116276	070	" t =35°C
_	•	24	Name	/				90397		" "
	08		-	5,3/17				91461		
_		42	-	5,2/				90752		**************************************
	11	59	-						270	

TABLE 9 Milos M-2. Production test December 1984. Results of monomer silica determinations in samples collected at different times.

Date	Sample	Po	SiO2 mg/	kg after	
	no.	bar abs.	O days	l day	4 days
84-12-05	1	8	950	550	
_	2	_	887	575	
	3	-	825	600	
06	16	_	500	133,5	75
05	5	2,5	875	675	
_	6	-	787	662	
-	. 7	-	719	656	
_	9	1,0	750	575	
-	10	_	662	625	
	•				

TABLE 10 Milos M-2. Results of chemical analysis of NEA brine sample from 8 bar abs. line 1984-12-12.

Ps bara	H kJ/kg	Conductivity ohmm/°C			K mg/kg		Mg mg/kg	SO4 mg/kg	Cl mg/kg	F mg/kg	Tot dissolve solids mg/kg
7.0	1000	0.10/21.2	831	29308	8497	3971	2.43	11.7	56227	2.16	102317
Br mg/k	Fe g mg/k	Li Sr g mg/kg mg/kg		Conde Na m							

21.7

67.1 35.6

17.0 74.2

169

TABLE 11 (Mitsubishi Heavy Industries, Nagasaki Shipyard Engine Works 1985)

DESIGN CONDITION OF HOT WATER

DESIGN PRESS. : 25 atg
 OPERATING PRESS.: 16.3 ata
 DESIGN TEMP. : 188 °C
 OPERATING TEMP. : 171 °C

5) DESIGN H.W. FLOW: 25 T/H

6) CHEMICAL COMPOSITION OF BRINE

CHIMITOTIC COLLEGE TO THE		
Conductivity	μMKos/cm	137,500
РН		5.5 (97°F)
Total Dissolved Solid	ppm	152,160.00
(TDS) in 356°F		•
Total Hardness in $CaCO_3$	ppm	14,435.5
Bicarbonate ions HCO3	ppm	3.66
Silica SiO ₂	ppm	700.00
Dissolved CO ₂	ppm	· -
Dissolved H ₂ S	ppm	-
Calcium Ca	ppm	5,731.44
Magnesium Mg	ppm	33.00
Sodium Na	ppm	44,735.00
Potassium K	ppm	10,166.00
Chloride ions Cl-	ppm	88,384.05
Sulfate ions SO_4^{-2}	ppm	129.68
Ammonia NH ₄	ppm	52.50
Boron B	ppm	280.00
Bluoride ion F	ppm	3.00
Strontium Sr	ppm	90.00
Barium	ppm	21.2
Total Iron Fe	ppm	16.90
Aluminum Al	ppm	0
Lead Pb	ppm	0
Lithium Li	ppm	93.50
Zinc Zn	ppm	2.00

TABLE 12 Milos M1-2. Dissolved solid composition in deep water. Calculated for samples A, B and C (see footnote) using WATCH l. All values in mq/kq.

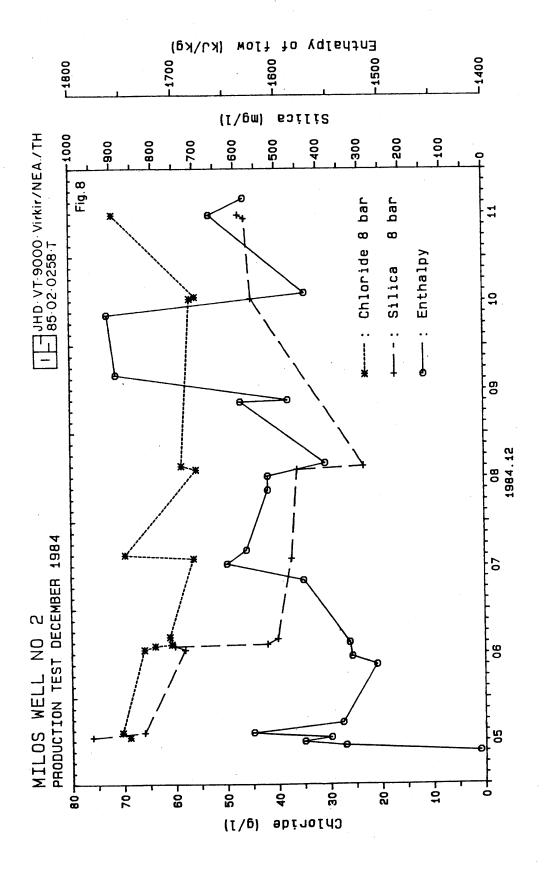
Sample	SiO2	Na	К	Ca	Mg	S04	Cl	F	TDS	Al	В	Fe
A	535	23054	5173	3029	26,2	47,5	45549	1,51	75588	0,19	62,1	2,75
В	450	15879	4603	2152	1,32	6,33	30462	1,17	55436	-	_	9,20
С	454	29025	6596	3718	21,4	84,3	57340	1,95	98724	-	182	11,0

TABLE 13 Milos M-2. Log solubility products of selected minerals in deep water. Calculated for samples A, B, and C (see footnote) using WATCH1.

Sample	e Minerals A	nhydrite	Calcite F	luorite	Pyrite W	ollastor	ite Marcasi	te Quartz
	Saturation							
	value	-9,396	-14,600	-11,360	8,400	6,431	23,189	-1,849
Α	Calculated value	-8,697	-12,383	-12,383	-22,604	6,624	-22,604	-2,051
		•	,	•	,		10.740	0 105
В	Calculated value	-9,626	-13,114	-13,675	-10,349	5,178	-10,349	- 2 , 125
С	Calculated value	-8,438	-13,866	-12,571	-17,320	6,159	-17,320	-1,122

Footnote to tables 12 and 13.

- Sample A. Composition based on previous tests. A composite sample based on analytical results for samples taken 81-11-16, 83-09-23 and 83-09-24. Temperature of inflow is assumed to be 282°C, and a silica concentration of 990 mg/kg accordingly assigned to the sample.
- Sample B. NEA brine sample. pH, CO2 and H2S based on field measurements by contractors (Table 1), and gas concentrations on previous samples (Mitsubishi Heavy Industries, Nagasaki Shipyard & Engine Works 1984).
- Sample C. Based on Design condition (Table 11) and previous gas samples.



7 NOTE ON POSSIBLE DEPOSITION OF ANHYDRITE FROM SEAWATER INTO A GEOTHERMAL WELL

7 NOTE ON POSSIBLE DEPOSITION OF ANHYDRITE FROM SEAWATER INJECTED INTO A GEOTHERMAL WELL

Anhydrite (CaSO4) deposition is known to be a problem in cases where seawater is heated. From practical experience it is expected that such deposition starts at or below $100\,^{\circ}\text{C}$ and is rapid.

Blount and Dickson (1969) have published data on anhydrite solubility at temperatures ranging from $100-450\,^{\circ}\text{C}$ in sodium chloride solutions (NaCl-H2O).

The following calculations are based on their data to show how much anhydrite can be expected to be deposited from seawater and mixtures of seawater and Milos freshwater pumped at the rate of 25 ton/h for 4 weeks into a geothermal well. This is the average rate expected for the proposed injectivity test for well M-l, Milos.

The following assumptions are made:

Seawater is a 0.5 M NaCl solution

Calcium concentration in seawater: 400 mg/l Sulfate concentration in seawater: 2600 mg/l

Calcium concentration in Milos freshwater: 100 mg/l

The results of these calculations are given in table 14.

TABLE 14 Predicted amount of anhydrite deposition after 4 weeks pumping of seawater at 25 ton/hr at different temperatures.

Anhydrite deposited, (tons) from:

Temp. °C	seawater	l+l mixture seawater and Milos freshwater	1+3 mixture seawater and Milos freshwater
100	0	0	0
150	6,4	4,1	3 , 0
200	15,1	9,8	7,1
250	19,2	12,2	8,8
300	21,0	13,3	9,4

Rough calculations that have been made regarding the effect of temperature indicate that the temperature at the main inflow at 1150 m would go down to $50-100^{\circ}$ C after about 6-8 hrs of pumping (25 ton/h), and stay at

that for the rest of the time.

The injected water would, however, heat up rapidly once it gets into the formation. How rapidly depends on the nature of the permeability, but if the seawater escapes through a single fissure it would flow $20\text{--}30\,\text{m}$ away from the well, before reaching a temperature of $150\text{--}200\,^{\circ}\text{C}$, but in a situation, where the flow is in all directions, the corresponding distance would be $5\text{--}10\,\text{m}$.

Thus the danger of plugging the formation near the well inflow is considerable.

8 SUGGESTIONS FOR THE REPAIR OF A LEAK

8 SUGGESTIONS FOR THE REPAIR OF A LEAK ON THE WELLHEAD OF M-1 ON MILOS.

A pinhole leak has appeared on the casing head of geothermal well M-l on Milos. Geohermal brine is oozing through the hole at a low rate. The casing head, $13\ 3/8$ ", has two 2" API 3000 side outlets that are threaded and then welded. The leakage is probably due to seepage past the threads and through a pinhole in the weld. This leak should be repaired as the well is under pressure (23 bars) and the situation can only deteriorate. Access to the leak is difficult as shown in Fig. 9.

Leaks on the side outlets and kill line valves were quite common in Iceland in the early days of geothermal development. This problem was solved by having the casing head without side outlets and to locate the outlets between the master valves instead. The kill line valves can thus be serviced without killing the well.

It is suggested that PPC consider closing off the side outlets of existing wells when the opportunity arises e.g. when the well is quenched.

As requested suggestions of possible methods of repair have been listed. These are illustrated in Fig. 9.

1. Killing the well.

The well has a WHP of 23 bars and is cased off to 850 m depth. The pressure can only be reduced to about 9 bars by pumping cold water into the well and thus the well must be quenched by use of heavy mud or heavy brine. Once the well has safely been quenched the side outlets should be plugged with a solid plug and welded.

2. Temporary repair.

Just after the injection well test it may be possible to flow the well to reduce the WHP. By peening the area around the weld the leak could be reduced enough to allow welding of the hole. This should be regarded as a temporary repair.

3. Welding a patch.

A patch consisting of a portion of a pipe of I.D. 65 mm and a nipple can be welded over the hole. The water seepage will make the welding nearly impossible, but by pumping compressed air into the well, thus lowering the water table a few meters the job would be made easier. After the welding is complete the nipple can be closed with a valve. This should also be considered as a temporary repair.

4. Use of packers.

As the well is only lukewarm a casing packer could be set in the 9

5/8" production casing by installing a special spool and a rotating head on the wellhead. A small drilling rig would have to be brought in for the job. As there is casing damage at 78 m depth water may seep through the annulus to the surface. This method of repair has the advantage that the well does not have to be quenched, but the casing damage makes success uncertain.

5. Small packer.

The oil-industry makes use of small hand held packers to be placed in the side-outlets of wells so that repairs can be done. The packer is run through the kill line valve and placed in the 2" pipe. This is a neat solution. However, because the leak is expected in the threaded portion it cannot be stopped with this method.

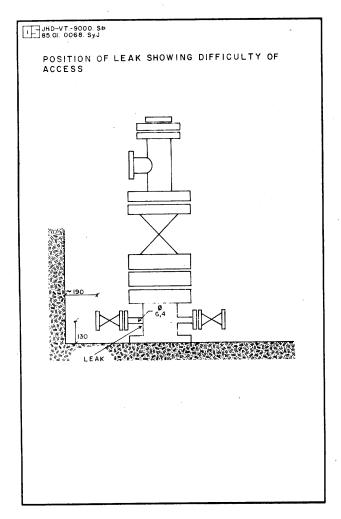
6. Sealing.

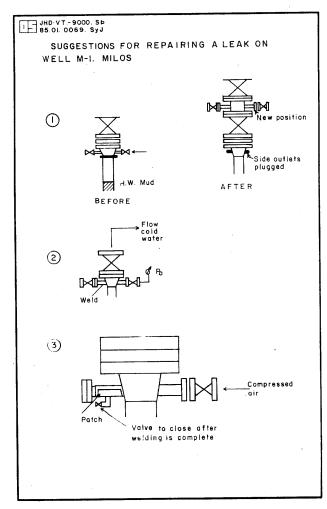
Specialized service companies perform sealing of leaks with the equipment under pressure (Furamite U.K.). This type of repair has once been used in Iceland with success.

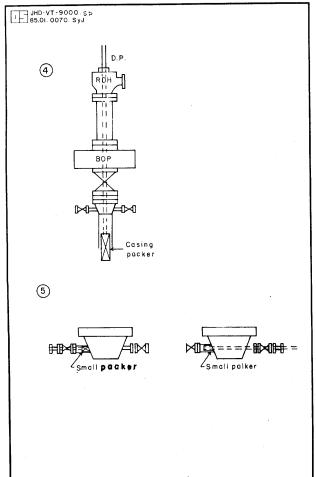
7. Improving access to the leak.

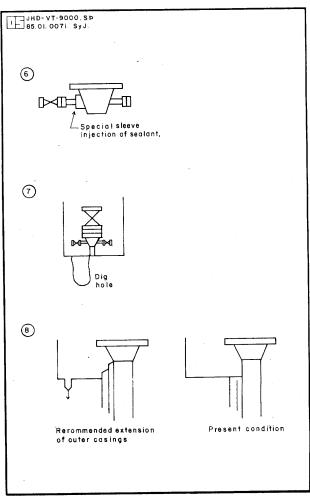
Working on the repair will be extremely difficult, because of the inaccessibility of the leak, which is on the bottom of the pipe only 10 cm from the floor. The access could be improved by digging a hole around the side outlet so that a person can work upright. This hole will also allow inspection of the outer casings and the outside of the 13 3/8" casing. This is the most probable location for corrosion damage. It is recommended that such inspection on wells M-1, 2 and 3 be done, as the cellars are cracked and all rainwater and brine from leaks seeps into the ground.

8. A detailed specification should be made prior to carrying out repair as it is a critical operation.









9 MEMOS FROM CONSULTANTS' VISIT

9 MEMOS FROM CONSULTANTS' VISIT

9.1 MEETING AT PPC IN ATHENS NOV 30 1984

Present: P. Adamis, G. Spiliotis, F. Vrouzi, J. Eroy, W.A.J. Mahon, S. Thorhallsson & H. Ármannsson.

9.1.1 Injectivity test.

The subject of well damage due to the use of seawater for the injection was discussed. PPC is unable to supply more than 6-7 m3/hr of freshwater from local wells and a storage capacity of 6000 m3 at well MZ-1. The supply of fresh water with a tanker from Athens is under investigation (12.000 m3). It was revealed that the subject of substituting seawater for freshwater for the test had been discussed and approved by two Mechanical Engineers from MHI/GEOSPAC.

Mr. W.A.J. Mahon says that the two main objectives of the injectivity not to damage the well, and to prove its injection capacity. Approximately 15.000-20.000 m3 are needed for the test. Mahon said that the pump may be too small, but Mr. Spiliotis pointed out that MHI/GEOSPAC engineers had approved the present centrifugal pumps was to supply additional ones if these were and that MHI furthermore said that seawater had been used for the inadequate. Не drilling fluid, and that the well had been a good producer (50 t/hr steam, 80 t/hr brine). The well was produced for 5-7 days in December 1980 and has since then been tested twice by PPC for 1-1.5 months time, increasing its output each time. Considering the lack of freshwater Mr. W.A.J. Mahon saw no reason to change the programme, as he considered the possible effect on the reservoir small.

Mr. S. Thorhallsson recommended that local freshwater be used for the initial test of step rate injection testing, and that seawater should be pumped only for as short a period as possible. He said that the step rate test could perhaps be completed in three days after the well had been cooled, and a test of less than one weeks` duration was preferable to the scheduled five weeks test proposed by MHI/GEPOSPAC.

9.1.2 Production test.

Mr. W.A.J. Mahon considers a production test of one week's duration sufficient to collect representative brine samples, as he had been informed that this well stabilises very quickly. When the VIRKIR/NEA plot of the test from September 1983 where it was shown that the well had not yet reached stability after the first week of flow was presented

to the meeting. Mr. Spiliotis explained that this was due to readjustment of the valves to obtain a certain flow. Mr. S. Thorhallsson attributed this change to the flashing of fluid in the formation too and asked whether the flow period could be extended. When asked again by Mr. Spiliotis wether the 7 days was long enough, Mr. W.A.J. Mahon confirmed this.

9.1.3 Brine test.

Mr. S. Thorhallsson pointed to the weakness of the brine studies and procedures, as no detailed suggestions have been made by the contractor, as to the tests to be carried out. The only comment was that the vast amount of information on record plus the experience gained by GEOSPAC in Fushime Japan among other places, would be used to design the brine treatment process. Mr. J. Eroy showed a telex. from MHI saying "Therefore we would like to select the best treatment system and instal it before doing the brine test." This test is to be moved forward, and performed in June 1985. In the same telex. MHI says that they are planning on testing a magnetohydrodynamics (MHD) process for stabilizing silica. Further description is lacking. The pond test is now scheduled for February 1985, as well as the injection trial and tracer test.

9.1.4 Chemical sampling and analysis.

Mr. S. Thorhallsson pointed out that detailed procedures have not been submitted by MHI/GEOSPAC for this part of the production test as stated in the MHI document (sampling and analysis, particle characterization). Mr. W.A.J. Mahon said that the standard procedures would have to be modified, and therefore could not be given at this time. He will stay in Greece until December 15 and will prepare these for PPC before departure.

9.1.5 Turbine.

The turbine design is the following: Inlet pressure is to be $8.0~kg/cm^2$ a: at a steam flow of 17.020~kg/h, and the corresponding well production is 40.8~t/hr at $47.9~kg/cm^2$ a. An enthalpy of 377.3~kcal/kg is assumed.

9.1.6 Tracer test.

On the subject of radioactive tracers, Mr. W.A.J. Mahon said that the test procedure was possibly being reevaluated by W. McCabe in New

Zealand. He said that returns had been observed in N.Z. over a distance of l km in approximately one month.

9.1.7 Nisyros

Before the meeting the subject of gas accumulation and increase in pressure of a well at NISYROS was discussed. A well of 1450 m depth, cased to 1044 m has had the WHP increase from 44 bars to 79 bars, and the question of bleeding was discussed. Based on the casing depth Mr. S. Thorhallsson said that the pressure could be expected to reach roughly 100 bars, and he recommended to bleed the gas continuously, through an orifice and/or a needle valve and to maintain the pressure at approximately 60 bars.

9.2 MEETING AT MILOS 1/12 1984

Present: C. Biniaris, N. Koutroupis, F. Vrouzi, S. Thorhallsson & H. Ármannsson.

9.2.1 Temperature logs.

S.Thorhallsson asked for temperature logs of wells M-1 and M-2. It was revealed that no previous measurements had been made of the well in the shut-in condition. Some measurements were made in M-2 during a flow test (1200 m, 23,5 kg/cm2, 211 $^{\circ}$ C, flow during measurement 48 t/h at WHP 12 kg/cm2, 1981.6.19) and another log made two days later with the well closed, showing a substantial temperature increase. This indicates flashing in the formation.

9.2.2 Heating up of well.

Previous heating up measurements were inspected. Two days heating up has been practised (2-3 C/hr) by bleeding off on up to four 1/2" pipes connected to the kill line valves. Maximum WHP during early discharge has reached 49 bars, and a temperature of 250°C. Heating up was to start to-day. The WHP now is 24 bars g and the well head is only lukewarm.

9.2.3 Well test.

The well is to be tested at $18\,$ t/hr steam, and $23\,$ t/hr of water. Previous measurements (1984.9.20) showed 40.7 t/hr at WHP 55 kg/cm2.

9.2.4 Anhydrite deposition.

The subject of anhydrite deposition was discussed again, as no definte decision has been made. The concentration of SO4 in seawater is roughly 2600 ppm but the geothermal brine contains only 88 ppm, due to anhydrite deposition in the reservoir. By analogy up to $1 \, \text{kg/m3}$ can be deposited from the seawater or in the range of 15-20 tonnes during the injectivity test.

9.3 FIELD INSPECTION 1/12 1984

Two trips were made to well M-2 for inspection. The following observations were made.

9.3.1 Logs

The second log was in progress. Yesterday the maximum temperature was measured to be 317°C. The last 3-4 measuring points were lost due to clock failure, caused by leaky seals.

9.3.2 Scaling and deposits.

Scaling in the flowline was inspected at two points.

- a. Scaling on the high pressure side of the second choking valve was negligible, but substantial on the low pressure side. The deposit was black and approximately 5 mm thick. A sample was collected.
- b. At the silencer inlet just upstream of the critical lip negligible scaling was observed, but there was some scaling on the lip itself. More significantly the lip had been extended by building up of scale from 3.2 mm to 7 mm from the face to the 1/4" Pc hole. This may give enhanced estimates of flow.
- c. Large deposits of silica had been removed from the silencer of which a sample was taken.

9.3.3 Lip pressure pipe.

A new lip pressure pipe was inspected. Inside diameter was measured 124.5 mm, and the distance to the Pc hole 3.5 mm. The end was somewhat rounded, and the straight section was 3 mm. (An old lip pressure pipe had an ID of 94.5 mm (see paragr. 2)).

9.3.4.Well head inspection.

The well head was inspected, and found to be in a good conditon, except for the 4" valve on top of the Christmas tree which is only 600 lb ASA. This valve should be replaced. The $1\ 1/4$ " connection to the flowline requested for insertion of a coupon turned out to be only 1", and a modification was requested.

9.4 DEC 2, 1984:

9.4.1 Caliper basket.

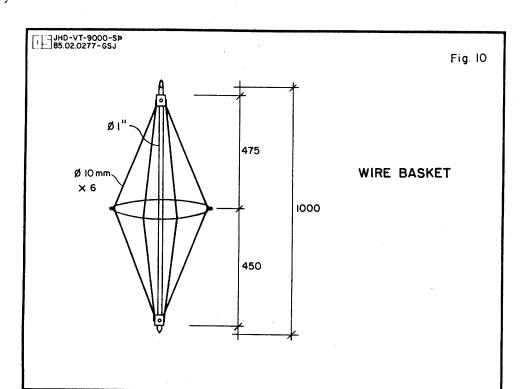
A sketch (Fig. 10) of a wire basket of different diameters to be used for a caliper survey was made for PPC. The tool is designed on the same principle as tools used in Iceland. The diameter is selected to show scales that are greater than 5 mm.

The following baskets are required:

 $13\ 3/8$ "(drift i.d. $313.9\ mm$) casing - $305\ mm$, 9 5/8"(drift i.d. $212.8\ mm$) casing- $205\ mm$, 7"(drift i.d. $173.8\ mm$) casing- $160\ mm$ diameter of wire basket. It was recommended that the tool be run in well M-1, the reinjection well, both before and after the injection test and in well M-2 after the production test. The tool will be made in a local shop, and measurements performed by PPC.

9.4.2 Logging.

Inspection of the temperature log made yesterday revealed 317°C at an unspecified depth below 1050 m. As no temperature logs of the well in a shut-in condition are available, it was suggested that the temperature log be rerun. Inadequate sealing has been a recurring problem with the Kuster instruments supplied by MHI/GEOSPAC. The instruments used are modified to use a copper sealing ring, and a Viton O-ring. The resulting leakage has caused the clock to stop. Both the pressure and temperature logs of December 1 were faulty, and in the t and p logs to-day slight leakage was also observed, but this apparently did not affect the readings. This delay has postponed the heating up process one day.



9.4.3 Heating up of well.

TABLE 15 Previous heating up data

	First test	Second test	Third test
Heating-up period (hr)	37	74	ca 70
Casing elongation (cm	1)	10	13
WHT max (°C)	220	230	=======================================

Heating up was started at 15:45 by openig one 1/2" valve. Based on previous experience a heating up period of two days is planned.

9.4.4 Flow line preparation.

The flow line was cleaned in three places to allow inspection of scale accumulation during the flow test. A sampling point for the collection of samples of water and steam on the 8 bar line was selected, as the point shown in the document 1.0 PROCEDURE FOR PRODUCTION WELL TEST (MHI/GEOSPAC 1984) was found unsuitable.

9.4.5 Pressure rating of well head.

PPC has decided to upgrade the pressure class for the well head to ASA 900 by installing a new 2" valve instead of the 4"x600 lb. valve. The recovery tube and lubricator to be supplied by MHI/GEOSPAC have not been delivered, and consequently the PPC parts are being used.

9.4.6 Other wells.

An inspection tour was made with N.K., T.M., S.T, H.A. of wells M-1, M-3 and MZ-1. All the wells are under pressure, full of water, well heads luke warm and WHP gauges installed. T.S. has recently measured the WHPS, which are in the range 15-25 bars. The injection pump at well M-1 was looked over, and found to have valves of ND 25 cass. The centrifugal pump has a 290 kW motor, 1485 rpm.

9.4.7 Leakage on casing head of well M-l.

There is a leakage on the 2" kill line welded to the casing head of well M-1. The 2" pipe is screwed, and later welded to the casing head. The leak is located on the lower side of the pipe, at the weld. N.K. has asked S.T. to submit a proposal for possible methods of repairing the leakage.

9.5 MEETING AT MILOS. 1984.12.3

Present: N. Koutroupis, C. Biniaris, F. Vrouzi, S. Thorhallsson & H. Ármannsson.

A preliminary discussion of the document from MHI/GEOSPAC titled "Procedure for production well test" dated 23 oct. 1984 took place. PPC personel had not received a copy from MHI/GEOSPAC until after their arrival at Milos. The main points raised by VIRKIR/NEA are the following:

- a. The test is only planned for a single set of operating conditions (based on constant well head preessure), and is of short duration. Results of previous tests show different enthalpies for discharge at different WHPs. It was recommended that the test be for constant output (not constant pressure) and that it should be made clear whose responsibility it was to control the valve. N.K. said that the intended constant pressure would be very difficult to achieve.
- b. Some equipment to be supplied by MHI/GEOSPAC is not on location: Recovery tube, choke valve, wireline. It was stressed by VIRKIR/NEA that PPC should bear no responsibility for the operation of similar equipment borrowed from PPC.
- c. It was recommended that a sampling location close to the well head be added, allowing collection of samples at full WHP, as this would provide a more representative samples for the calculation of deep fluid composition.
- d. A meeting with the Geospac representative was recommended to discuss their document, and finalize details of the production well test. This meeting was held from 13:00 to 18:00. The following points were discussed.
 - -Equipment to be supplied by the contractor.
 - -Flow test (our earlier recommendation of constant output was approved).
 - -Replacement of ASA 600 lb valve with API 2000 valve.
 - -Duration of test (results of earlier output data were discussed).

TABLE 16

Beginning of heating period: 84.12.2 at 17:30 hr. Data

date 12.2 12.3 12.4 time 17:30 17:00 10:00

WHP bar 24 26.7 28 WHT C 75 175 188

Elongation cm 0 5

average rate of heating 5-7°C/hr

9.5 MEETING AT MILOS 1984.12.06.

Present: C. Biniaris, N. Koutroupis, D. Cotsoni, C. Leonis, St. Xenopoulos, K. Dimitropoulos, W.A.J. Mahon, A. Slatter, C. Leonis, S. Thorhallsson & H. Armannsson

9.5.1 Production test procedure.

After some discussions it was decided to maintain constant well output, and to compensate for the decline in output by adjusting the throttle valve twice daily. The contractor approved this and of the adjustments being made, (the plan called for constant WHP).

9.5.2 PPC supplies

The centrifugal injection pump has been tested to 24 bars pressure, and all the facilities to be supplied by PPC are ready, according to PPC.

9.5.3 Logging cable

A. Slatter voiced concern that the logging cable now in use (borrowed from PPC) is not safe for caliper logs due to its small diameter.

9.6.4 Anhydrite deposition

H. Ármannsson submitted results of calculations, showing the potential for anhydrite scaling. These results are reported separately (chapter 7).

9.6 MEETING AT MILOS 1984.12.10

Present: C. Biniaris, N. Koutroupis, W.A.J. Mahon., T. Slatter & H. Armannsson

9.6.1 Subject.

To question Geospac representatives on their preliminary results, and their possible implications. Their opinions follow.

9.6.2 Output.

This one week test is not long enough to obtain stable output at a constant pressure. The enthalpy fluctuates but on the whole it is increasing. Over a long testing period (e.g. l year) it can be expected to increase up to or above 2000 kJ/kg.

9.6.3 Chemistry.

In spite of enthalpy fluctuations the chemistry of the fluids appears to be stable. Further samples for chemical analysis should not be necessary, since composition at different enthalpies and pressures can be extrapolated from the present results. Silica polymerisation is substantial and fast. It occurs already in the 8 bar a line. However results on total silica have not been obtained, since the analyses will be done in the Athenes laboratory. It turned out that contrary to the Geospac representative's belief the samples had not yet been sent to Athens for total silica analysis. It was decided that sending them would be a priority, since a lot depended on the results.

As enthalpy is expected to rise, the polymerisation problem can only be expected to get worse during the course of time.

9.6.4 Brine treatment.

There is no way that the brine can be reinjected directly from the separator due to silica depostion. Due to fast settling rate ponding might be successful.

9.6.5 Separators.

A single separator at 8 bar a cannot be employed due to the fast polymerisation and deposition rate of silica. Therefore according to W.A.J. Mahon double separation will be necessary, i.e. high pressure

and then the 8 bar a separator. There will be some carryover from the separators containing e.g. damaging chloride. Therefore he recommends a long pipeline (at least 100 m) between the separator and the turbine from which the damaging liquid will be removed by traps. It was noted that in the present MHI-drawings this pipeline is nowhere near 100 m long.

9.6.6 Further work.

Next step should be brine treatment tests. As the chemistry of the brine has been characterized, answers and solutions to problems should be obtained by well prepared tests, such as coupon insertion at different pressures.

It was stated with regard to the immediate future, that Mr. A. Slatter's contract runs out 22nd December 1984, and that he will do no measurements after that time.

9.7 MEETING AT PPC IN ATHENS 1984.12.12

Present: P.N. Adamis, G. Spiliotis & S. Thorhallsson.

9.7.1 Nisyros

The subject of VIRKIR/NEA collaboration in the further study of Nisyros wells was discussed. Spiliotis requests that we prepare a short proposal on the further testing of the wells in order to complete the bid documents. Greece has obtained EEC financing for this project, which is good for the next four years. In this time the power plant must be built, and cables laid to the nearby islands. The proposed size of the plant is 3 MW.

Two wells have been drilled, and the final reports by Geotermia Italiana for both wells were pbtaomed. Nisyros l produced initially superheated steam and buried the silencer in a mound of dust and silica in four days. Using heat crayons they estimated the WHT to be $420\,^{\circ}\text{C}$. The well was filled in and may also have collapsed, and subsequent tests have given better steam. The output was reportedly at a depth of $1800\,\text{m}$ 10 t/hr steam and 2 t/hr brine (test duration 4--5 days). After the collapse and repair to $1550\,\text{m}$ the output was 8 t/hr steam and 8 t/hr brine (test duration $1.5\,\text{m}$ months).

Well Nisyros 2 was drilled to 1540 m and had an initial production of 33 t/hr of steam and 30 t/hr of brine (test duration 3-5 days). The

second test lasted for 1.5 months, and showed an output of 28 t/hr steam and 33 t/hr brine. Both wells had to be started by air-lift. Nisyros 2 has in the last few days increased its pressure by up to 4 bars a day, and when asked for an opinion on what to do they were told to expect the pressure to stabilize at 80-100 bars. Due to jet perforations at a depth of 100-200 m it is considered safer to bleed the pressure off approximately 60 bars by use of a small needle valve to. PPC in the meantime sent a geologist to the well and he bled the pressure off quickly as can be seen in the pressure logs he kept from 11/22 to 12/3. The well has a WKM expansion spool, and the pressure on the outer casing is 40 bars (see table).

The second main interest of PPC is to determine the possibilities of disposing of the brine into some phreatic craters within the caldera, or else to dispose of the brine into wells that would be drilled to 500 m with small rigs they have available. They would also like to have a VIRKIR/NEA proposal on effluent disposal.

Tourism is a factor, as the caldera and fumaroles and steam vents are frequented by tourists in the summer. PPC will telex to VIRKIR/NEA a message describing their intentions, and they estimated the probability that VIRKIR/NEA would do the work as 80%. This would be easier within the present contract, or one based on the same rates. I suggested that Valgardur visit the island after his mission to Milos.

9.7.2 Water supply for injectivity test

The subject of water supply for the Milos injectivity test was discussed and after consulting Valgardur. I gave the following opinion: To inject with freshwater for approx 3 days, and not to inject seawater.

9.8 MEETING IN ATHENS 1984.12.14

Present: J. Eroy, W.A.J. Mahon, P.N. Adamis, G.Spiliotis, F.Vrousi, D. Cotsoni + 3 other PPC reprentatives & H.Ármannsson.

9.8.1 Subject.

Status report from W.A.J. Mahon and MHI representative regarding production test at Milos M-2, and possibilities regarding the continuation of the project.

9.8.2 Injectivity test.

A telex from MHI, Japan was presented, where it was stated that fresh water would be used for reinjection test, which therefore would be postponed. Instructions are made regarding the filling of the M-l pond with fresh water. It is moreover concluded that it takes about 90 days to pump enough water into the M-l pond, so that the reinjection test will start 20th March 1985, if filling with fresh water starts 20th December 1984. The meeting was informed that the filling would start the next day. Water from cold water well B, drilled 1979, would be used, and its chemical composition carefully monitored, especially with regard to calcium and chloride composition.

9.8.3 Silica deposition.

It was stated that the total concentration of silica at the silencer outlet could easily be controlled and kept to ca 300 ppm, which is regarded as neither dangerous to well nor reservoir in the event of reinjection. On the other hand it was put foreward that direct hot reinjection without the precipitation of silica was not possible. W.A.J. Mahon was satisfied that the chemical composition of the brine obeyed known chemical principles.

9.8.4 Well head pressure during production.

Well head pressure during production will have to be kept at 45-50 bar to prevent silica deposition in the well. The fluid would then be flashed at the separator pressure (8 bar a). As this is not the system originally proposed by MHI it was requested that MHI included such changes in a report. It was then stated that W.A.J. Mahon would present his report to the MHI engineers, who then would take his comments into account. When questioned about when his report would be ready. W.A.J. Mahon replied, Christmas Day.

9.8.5 Magnetohydrodynamics (MHD) brine treatment system.

When questioned about this system, W.A.J. Mahon replied that he was not familiar with it, but thought that any testing of new technological possibilities was positive and for this reason the tests should be carried out. The MHI representative said that any damage or delay due to such tests was the full responsibility of MHI.

9.8.6 Milos M-2. Leak on high-pressure line weld.

The PPC representatives informed the meeting that the production test on Milos, M-2, would not be stopped yet to facilitate the repair of the leaking weld on the high-pressure line. There were hopes that the staffing box due to be supplied by MHI would arrive very soon, and then the opportunity for repair without closure would present itself. For the time being points on a back pressure curve for the well flow were being established. Mr. J. Eroy of MHI said that everything possible was being done to accelerate the process of clearing the staffing box through the customs.

9.8.7 Detailed analytical procedures.

W.A.J. Mahon stated that the detailed procedures for sampling and analysis requested at previous meetings could soon be presented.

REFERENCES

REFERENCES

- Arnórsson, S., Sigurðsson, S. & Svavarsson, H., 1982: The Chemistry of geothermal waters in Iceland I. Calculation of aqueous speciation from O° to 370°C. Geochim. Cosmochim. Acta 46. 1513-1532
- Blount, C.W. & Dickson, T.W., 1969: The solubility of anhydrite (CaSO4) in NaCl-H2O from 100-450°C and 1 to 1000 bar. Geochim. Cosmochim. Acta 33, 227-245.
- Ellis, A.J. & Mahon, W.A.J., 1977: <u>Chemistry and geothermal systems</u>. Academic Press. New York, San Fransisco, London, 392 p.
- MHI/GEOSPAC 1984: Milos geothermal development 1.0. Procedure for production well test.
- Mitsubishi Heavy Industries, Ltd. Nagasaki, Shipyard & Engine Works 1984: Brine reinjection system for Public Power Corporation Greece Milos Island Geothermal P/P. Document no. PG-TI-2. 25 pp.
- Mitsubishi Heavy Industries & Nagasaki Shipyard & Engine Works 1985: Brine treatment.
- Muffler, L.P.J. & White, D.E. 1969: Geol. Soc. Am. Bull. 80, 152
- Patterson, C. S., Slocum, G.H., Busey, R.H. & Mesmer, R.E. 1982: Carbonate equilibria in hydrothermal systems first ionization of carbonic acid in NaCl media to 300°C. Geochim. Cosmochim. Acta 46. 1653-1663.
- Public Power Corporation & ENEL 1981: Milos Geothermal Project.

 Report on the well Milos2. No. GR/MI-11.

APPENDIX 1

VIRKIR/ORKUSTOFNUN Document No.750-34 1984.11.09

COMMENTS AND RECOMMENDATIONS ON:

TEST PROCEDURE OF WELL CHARACTERISTICS AND BRINE STUDIES. DOCUMENT 9700-2737A, DATED OCT 1984. SUBMITTED BY MHI AND GEOSPAC TO PUBLIC POWER CORPORATION GREECE.

INTRODUCTION.

The cited document sent by PPC to VIRKIR/ORKUSTOFNUN has now been reviewed as requested. The document outlines the tests and procedures to be used in fulfilling part of the MHI contract for the supply of a 2 MW geothermal power plant for the island of Milos. The document and information already submitted for review testifies to the high competence of MHI and GEOSPAC in meeting the contractural obligations. It is in the area of brine treatment and disposal by reinjection where present knowledge is limited, and thus requiring extensive field tests. It is also in this area where the cited document is quite vague, further discussions are recommended to prepare more detailed descriptions of the engineering/scientific work to be performed in this area. It should also be pointed out that a discharge period of up to one year is needed to determine long term production characteristics, and scaling rates in wells and surface equipment.

1. PRODUCTION WELL TEST.

The 7 day production test is to be performed at the proposed production pressure for the 2 MW plant. There seems to be some confilct in documents submitted by MHI and GEOSPSAC to PPC, as to whether the test is to be at wellhead pressure (WHP) 8 bars or 35.5 bars. This obviously affects the diameter selection of the lip pipe. On one GENZL sketch the pipe is specified to be 7" in diameter. This is too large and will cause low lip pressure readings. Results of the output test of sept. 1983 were 42 t/h at WHP 37 bars. A suitable lip pipe dia. is 5.5" as indicated in the GENZL well measurement programme.

Recommendations: The operating conditions must be clarified and a suitable lip pipe diameter selected. The end of the lip pipe should be machined on a lathe to produce a smooth and circular inside surface some $20\,$ cm long, and care should be taken to locate the 1/4" tap drill hole exactly 1/4" from the lip.

2. REINJECTION WELL TEST.

Seawater to be injected may form anhydrite deposits where the temperature exceeds 70 C. Should this take place within the well or in the reservoir close to the well, damage may result.

Recommendations: We cannot recommend seawater for the reinjection well test. Clean freshwater should be used. The amount of water to be injected can be reduced, if supply is limited.

3. CALIPER SURVEY.

No mention is made of caliper surveys of the wells.

Recommendations: Caliper surveys with wire baskets of full casing diameter, should be made prior to the flow- and reinjection tests and on completion of the tests. Smaller diameter baskets should be run if scaling in the wells is indicated.

4. TEST PERIOD.

The proposed flow test of 7 day's duration is not adequate to define stable production characteristics, or yield representative samples for analyses, as flashing in the reservoir is anticipated.

Recommendations: Increase the duration of the flow test to at least 28 days. The number of samples for total analysis should be increased from what was proposed for days 3 and 7 only, to additional days 1, 14 and 28. Lithium and boron should also be included in the total analyses. A reduction in the number (56) of C1, SiO2 and TDS samples should also be considered, but Na, K and B should be included in this lot. Two samples per day are considered adequate (vs. 8 samples).

5. BRINE TREATMENT.

The plan for brine characterisation is incomplete, and the disposal methods focus on ponding or hot injection. No serious attempt is made to collect vital background data by carrying out bench scale studies in the field at the time of the first production test.

Recommendations: Bench scale studies should be made of the rate of monomer decrease, growth of silica particles and sedimentation, with special emphasis on the effect of pH, temperature, condensate addition etc. To monitor scaling rates special coupons should be inserted through 2" valves with devices that allow withdrawal of the coupons under pressure for periodic inspection. The pond test scheduled for febr. 1985 is late in the program and should preferably take place during the first production test. Should the bench scale tests not be within the scope of the MHI/PPC contract, we recommend that PPC specialists undertake the tests.

6. REINJECTION.

The limited amount of brine produced from well M2 (maximum production in sept. 1983, 20 t/h), and the long distance from the injection well M1 to M2 (1.2 km) will make detection of returns of the short half-life radioactive tracer unlikely.

Recommendations: Before embarking on these tests the question of, amounts added, detection limits, and expected travel time, should be discussed with GEOSPAC.

7. CHEMICAL SAMPLING AND ANALYSIS.

Repeated mention is made of the doubtful value of earlier determinations for silica from well M2. This may be due to faulty sampling of silica. It is anticipated that the silica may already have polymerized to some extent when collected at the surface. It is necessary to treat samples with hydroxide to disintegrate the polymenrs before analysis. It seems best to dilute all samples 10 timens when collected and add NaOH. Turning the sample bassic is likely to cause some precipitation of calcium hydroxide, and even calcium silicate, due to the high calcium content of the brine. If this is the case, it will be necessary to collect the precipitate quantitatively from a known volume of sample and analyse it gravimetrically for silica. This would involve digesting the sample with 6 M HCl or fusion with Na2CO3, dry ashing followed by treatment with HF.

MHI base their recommendation of "hot injection" on the low silica value of 400 ppm (MHI doc. PG-TI-2, june 1984). This may also affect the guarantee in the contract with MHI relating to the brine treatment.

In a short description of preferred analytical procedures submitted by GEOSPAC colourimetry is recommended for the SO4 analysis. In our experience gravimetry, however, is preferable to colourimetry for brines, due to interference of cations other than barium on the colour formation. Also, analyses of H2S and CO2 should be carried out by titrations with mercuric acetate and hydrochloric acid respectively. In calculating CO2 (total carbonate) it is important to correct for the interference from weak acids in solution other thean CO2.

Recommendations: PPC request that GEOSPAC submit detailed procedures for sampling and analysis of the steam and brine as stated in the contract. PPC should furthermore show caution in agreeing to what is called "a fixed mutually agreed scaling rate". Criteria for adequate treatment for long term injection is yet to be established, and experience from Iceland shows that a scaling rate of no more than 4 mm per year in surface equipment can clog a higly permeable reinjection well in a few months.

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mr d kaloyannis, director public power corporation direction of alternative energy forms

please receive in the following our comments to the documents racieved. the report is not to be regarded as the final word on this subject. none of our experts have yet been to greece, and the comments and recommendations may therefore reflect the rathor limited information we have at our disposal. after further consultations with ppc and the contractor mhi/geospac we feel we will be in a better position to contribute to the project.

CANFILEE INTER

introduction.

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recommendation: ppc request that geospac submit detailed procedures for sampling and analysis of the steam and brine as state: ppc should furthermore show caution in agreeing in the contract. to what is called 'a fixed mutually agreed scaling rate'.
criteria for adequate treatment for long term injection is yet to
be established, and experience from iceland shows that a scaling rate of no more than 4 mm per year in surface equipment can clog a highly permeable reinjection well in a few months.

hope this was well received.

best regards for virkir/nea a svanbjornsson

773 215153 dei gr 2012 virkir is 2012 virkir is sth/sth telex 1222 attn kaloyannis

spilotis

according to request by mrs vrouzii the following information is forwarded.

bench scale studies of silica behaviour in brine.

the method for determination of silica should be checked and a good value for total silica in brine obtained before start of the bench scale study.

- test of monomer decrease rate.
- 1.1 acid-base titration curve
- 1.3
- effect of temperature. tests at 100, 80, 50, 20 deg c effect of ph at 80 deg c and ph of 10, 8, 5 and 4 effect of addition silica particles at selected ph and deg c 1.4
- effect of condensate addition at 80 deg c and 20 o/o, 40 o/o and 60 o/o condensate addition
- 2. deposition test
- 2.1 growth of silica particles, determined by filtration and gravimetry
- coupons in 3 bar pipe, to determine scaling rate 2.2
- gravity settling rate measured in a graduated cylinder 2.3
- effect of addition of silica particles on settling rate
- pand test (as per mni/geospac proposal)
- the following time estimate is made for orientation as to the 3. workload expected in carrying out the bench scale studies outlined in this tlx. a more detailed estimate should be made by the party performing the work.

time estimate (at site, mandays)

item	t1me	- 1944 1954	- 1984 - 1984		
1.1+1.2	4 days				
1.4	2 3				
2.1	2 -				
2.4	2				
	n.a. 22 days no	t including pond te	\$		

4. equipment colourimeter (410 nm), oh meter, thermometer, analytical balance, constant temp. bath, ir heating bulb, membrane filter assembly, desicator, separator (steam/water), cooling coil, pressure gauge, test coupons and inserting device, analytical reagents and equipment glasswave.

sverrir thornallsson

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APPENDIX 2

Interim report no 1. from VIRKIR/NEA to PPC.

1984.12.08

PRODUCTION WELL TEST M-2.
PROGRESS REPORT AFTER 3 DAYS OF TESTING.

1. The first phase of the MHI/GEOSPAC contract is under way at Milos. VIRKIR/NEA has had two experts on Milos for the production test, Mr. Sverrir Thorhallsson and Dr. Halldor Armannsson to witness its execution, and make recommendations, as stipulated in the contract between PPC and VIRKIR/NEA. The consultants had earlier sent recommendations to PPC regarding this test (see appendix I).

2. Meetings.

Several meetings have been held by PPC, the contractor and the consultants. The main topic of discussion has been the program proposed by MHI/GEOSPAC. Memos of the meetings have been kept and will be included in our report.

3. Preliminary results.

- -A temperature log was made of well M-2 and a maximum temperature of 318°C was recorded at 1150 m depth. This is the first temperature and pressure log of the fully hot well in a shut-in condition.
- -The well shows a temperature inversion below 1200 m.
- -Silica concentrations of up to 950 ppm have been measured in the brine at 8 bars a.
- -The initial wellhead pressure is slightly higher than expected or roughly 57 bars for an output of 17 t/h of steam.

4. Work of contractor.

- -The contractor arrived at Milos $28 \, \text{th}$ of November with equipment (Mr. A. Slatter).
- -Mr. W.A.J. Mahon arrived at Milos 30th of November. One week's preparation time at the site for the measurement engineeer suggested in the contractor's work schedule turned out to be only 3 days.
- -The contractor arrived with the required equipment in good condition, except the recovery tube and logging cable which are not yet at Milos. Use has been made of PPC equipment, but the PPC cable diameter is smaller and the recovery tube requires scaffolding.

- -The clocks in the logging instruments have failed two times so far due to leakage of seals in the probes, thus delaying the start of the production test for one day.
- -Detailed description by GEOSPAC of the production and reinjection tests to be performed were only received by PPC and the consultant after the arrival of Mr. W.A.J. Mahon at Milos.
- -The work of the contractor MHI/GEOSPAC and subcontractor (I.G.M.E) has been of a high professional standard.

5. Work of PPC.

- -The modifications and work that was given to PPC to finish in time for the test, was completed.
- -The PPC personnel and facilities were on site.

6. Heating up of well.

The heating up of the well was carried out in accordance with good practice.

7. Wellhead.

The pressure class of one wellhead valve was changed to API 5000.

8. Unresolved problems

One of the original recommendations of VIRKIR/NEA was that fresh water should be injected during the injectivity test instead of sea water as seemed to be the intention. In fact the use of fresh water is mentioned in the contract. In view of the possible damage to the injection well using sea water, it was recommended that PPC ask MHI whether the latter would assume full responsibility in case of such damage.

This matter has been discussed in great detail and PPC and MHI have not yet found a mutually agreeable solution to this problem. This has caused uncertainty as regards the starting date of the injectivity test. It is undesirable that such conflict can arise at such a late stage and the absence of authoritative personnel at meetings where the matter has been discussed has greatly hampered its progress. Another reccommendation was that bench scale studies be carried out during the first production test, but MHI deemed this unnecessary. Just how and when MHI is going to selcet and design a brine treatment process is unclear without the results of such tests.

APPENDIX 3

Milos Interim report no. 2 on 1984.12.8-13

From: VIRKIR/NEA

To: PPC

1. Introduction

As a part of the agreement between VIRKIR/NEA and PPC. Mr. S. Thorhallsson & Dr. H. Ármannsson have already given a witness account on the production test at well M-2, Milos up to the third day of production. The latter stayed until the end of the chemical sampling programme, and the following completes the above account.

2. Meetings

A meeting was held with the contractor's representatives 1984.12.10. A memo was kept and will appear in a fuller report on the consultants' visit.

3. Results of chemical analyses

The original sampling schedule could not be adhered to due to scarcity of personnel and apparatus. That schedule however, was much too stringent, and adequate information for the present purpose should have been obtained from the sampling programme actually carried out.

The results of the on site analyses were not reported to PPC on a regular basis so that an opinion of their significance has to be given with reservations, since the opportunity to study them in detail has not yet come.

Mr. W.A.J. Mahon is of the opinion that even though the enthalpy of the well is expected to rise during a longer production period little further information on the relevant chemical characteristics would be gained by a longer sampling programme, since the chemistry of the well appears to be relatively stable judging by his preliminary results. With the above reservations the consultants are of the same opinion.

4. Methods of sampling and analysis

The detailed description of sampling and analytical techniques mentioned in the contract between PPC and MHI, and requested at the meeting with PPC and the contractors in Athens 1984.11.29 has not yet been presented. A check on the method used on site has been by eye-witnessing.

As stated in the earlier account this analytical work has been performed with a high degree of professionalism. criticism will, however, be made regarding sampling for the carbon dioxide and hydrogen sulphide. determination of pH, Plastic bottles were used and transported from the well site to the temporary laboratory at the Adamas office. In our experience substantial changes in the concentrations of these constituents can take place upon such treatment. Doubtful values for affect the reliability of calculations of speciation and total composition of deep brine, but do not harm the main object of the i.e. to establish the silica and chloride present exercise, concentrations of the brine at various pressure points to aid a decision on the desirability and mode of brine treatment prior to reinjecton.

The separator used was not designed to withstand pressures as high as the well head pressure recorded (ca 57 bar), so that no sampling could be done on the high pressure line. As it happened it would have been useful to obtain such a sample since there the silica would be expected to be in monomeric form only, but it seems to have already started to polymerise in the 8 bar line.

A further note of criticism may be added on the non-availability of membrane filters but use of these is standard practice.

5. Bench scale studies for brine characterization

One of VIRKIR/NEA's original criticisms of the proposed test procedure of well characteristics and brine studies (Document 9700-2737A, Oct., 1984 submitted by MHI/Geospac to PPC) was that the plan for brine characterization was incomplete and bench scale studies on silica deposition and monitoring of scaling rates by coupon insertion was recommended during the first production test. This recommendation was followed by a telex on November 19th 1984, where procedures, necessary apparatus and manpower needed were specified after a request for this from PPC.

It was recommended that these tests be performed by PPC personnel, if the contractors did not agree to carry them out. At the Athens meeting 1984.11.29, the contractors stated that they did not feel that these tests were necessary at this stage. On our arrival in Milos it was apparent that the apparatus and manpower specified in the aforementioned telex had not been made available and it was our understanding that these tests were not to be included in the well production test programme. On December 8th, PPC informed us that an agreement had already been reached between VIRKIR/NEA and

PPC that the consultants would supervise such tests performed by PPC personnel. In our understanding such work is outside the scope of the work contract between VIRKIR/NEA and PPC.

It was, however, decided that the consultants would take on such supervision and perform as many of the tests as would be possible with the limited apparatus and manpower available during the short period that was left.

The following tests were performed with brine samples collected from the silencer outlet.

- a) Titration curve for 50 ml 0.1N NaOH and 0.1N HCl.
- b) Rate of monomer decrease of untreated brines at temperatures 19°C and 56 3°C.
- c) Rate of monomer decrease at temperature 47 5°C and pH=8.
- d) Settling rate determination attempted on untreated brine and obtained with flocculate at pH=8 (t° = 30-40°C).
- e) Attempt to assess rate of precipitate formation by first filtering a fresh sample, and the resulting filtrate after standing overnight. The results of this test are liable to be inaccurate due to inadequate apparatus.
- f) It had already been agreed that scaling rate test coupons and apparatus for their insertion be supplied and operated by the consultants. This was done.

Preliminary results of tests a) to d) have been submitted to PPC in the form of graphs. Tests e) and f) will be completed in Iceland and results sent to PPC as soon as they become available.

6. Type of fluid used in injectivity test

As is apparent from memos from meetings and earlier accounts one of the main topics of discussion during our stay regards the fluid used during the proposed injectivity test. VIRKIR/NEA's original recommendation was that clean, fresh water should be used, not sea water. On arrival in Greece, it was apparent that the provision of fresh water for such a long period of injection would prove extremely difficult. We, therefore proposed that if sea water had to be used, the injection time should be cut to a minimum, preferably not more than one week. A note was presented to PPC with calculations of possible amounts of anhydrite deposition at different temperatures from the quantity of sea water originally proposed for the injectivity test. It was shown that high enough temperature could prevail close to the well inflow during the injection to cause a danger of plugging the formation and thus

damaging the well.

As preliminary tests suggested that the rate of silica precipitation from the brine was fast, a compromise solution was suggested i.e. to pond brine and use it for the injectivity test. Although this may seem a more attractive proposition than the use of sea water it must be stated that the above tests are preliminary and much more extensive studies must be performed on the brine before its reinjection can be recommended. As, however, the use of sea water has now been rejected, our present recommendation is to use the amount of fresh water that can be made available, and let that determine the duration of the test.

It is suggested that fresh water from pumping well B constructed for the Milos geothermal project in 1979, be used as a source of injection water. Analysis of the water is published in a PPC report dated 12th February 1980. Although this could not be described as a "clean fresh water", as was originally recommended, it is certainly the best available. Inspection of the data reveals that there is a danger of small anhydrite deposition at temperatures above 250°C, but this is not a serious danger as regards the plugging of the formation.

7. Visit to IGME

One of the original briefs for the present stay in Greece was a visit to the Institute of Geology and Mineral Exploration (IGME) where most of the chemical analysis of the samples obtained during the production test will be carried out. Such a visit has been arranged for 1984.12.14., and will be reported on in the fuller report of the consultants` visit.

1984.12.13

Halldór Ármannsson

APPENDIX 4

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Milos Geothermal Power Project

Scope of Work - Chemical Analysis

VARDAR 750-31									
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1. Production Well Test - 7 day discharge.

Field Analysis

H2S 2 Determinations (Days 3 and 7) 2 Determinations (Days 3 and 7) 2 Determinations (Days 3 and 7)

CO²

2 Determinations (Days 3 and 7)

Chloride

56 Determinations (8 per day)

Silica

56 Determinations (8 per day)

Silica 56 Determinations (6 PH & Temperature -All aqueous samples

Laboratory Analysis

Brine

Potassium 2 Determinations

Sodium 2 Determinations

Calcium 2 Determinations

Magnesium 2 Determinations

Sulphate 2 Determinations

Ammonia 2 Determinations

Ammonia 2 Determinations (optional Field Analysis Total Disolved Solids 56 Determinations (optional Field Analysis

Residual gases-O² 2 Determinations

N² 2 Determinations

H² 2 Determinations

Methane 2 Determinations

CO 2 Determinations

Dissolved Oxygen 2 Determinations

Carbonate 2 Determinations

Sulphide 2 Determinations

Brine Test (Assume 7 day period)

Confirmation of all analysis from production well test.
 -Assume same number of field and Laboratory analysis determinations as for Production Well Test.

(ii) Addtional Field Analysis

Silica - 56 Determinations
Chloride - 56 Determinations

Pipe scale - 21 Visual Inspections

PH & Temperature - 56 Determinations

(iii) Additional Laboratory Analysis

Analyse Sample of Pipe Scale - 3 Determinations Incl. Weight and Thickness.

3. Reinjection Test (30 day period)

(i) Field Analysis

H'S - 4 Determinations

CO' - 4 Determinations

Silica - 90 Determinations

Chloride - 90 Determinations

Pipe scale - 12 Visual Inspection

PH & Temperature - 90 Determinations

(ii) Laboratory Analysis

Analyse Sample of Pipe Scale - 3 Determinations Incl. Weight and Thickness.

Ka, Na, Ca, Mg, Sulphate - 4 Determinations each
Ammonia, Total Disolved Solids- 4 Determinations

Preferred Analytical Procedures

- 1) Hydrogen Sulphide-Titrimetry using Iodine/Thiosulphate
- 2) Carbon Dioxide/Bicarbonate/Carbonate-Titrimetry using caustic soda/hydrochloric acid.
 - Note: Titrimetry preferable to gas chromography as less problems with collection and analysis. Geospac experience shows gas chromography to be less reliable at low gas levels and results liable to interference from water, but may be acceptable subject to specific laboratory procedure approval.

- 3) Sodium/Potassium-Flame Photometry (AA Acceptable)
- 4) Sulphate-Colourimetry using Barium Chromate or Barium Chloride Note: Geospac experience is that gravimetry method may have large interference from other solids in solution.
- 5) Silica Colourimetry using ammonium molybuate(Oxalic Acid. Note: Kitsets available.
- 6) Total Solids Gravimetry at 105°C.
- 7) Chloride Titrimetry using silver nitrate/potassium chromate.
- 8) Calcium & Magnesium Atomic Absorbtion.
- 9) Ammonia Using Nessler Reagent

Note: Highly Saline Waters could cause interference using specific ion electrode method.

For other components requiring analysis, laboratory to submit procedure for approval.

EQUIPMENT

Geospac will supply the following items:

- (i) Webre Sample Separator
- (ii) Gas collection apparatus including rotoflo flasks
 5 litre collection vessels, and safe y equipment.
 - Note: Laboratory required to supply butyl rubber tube and sealing clips as follows:
 - 21 mm O.D., 7 mm I.D. 2 metre
 - 27 mm O.D., 21 mm I.D. 2 metre
 - 14 mm O.D., 5 mm I.D. 2 metre

Also 1 pair of forceps.

- (iii) Plastic sample collection Bottles.
 - Note: Laboratory to supply pre-weighed glass collection bottles for total dissolved solids determinations.
- (iv) A portable deionised water column and resin for field use.

All other glass ware, chemicals and equipment mentioned in the attached telex and other items that may be required to facilitate the sample analysis will be provided by the laboratory for both field and laboratory use.

Schedule

The Production Well test, Brine test and reinjection test will be carried out during separate periods.

Field results will be determined on a daily basis and laboratory determinations must be completed and the results submitted within 15 days of receipt of sample.

Costs

The Laboratory is to quote for the following services.

(Note: A Geospac Chemist will be on site for the production and Brine tests and at the beginning of the reinjection test).

(i) Production Well Test:

Field Analysis

Daily rate of Chemist incl. travel and subsistence Daily rate for materials and equipment Cost per determination for each component specified TOTAL COST FOR THIS SECTION

Laboratory Analysis

Cost per determination for each component specified TOTAL COST FOR THIS SECTION

(ii) Brine Test

Field and Laboratory Analysis costs same format as (i) above.

(iii) Reinjection Test

Field and Laboratory Analysis costs same format as (i),(ii) above.

(iv) Total Quotation-Sum of (i), (ii), (iii) above.

APPENDIX 5

SAMPLING AND ANALYTICAL METHODS

Orkustofnun - National Energy Authority Geothermal Division. 1984 10.12 HA/TH

1. SAMPLING - GENERAL

1.1 SAMPLING POINT

shall be a horizontal outlet (>1/2") on the line, ideally about 1.5 m from T-joint on well-head.

1.2 SEPARATION

of liquid and vapor phase should be carried out under pressure with minimal pressure drop between pipeline and separator (Valve fully open). The separator should be insulated to prevent condensation.

1.3 COOLING

The separated steam and liquid phase shall be cooled down to ambient temperature in small diameter stainless steel spiral tubes.

1.4 SEPARATION EFFICIENCY

To check for separation efficiency during sampling no bubbles should be observed in the liquid phase flow and the steam cone should be checked for dryness.

The sodium or chloride concentration of the condensate fraction is determined and compared with that of the water fraction as a further sampling efficiency test (see below).

1.5 SAMPLE FRACTIONS

Steam can be collected by one of two methods (2.1 and 2.2-2.3 respectively). The first method involves sampling into NaOH solution in an evacuated flask. The second method involves separate collection of condensed steam and non-condensable gases. Sampling of the liquid phase is described under 2.4.

1.6 PRECAUTIONS

Before sampling always rinse the sample container three times with the fluid to be sampled. Fill the gas sample tubes completely and leave no space for air. Always write down the sampling temperature and pressure. Well head pressure, enthalpy and flow at the time of sampling have to be known.

2. SAMPLING OF DIFFERENT FRACTIONS

2.1 STEAM

Add 50 ml 40% sodium hydroxide solution to a round bottomed flask and evacuate. Collect gas and condensate until the pressure inside the flask is slightly below atmospheric pressure. Shake vigorously.

2.2 NON-CONDENSABLE GASES

Fill gas sampling tube with condensate, reverse the tube (or flow) and drive the condensate out with the gas.

2.3 CONDENSATE

Collect samples for the determination of pH and volatile constituents into a gas sampling tube. Collect a separate 100 ml sample into a plastic bottle for the determination of sodium, as a check on sampling efficiency.

2.4 LIQUID PHASE

Collect samples (Ru = Raw, untreated) for the determination of pH and volatile constituents into gas sampling tubes, but the rest into four plastic bottles marked as follows.

Rd: raw, diluted 1/10 with distilled water for SiO₂ determination

Fu: filtered, through 0,45 um membrane filter, untreated.

Fp: filtered, precipitated by adding 10 ml 0,2 M ZnAc₂ to a 500 ml volumetric flask and filling to the mark with the sample (for sulphate analysis)

Fa: filtered, acidified by adding 1 ml 6N HCl to a 500 ml volumetric flask and filling to the mark with the sample

Thus the following determinations are done on the different samples.

Ru: pH, CO₂, H₂S

Rd: Si0₂

Fu: F, conductivity, total dissolved solids

Fp: C1-, S0₄

Fa: Na, K, Ca, Mg

3. ANALYTICAL METHODS FOR STEAM FRACTION

3.1 CARBON DIOXIDE

To 2 ml of the sample and 2 drops of 30% H_2O_2 (to destroy H_2S). Allow to stand for 1 min. then dilute to 50 ml. Adjust the pH to 8,2 with hydrochloric acid, and titrate from pH 8,2 to pH 3,8 with 0.1 N HCl using a glass electrode. Subtract blank contribution.

3.2 HYDROGEN SULPHIDE

Add 0.1 - 0.5 ml of the sample solution (2.1) to 10 ml distilled water. Add 5 ml 5N sodium hydroxide solution, 5 ml acetone and a few dithizone crystals. Titrate with 0,001 M mercuric acetate.

4. ANALYTICAL METHODS FOR NON-CONDENSABLE GASES

Gas chromatography employing a Poropak column for acid gases (CO_2 , H_2S), and a Molecular Sieve column for other gases (H_2 , N_2 , O_2 , CH_4). Hydrogen is extracted from the helium carrier gas stream through a palladium tube and detected in a nitrogen gas stream with thermal conductivity detectors.

5. ANALYTICAL METHODS FOR CONDENSATE FRACTION

5.1 pH

Use glass electrode, calibrate with buffers (pH = 4.7 and 9)

5.2 CARBON DIOXIDE

Run 50 ml of sample into a volumetric flask, containing 0,4 ml 5N NaOH, immediately upon opening the sampling tube. Titrate from pH 8,2 to pH 3,8 with 0,1 N HCl using a glass electrode. Subtract blank and hydrogen sulphide contributions.

5.3 HYDROGEN SULPHIDE

Run 50 ml of sample into a volumetric flask, containing 0.4 ml 5N NaOH, immediately upon opening the sampling tube. Add 0.1 - 1 ml to ca 10 ml water. Add 5 ml 5N sodium hydroxide solution, 5 ml acetone and a few dithizone crystals. Titrate with 0.001 M mercuric acetate as soon as possible.

5.4 SODIUM

Either determine directly flame - photometrically or at 589 nm by AAS adding a large excess of a lithium salt.

6. ANALYTICAL METHODS FOR LIQUID PHASE

6.1 pH

Use glass electrode, calibrate with buffers (pH = 4,7 and 9).

6.2 CARBON DIOXIDE

Titrate 50 ml of sample from pH 8,2 to pH 3,8 with 0,1 N HCl. Subtract on a theoretical basis interferences from water, hydrogen sulphide, silica and boron.

6.3 HYDROGEN SULPHIDE

Run 50 ml of sample into a volumetric flask, containing 0,4 ml 5N NaOH, immediately upon opening the sampling tube. To 1-50 ml add 5 ml 5N NaOH solution, 5 ml acetone and a few dithizone crystals. Titrate with 0,001 M mercuric acetate.

6.4 SILICA

Dilute sample 10 times upon collection (giving < 100 ppm $\mathrm{Si0}_2$) to avoid polymerization (Rd). If $\mathrm{H}_2\mathrm{S}$ is present in significath amounts (1 ppm) add 0.1 N iodine to 10 ml of diluted sample to oxidize sulphide (till iodine colour is persistent) and then 0,05N sodium thiosulphate solution to destroy excess iodine. Add 2 ml 10% ammonium molybdate solution and 1 ml 6 N hydrochloric acid, dilute to 50 ml and determine spectrophotometrically at 410 nm. For control purposes boil a few samples with NaOH before determination (total silica). If results are higher this way, all samples will have to be treated thus.

6.5 SULPHATE

Filter sample (Fp) and pass filtrate through a cation exchange resin. Add 20 ml propanol-2 and 1-2 drops 0,2% thorin solution to 5 ml sample. Titrate with 0.005 N barium perchlorate solution. In saline waters sulphate must be determined gravimetrically as barium sulphate.

6.6 CHLORIDE

Filter sample (Fp). If H_2S is present significant amounts add 1N H_2SO_4 to filtrate and heat on a water bath to remove sulphide. Take care that pH is not higher than 8.2. Employ Mohr titration with $AgNO_3$ and potassium chromate indicator.

or

Filter sample (Fp), acidify the filtrate with nitric acid and blow free of H₂S with air, add 30% hydrogen peroxide to remove all traces of sulphide. Add a measured excess of silver nitrate. Remove the silver chloride precipitate by centrifugation (must be white; brownish color indicates sulphide), and determine silver in the remaining solution by AAS at 328,1 nm. Calculate the chloride concentration from the difference in silver concentrations between blank and solutions.

6.7 SODIUM

Determine a suitably diluted sample at 589 nm by AAS adding a large excess of a lithium salt. Flame photometry may also be employed.

6.8 POTASSIUM

Determine a suitably diluted sample (Fa) at 766,5 nm by AAS. Flame photometry may also be employed.

6.9 CALCIUM

Determine a suitably diluted sample (Fa) at 422,7 nm by ASS, adding 2 ml 5% lanthanum oxide solution to 10 ml of diluted sample to overcome interferences.

6.10 MAGNESIUM

Similarly add to diluted sample (Fa) lanthanum oxide solution and determine at 284,2 nm by AAS.

6.11 FLUORIDE

Add TISAB buffer to sample (Fu) and standards and determine concentrations by means of fluoride selectrode.

6.12 CONDUCTIVITY

Use conductivity bridge or suitable electronic equipment on samples (Fu).

6.13 DISSOLVED SOLIDS

Evaporate sample (Fu) to dryness at 105°C and determine gravimetrically.

7. ANALYTICAL METHODS FOR SOME MINOR CONSTITUENTS

7.1 BORON

Determined spectrophotometrically in condensate and liquid (Fu) fractions with either curcumin or methylene blue.

7.2 AMMONIA

Determined in condensate and liquid (Ru) fractions, spectrophotometrically as indophenol blue, preferably in a closed circuit set up, such as an Auto-Analyser, as soon as possible after collection. If any storage is necessary, samples will have to be frozen.

Alternatively ammonia can be determined in the field with a specific ion electrode after the addition of sodium hydroxide to the sample.

7.3 ARSENIC

Determined spectrophotometrically with silver diethyldithiocarbonate after generation of arsine with sodium borohydride in condensate and liquid fractions to which potassium permanganate and nitric acid are added upon collection.

7.4 ALUMINIUM

Determined fluorometrically in liquid fraction sample (Fa) with lumogallion.

7.5 MERCURY

Determined by flameless AAS after amalgamation on gold in steam and water (filtered) fractions which are specifically collected into a permanganate solution acidified with nitric acid.

7.6 IRON

Determined by AAS or spectrophotometrically with phenanthroline on liquid sample (Fa).

7.7 MANGANESE

Determined by AAS or spectrophotometrically by periodate oxidation of malachite green leuco base to malachite green.

7.8 CADMIUM, ZINC, COPPER, LEAD, COBALT, NICKEL AND SILVER

By AAS on liquid fraction, preferably after on site extraction with dithizone/chloroform or APDC/MIBK, or after a similar extraction of stored sample (Fa).

7.9 NITRITE AND NITRATE

Spectrophotometrically on liquid sample (Fu) after diazotization and coupling with sulphanilamide and N-(1-napthyl) ethylenediamine directly for nitrite, but after reduction with a cadmium-copper column for nitrate.

7.10 PHOSPHATE

Spectrophotometrically with ammonium molydate, ascorbic acid and potassium antimonyltartrate on liquid sample (Fa).

7.11 OTHER METALS

The possibility of analysis for antimony, chromium and vanadium has arisen, but no simple method can be recommended for the relatively low concentrations which could be expected in geothermal waters.

7.12 ION CHROMATOGRAPHY

NEA has available an ion chromatograph. Where such an instrument is available, it can be recommended for the analysis of most common anions, e.g. Cl⁻, Br⁻, I⁻, F⁻, NO₂⁻, NO₃⁻ (Fu) and SO₄⁻² (Fp).