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SCALING PROBLEMS WHICH COULD APPEAR AT GEOTHERMAL WATER UTILIZATION IN WESTERN PART OF ROMANIA

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ABSTRACT

This paper presents the research made upon the scaling problems which could appear at geothermal water utilization in western part of Romania. Emphasis was placed on the geothermal fields of Borş and Ciumeghiu.

Geothermal waters from two production wells were sampled during years and analysed using standard methods. The chemical monitoring has given the chemical changes that may later lead to scaling. Based on the chemical composition of these waters, by using a chemical computer program were assessed in time the scaling depositions which could appear at geothermal utilization when the temperature decreases. Severe scaling problems have been encountered.

Scaling monitoring device were installed into two wells for one year. The scale deposits were analysed thermic differential and by X-ray diffraction. The experimental results were compared to those that were obtained by using the computer program.

1. INTRODUCTION

Geothermal energy is currently utilized in many parts of the world not only for space and process heat for residential, commercial and industrial uses, but also for electricity generation.

Geothermal energy utilization has increased due to the low cost. Thermal energy delivered in large volumes near a geothermal reservoir might cost as little as one-fifth that of fossil fuels. It also has the advantage over other available domestic resources that is an unpolluted resource.

The main geothermal reservoir exploited in Romania is located in the western part of the country. The Borş reservoir is an integrated part of this principal reservoir. The reservoirs are usually named after towns or villages located in or close to the respective geothermal field. The Ciumeghiu geothermal reservoir is also located in the western plain of Romania, south of Oradea.

In Romania geothermal energy is used in various domains. The main uses are space heating and warm water preparation for domestic use, greenhouse heating, wood drying, milk pasteurisation and fish farming. Geothermal waters from Borş and Ciumeghiu are especially used for greenhouse heating. Due to the temperature decrease during utilization of these waters, depositions could appear in process equipment, piping, disposal channels.

2. FLUID CHEMISTRY

Geothermal waters from two production wells from Borş and Ciumeghiu were sampled and analysed by the following analytical methods:

- total carbonate was determined by electrometric titration
- hydrogen sulphide was determined by titration using dithizone
- ammonium – spectrophotometric determination at λ = 420 nm, using tetraiodomercuriat dipotassic
- sodium, potasium – flamephotometric determination, λ = 589 nm, respective λ = 767 nm
- magnesium, calcium – titration with EDTA
- boron – spectrophotometric determination using azomethine method; absorption was determined at 420 nm
- aluminium – spectrophotometric determination at λ = 535 nm by using eriocromcyaninum
- ferrum - spectrophotometric determination at λ = 510 nm, using phenantroline
- silica - spectrophotometric determination using ammonium molibdate; absorption was determined at 410 nm
- fluoride – selective electrode
- chloride, sulphide – titration using potassium chromate as indicator, respective thorin
- total dissolved solids – gravimetric analysis.

All samples were collected from thermal springs with artesian flowrate. The wellhead temperatures measured during collection of water samples ranged from 90°C to 115°C at Borş and from 84°C to 101°C at Ciumeghiu. The pH is neutral or slightly acid at Borş, except in 1989 and slightly basic at Ciumeghiu. All the analytical results are presented in table 1 and 2.

The chemical data from Borş show that sodium and chloride presents a very high concentration. The sulphate and silica are also in big amount. The mineralisation of geothermal water from Borş is around 11 g/l in most of the years which were taken for studies.

The analytical results from Ciumeghiu show a very high CO_2 concentration. The SiO_2 concentration is also rather high. Compared to the results from Borş they can notice the presence of boron in a higher concentration and sodium, chloride and sulphate are in big amount, but less than in geothermal water from Borş. Fluoride and hydrogen sulphide were detected in small amounts. The mineralisation is about 6-7 g/l.

Changes of the major components concentration with time, for geothermal waters from Borş, 529 and Ciumegiu, 4668 are presented as folows:

The calcium concentration in the geothermal water from well Borş-529 got a maximum value in 1988. Then the concentration decreased suddenly to 84 mg/l in 1989, but thereafter there was a tendency to increase with time. The calcium concentration in the geothermal water from well Ciumeghiu-4668 is lower than in well Borş-529. The Ca concentration increased from 1986 until 1993, when was recorded the maximum, about 46 mg/l. After that the concentration decreased a little and then, starting by 1995 the calcium concentration has continuously increased.

The CO_2 concentration at well Borş presents a similar tendency as calcium, starting by 1988. At the beginning the concentration was higher than in the last years. The minimum value of CO_2 was about 860 mg/l in 1989. After that year the CO_2 concentration increased to 1030-1070 mg/l. CO_2 presents a high concentration in geothermal water from Ciumeghiu, but its concentration has decreased from about 2900 mg/l in 1986 to about 2080 mg/l in 1998.

The sulphate concentration in geothermal water from Borş was maintained around 160-170 mg/l from 1988 until 1997. In 1998 it was recorded a low value for SO_4, about 120 mg/l. The sulphate concentration in geothermal water from Ciumeghiu was maintained in range 46-60 mg/l.

The sodium concentration changes in time like chloride concentration for the geothermal water from Borş but the values are between 3100-4500 mg/l. The concentration increased from 3100 mg/l in 1989 to 4200 mg/l in 1998. In geothermal water from Ciumeghiu the sodium concentration is a little bit smaller in 1993 than in 1986. After 1993 it decreased rapidly to about 1700 mg/l in 1995. Since 1995 the sodium concentration has increased continuously until 1998, when the concentration value was 2150 mg/l.

The chloride concentration in water from well Borş-529 was not stable, showing a low concentration in 1989, but before and after this year the Cl concentration was very high. Since 1989 there was a tendency to increase with time. The values of Cl concentration are around 6000 mg/l. This increase in chloride could be due to vaporization of the fluid passing through the aquifer. The range of chloride concentration in geothermal water from well Ciumeghiu-4668 is 600-1800 mg/l. The minimum value was recorded in 1995. In the last years the chloride concentration increased, beeing around 1800 mg/l in 1998.

In geothermal water from Borş the SiO_2 concentration was about 120 mg/l in 1987. In 1988 it had a low value, 80 mg/l and then it increased rapidly to 170 mg/l in 1989. After that the concentration values were between 140-170 mg/l. In geothermal water from Ciumeghiu the silica concentration has increased during the period 1986-1998 from about 110 mg/l to 180 mg/l.

In geothermal water from well Borş-529 the concentration of the major components has been increasing since 1989, only sulphate concentration has decreased. The tendency of the major components of geothermal water from well Ciumeghiu-4668 was to increase since 1995, except CO_2 which has decreased. Sulphate concentration hasn't changed too much.

3. STUDIES ABOUT THE INFLUENCE OF THE TEMPERATURE ON MINERAL DEPOSITIONS

The decrease in temperature of geothermal water parallels the solubility in the system, that means a supersaturation, resulting scale depositions. The composition and the mineralogical structure of these depositions depend on the chemical composition of geothermal water, the temperature of water and the composition of the distribution system material.

Based on the chemical composition of geothermal water, Watch program was used to predict the potential danger of scaling. The ionic balances for the samples calculated by the WATCH program gave values ranging from $-0.69 \div 5.88$ at Borş and $-1.09 \div 3.69$ at Ciumeghiu, which are acceptable for equilibrium calculations. The date could be used for interpretation. Based on data from table 1 and 2 the Watch program was used to calculate the saturation indexes, logQ/K for the minerals which could start to precipitate, assuming a conductive cooling in steps of about 20^0C. When Q=K the solution is exactly saturated or in equilibrium with the mineral in respect. If the water is in equilibrium most of the curves will intersect the saturation line at almost the same temperature. If there occur two or more main intersections, the fluid is likely to have reequilibrated at a lower temperature, still keeping memory of an equilibrium at higher temperature. Figures 1 and 2 show the dependence of saturation index on the temperature for different minerals.

In figure 1, the first diagram from Borş shows that most of the minerals calculated are found to be fairly close to saturation at chalcedony temperature. Wollastonite, chrysotile, andydrite and amorphous silica are undersaturated. Calcite is close to saturation at the wellhead temperature. The diagram from Borş in 1988 shows that calcite is slightly supersaturated at the wellhead temperature. We can expect calcite scaling. Talc is supersaturated at higher temperatures than 90^0C, but this does not create problems. In 1989 many minerals show equilibrium near the chalcedony temperature. Wollastonite, andydrite and amorphous silica are undersaturated as in the sample from 1987. At the wellhead temperature calcite is slightly supersaturated. Chrysotile and talc are supersaturated. The curves for quartz, chalcedony, amorphous silica, anhydrite, wollastonite are close to the saturation line at the wellhead temperature.

In 1993 at well Borş-529 at the measured temperature, 105^0C the curves for talc and chrysotile are scattered. Calcite is supersaturated. There were scaling problems. The curves for wollastonite, andydrite, amorphous silica are obviously undersaturated. Most of the minerals have the tendency to be close the equilibrium line at the measured temperature. In the sample from 1995 the diagrams are a little more scattered than in 1993. At the measured temperature there are scaling problems with calcite. The figure from 1996 shows that talc and chrysotile are supersaturated at the wellhead temperature, 99^0C. Supersaturation of calcite increased to a dangerous value at the measured temperature. The figure from 1997 presents the variation of calcite against temperature. There is supersaturation of calcite. There are still supersaturations of talc and chrysotile at the measured temperature, 94^0C. In 1998 the curve for chrysotile is modified compared to the previous years, so at the wellhead temperature, 90^0C chrysotile is undersaturated. Calcite still remained supersaturated. The other minerals are undersaturated or close to the saturation line at the measured temperature.

The values for log Q/K of calcite indicate scaling problems at well 529 from Borş during the period 1988-1998. At the measured temperature calcite scaling has been observed.

In the sample from well Ciumeghiu-4668, figure 2, in 1986 some minerals are close to saturation. Wollastonite, andydrite and amorphous silica are undersaturated. The water is slightly saturated with calcite at the measured temperature, 101°C. The figure from 1993 shows an equilibrium with the minerals at the wellhead temperature, 93°C. The diagram looks different to the previous. The equilibrium temperature for chalcedony corresponds to the measured temperature. The water is supersaturated with laumontite, microcline, albite, adularia, analcime and calcite.

In 1995 at the measured temperature the minerals are undersaturated, saturated or near the saturation line. The log Q/K for magnetite is very high, maybe due to the corrosion of the pipe. Calcite presents a dangerous value for the saturation index. The curves intersect between 60-80°C. This could be due to an increased importance of the colder aquifers in the production water. In 1996 the diagrams are scattered. At the wellhead temperature, 85°C could be observed the supersaturation of magnetite, talc, chrysotile, goethite and calcite. The equilibrium is perturbated probably due to the mixing of waters from aquifers at different temperatures.

In 1997 the pattern of diagrams is still similar like in 1996. They can say that minerals are not in equilibrium at the wellhead temperature, 85°C. In 1998 the curves remained very scattered. It could be a result of mixing of the geothermal water with solutions of different chemical compositions which would have the effect of disturbing the equilibrium. Wollastonite, anhydrite, fluorite are undersaturated, calcite and goethite are slightly supersaturated, chrysotile, talc and magnetite are supersaturated as well. The other minerals are close to the saturation line. Chalcedony crosses the equilibrium line at the measured temperature, 84°C. At any temperature precipitation of calcite may be inevitable.

Both in Borş and in Ciumeghiu they can notice the tendency of decreasing the temperature of the reservoirs.

4. STUDIES ABOUT SOLID DEPOSITIONS

Scale formation has been of grave concern in geothermal resource development and utilization as scales interfere with the production capacities of wells by clogging the boreholes and in other cases, the pipes. After the interpretation of the chemical data by using Watch program, scaling problems were expected both in Borş and Ciumeghiu.

Test plates were inserted at the wellheads of Borş-529 and Ciumeghiu-4668 in September 1997 and let there until May 1998. The test plates have been installed during the production of the wells. After the production was stopped the plates were removed and analysed by X-ray diffraction, giving information about the existence of crystals in the solid samples. The XRD studies were made using KαCu radiations. The diagram obtained for the solid depositions from well Borş-529, figure 3 shows there are aragonite crystals in the sample. The diagram obtained for the solid depositions from well Ciumeghiu-4668, figure 4 shows that there are calcite and magnesian crystals in the sample. The solid sample from Borş was also thermic-differential analysed. The diagram, figure 5 shows that at 600°C it starts a slow and continue decomposition process, which become stronger at 750°C. At 920°C the decomposition process is very accentuate. The mass loss is about 43,5%, that means that all depositions sample consists on $CaCO_3$ as main, the loss beeing CO_2.

5. CONCLUSIONS

Geothermal waters have a complex chemical composition depending on the aquifer. An assessment of potential scaling problems and an indication of conditions in the field were obtained through careful interpretation of the analytical data. Analysis made in many years for geothermal waters from well Borş-529 and Ciumeghiu-4668 have been calculated in the Watch program at production temperature and by cooling in steps of 20°C. The saturation indexes for many different minerals were calculated, establishing the minerals which would form depositions by cooling the geothermal water.

The structural analysis of depositions show that at the wellhead temperature the depositions are formed as main by a crystalline phase: aragonite at Borş and calcite, magnesian at Ciumeghiu.

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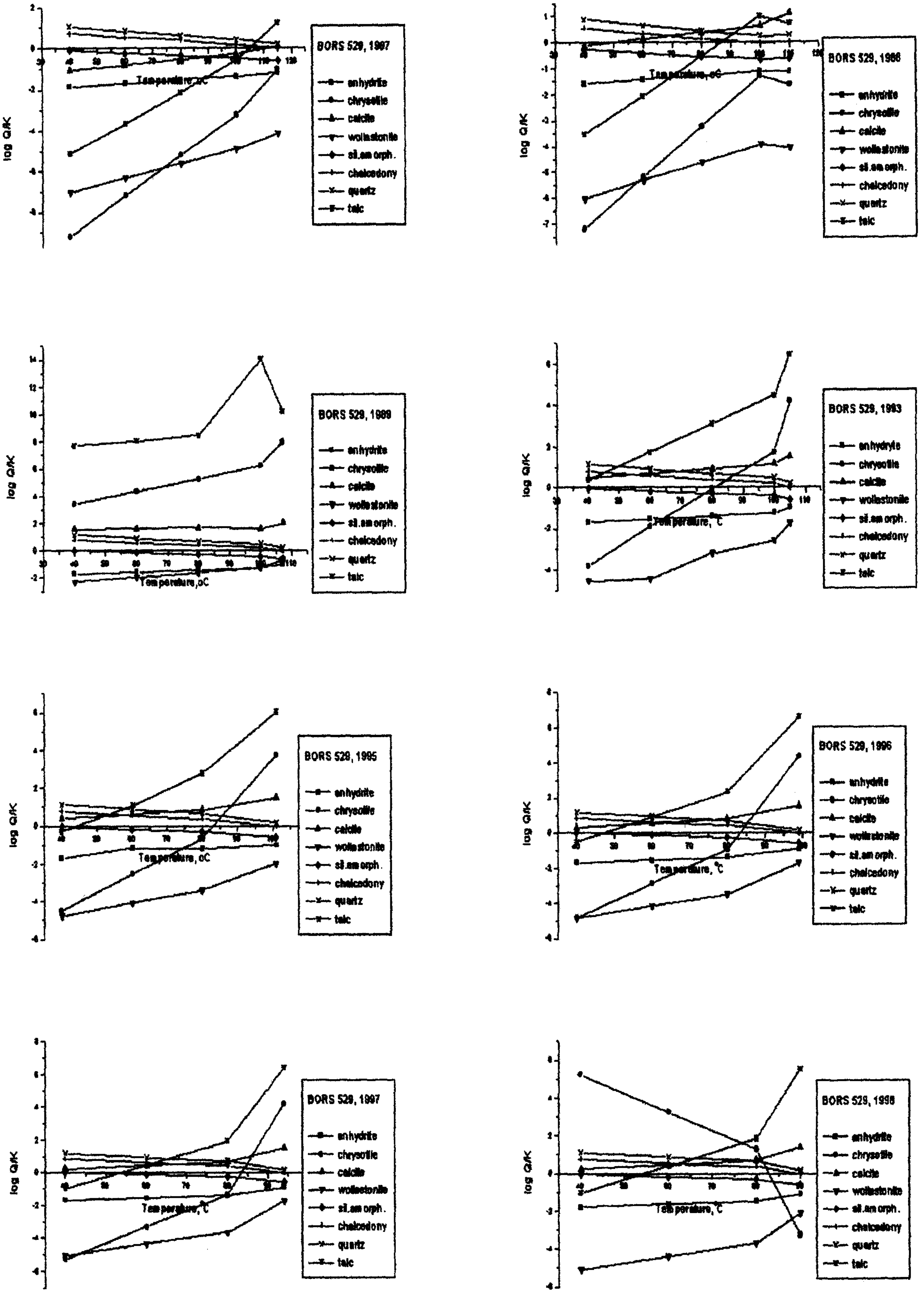

Figure 1. Log Q/K vs. temperature for geothermal water from well Borş-529, during 1987-1998

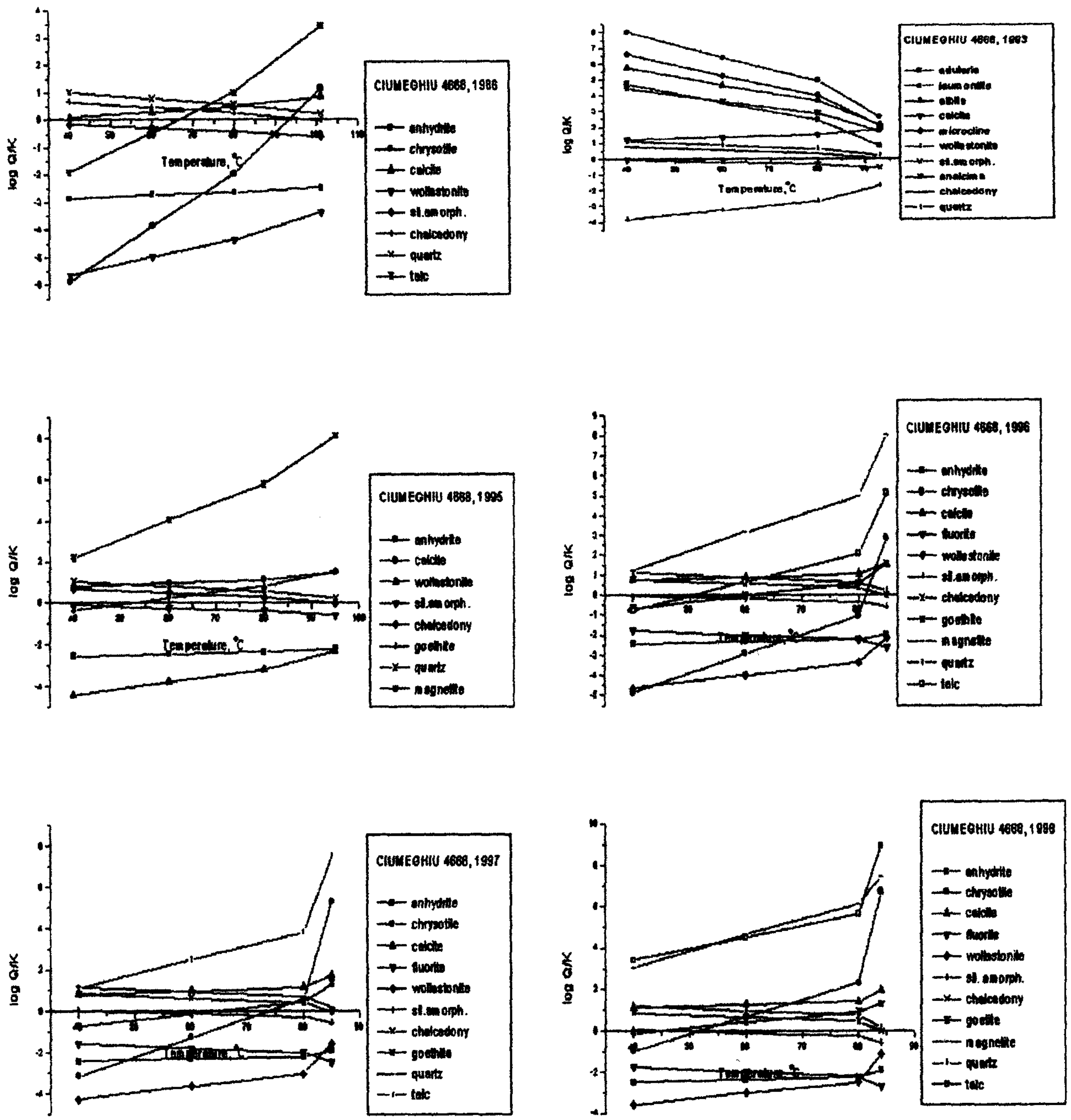

Figure 2. Log Q/K vs. temperature for geothermal water from well Ciumeghiu-4668, during 1986-1998

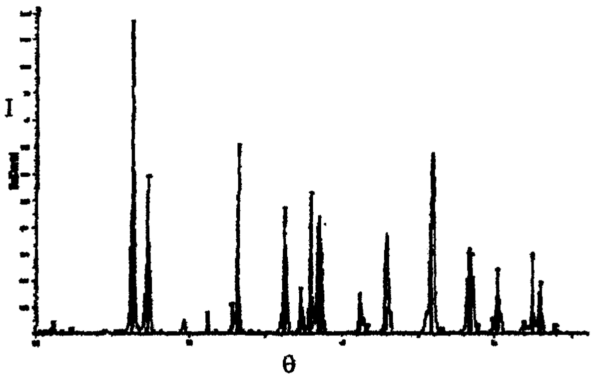

Figure 3. The XRD diagram for depositions from Borş.

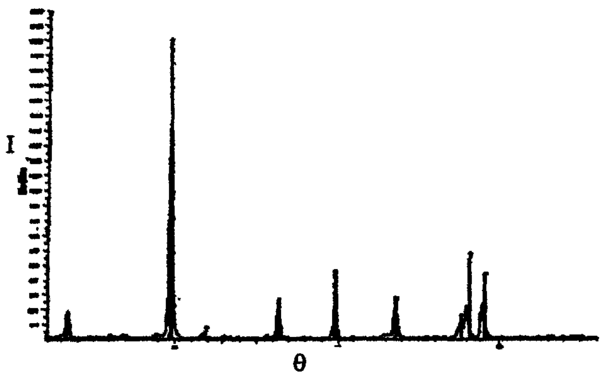

Figure 4. The XRD diagram for depositions from Ciumeghiu.

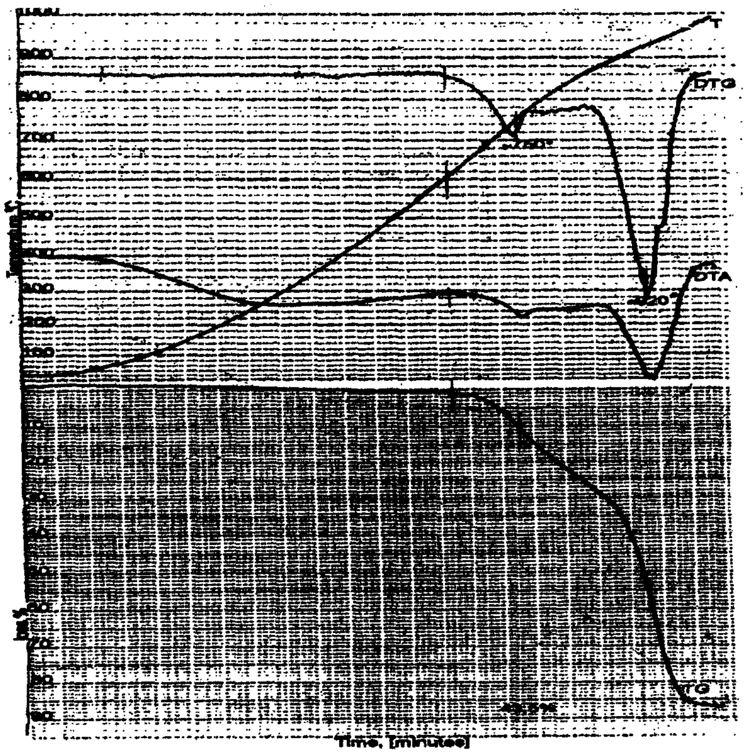

Figure 5. The thermic-differential diagram for depositions from Borş.

Table 1. The chemical composition of geothermal water from Borş, well 529 during the period 1987-1998, in mg/l.

	1987	1988	1989	1993	1995	1996	1997	1998
pH	6	6.5	8.5	7.2	7.1	7	6.9	6.9
CO_2	1169.96	1179.34	858	920	1032	1040	1073	1041
SiO_2	122	80	168	143.6	142.7	163.1	165.3	140
B	48.71	-	-	42.8	41.2	42.3	45.3	49.3
Na	4500	4000	3098	3680	3735	3833	4137	4200
K	220	550	300	267.7	270.3	283.2	320.5	381.5
NH_3	0.94	3.02	15.11	7.3	7.5	6.7	6.2	5.77
Mg	39.76	24.4	12.2	8.7	8.9	9.8	11.3	12.7
Ca	84.76	134	84	91	94	101.3	107.6	112.3
Fe	16.4	9.3	3	2.8	3.1	4.8	7.2	9.8
SO_4	135.4	170.3	170	168	163	160.8	158.8	121
Cl	6560	6205.5	4602	5107	5370	5543	6137	6248
TDS	11640	11200	8830	10357	10893	10997	11198.1	11203.5

Table 2. The chemical composition of geothermal water from Ciumeghiu, well 4668 during the period 1986-1998, in mg/l.

	1986	1993	1995	1996	1997	1998
pH	7.1	7.78	7.6	7.4	7.5	7.85
CO_2	2870.8	2736.6	2580.8	2390	2209.3	2080.3
H_2S	-	0.65	0.63	0.52	0.6	0.63
SiO_2	109	132	116	133.4	163	179
B	104.8	119.5	50.9	-	81.8	95.6
Na	2350	2206.22	1715	1815.8	1998	2150
K	40	38.2	30.3	30	34	33
NH_3	27	-	2.72	7.4	8.6	9.2
Mg	4	-	-	1.7	3.5	4.2
Ca	16.6	46	24	32.2	37.3	41.4
Al	-	1.39	-	-	-	-
Fe	0.42	2.8	0.17	0.2	0.12	0.14
F	-	-	-	0.8	0.98	0.75
SO_4	49.3	-	58	59.2	53.7	46.2
Cl	1580	1276	676	1060	1478.3	1790.2
TDS	6940	7327.15	5900	6130.5	6408.7	6514