

TYPES OF SCALING OCCURRING BY GEOTHERMAL UTILIZATION IN A LOW TEMPERATURE GEOTHERMAL FIELD

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ABSTRACT

The chemical composition of some geothermal waters from Romania were interpreted by using the Watch program, which gives information about the mineral equilibrium and a basis to assess possible scaling and corrosion problems.

The Ciumeghiu geothermal field was chosen for study. Chemical analysis from a well were selected for interpretation. Samples were taken and total analyses were made. The results were compared to results of former years by using the Watch program and the saturation index for different minerals calculated.

During exploitation of these waters, scale deposits were noticed. A solid sample of these depositions was analysed by X-ray diffraction, by infrared spectrometry and thermo-differential. For monitoring of scaling and corrosion a scaling device was proposed.

INTRODUCTION

The main geothermal reservoir exploited in Romania is located in the western part of the country. The Ciumeghiu geothermal reservoir is also located in the western plain of Romania, south to Oradea. The aquifer consists of gritstones at the average depth of 2200 m. Geothermal water is produced by artesian flow with a wellhead temperature in a range of 105⁰-80⁰C.

Geothermal waters from Ciumeghiu are especially used for greenhouse heating. Due to the temperature decrease during utilization of these waters, scaling problems could appear in process equipment, piping, disposal channels. The type of scaling depend on the chemical composition of geothermal waters.

FLUID CHEMISTRY

Geothermal waters from the production well 4668 from 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 $\lambda=420$ nm, using tetraiodomercuriat dipotassic;
- sodium, potassium – flamephotometric determination, $\lambda=589$ nm, respective 767 nm;
- calcium, magnesium – titration with EDTA;
- boron – spectrophotometric determination using azomethine method; absorption was determined at 420 nm;
- aluminium - spectrophotometric determination at $\lambda=535$ nm by using eriochromcyaninum;
- ferrum - spectrophotometric determination at $\lambda=510$ nm using phenantroline;
- silica - spectrophotometric determination using ammonium molibdate; absorption was detected at 410 nm;
- fluoride – selective electrode;
- chloride, sulphide – titration using potassium chromate as indicator, respective thorn;
- total dissolved solids – gravimetric analysis.

The results are presented in table 1. The wellhead temperatures measured during collection of water samples ranged from 84⁰C to 93⁰C. The pH is slightly basic at Ciumeghiu. Fluoride and hydrogen sulphide were detected in small amounts. They can notice the presence of boron. The mineralisation is about 6-7 g/l. Waters present a very high CO₂ concentration, but the concentration has decreased from about 2740 mg/l in 1993 to about 2045 mg/l in 1999. The SiO₂ concentration is also rather high. The silica concentration has increased during the studied period from about 110 mg/l to 180 mg/l.

The calcium concentration recorded the maximum in 1993 about 46 mg/l. After that the concentration decreased and starting by 1995 the calcium concentration has continuously increased. In the last year it reached again the value of 1993. Sodium, chloride and sulphate are in big amount. The sulphate concentration in geothermal water from Ciumeghiu was maintained in range 46-60 mg/l. After 1993

sodium concentration decreased rapidly to about 1700 mg/l. Since 1995 the sodium concentration has increased continuously until 1999, when the concentration reached 2250 mg/l. The range of chloride concentration in geothermal water from well Ciameghiu-4668 is 600-1900 mg/l. The minimum value was recorded in 1995. In the last years the chloride concentration increased, being around 1800 mg/l in 1998.

The tendency of the major components of geothermal water from well Ciameghiu-4668 was to increase since 1995, except CO₂ which has decreased and the sulphate concentration has not changed much.

STUDIES ABOUT THE INFLUENCE OF THE TEMPERATURE ON SCALE DEPOSITS

The decrease in temperature of geothermal water during utilization has a dangerous effect on the solubility in the system, that means a supersaturation, resulting scale depositions. The type of scaling 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 -1.09÷3.69 at Ciameghiu, which are acceptable for equilibrium calculations. The date could be used for interpretation. Based on data from table 1 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 20⁰C. 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. Figure 1 shows the dependence of saturation index on the temperature for different minerals.

The figure 1 in 1993 shows an equilibrium with the minerals at the wellhead temperature, 93⁰C. The diagram looks different to the others. 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 60-80⁰C. 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, 85⁰C could be observed the supersaturation of magnetite, talc, chrysotile, goethite and calcite. The equilibrium is perturbed 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, 85⁰C.

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, 84⁰C. At any temperature precipitation of calcite may be inevitable.

According to the diagram from 1999 cooling leads to supersaturation with respect to calcite, quartz, chalcedony. The potential for calcite scaling is very high. There is also supersaturation with respect to magnetite and talc at any temperatures. At the wellhead temperature there is a supersaturation with chrysotile, but cooling leads to undersaturation with respect to chrysotile. No best equilibrium temperature can be found. For a few minerals equilibrium is indicated at 40-60⁰C. Amorphous silica is fairly close to saturation when the temperature of geothermal water decreases. Fluorite and wollastonite remain undersaturated.

In Ciameghiu they can notice the tendency of decreasing the temperature of the reservoir.

DEPOSITIONS ANALYSIS

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 in Ciameghiu.

Test plates were inserted at the wellhead Ciameghiu-4668 in September 1997 and let there until May 1998. The test plates have been installed during the production of the well. 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 sample. The XRD studies were made using K α Cu radiations. The diagram obtained for the solid depositions from well Ciameghiu-4668, figure 2 shows that there are calcite and magnesian crystals in the sample. The

solid sample was also thermic-differential analysed. The thermogravimetric diagram, figure 4, indicates exothermic effects at about 255⁰C, 342⁰C and 390⁰C corresponding to 8.7% weight losses and endothermic effects with maximum at 467⁰C and 925⁰C. The thermic effect at 925⁰C corresponds to CaCO₃ decomposition. For a better understanding of the contain of this sample it was later made an infrared analyses. The infrared spectrometric analyses from Ciumeghiu, figure 3, indicates that the depositions are 95% Ca(Mg)CO₃. The acid insoluble residue was mostly organic paraffin hydrocarbons with minor amounts of polyester wax. It is this organic residue that explains the weight losses in the thermogravimetric analyses.

It is better to counteract scaling and corrosion problems before they occur. For monitoring of the field and possible scaling and corrosion it is recommended to take samples for complete analysis and also to use a special device (figure 5) for testing any scales which have formed. This device allows the coupons to the geothermal water without interrupting the flow, which is important when an uninterrupted supply of water is required.

CONCLUSIONS

Complete data are very important for any calculation and analysis. In this paper was used a chemical model to analyse scaling potential in the water from the low temperature geothermal field in Ciumeghiu.

A scale sample from the distribution system was analysed by X-ray diffraction, giving information about its origin as calcite, magnesian. A thermic-differential analysed and an infrared one confirmed that the scale deposit inside the distribution system is formed as main by a crystalline phase: calcite and

magnesian.

For monitoring of scaling and corrosion a special device should be installed in many sites of the network.

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Table 1. The chemical composition of geothermal water from Ciumeghiu, well 4668 during the period 1993-1999, in mg/l.

	1993	1995	1996	1997	1998	1999
pH	7.78	7.6	7.4	7.5	7.85	7.9
CO ₂	2736.6	2580.8	2390	2209.3	2080.3	2045
H ₂ S	0.65	0.63	0.52	0.6	0.63	0.7
SiO ₂	132	116	133.4	163	179	181
B	119.5	50.9	-	81.8	95.6	98.2
Na	2206.22	1715	1815.8	1998	2150	2250
K	38.2	30.3	30	34	33	33
NH ₃	-	2.72	7.4	8.6	9.2	8.2
Mg	-	-	1.7	3.5	4.2	4.5
Ca	46	24	32.2	37.3	41.4	45.6
Al	1.39	-	-	-	-	-
Fe	2.8	0.17	0.2	0.12	0.14	0.14
F	-	-	0.8	0.98	0.75	0.7
SO ₄	-	58	59.2	53.7	46.2	47
Cl	1276	676	1060	1478.3	1790.2	1902
TDS	7327.15	5900	6130.5	6408.7	6514	6574

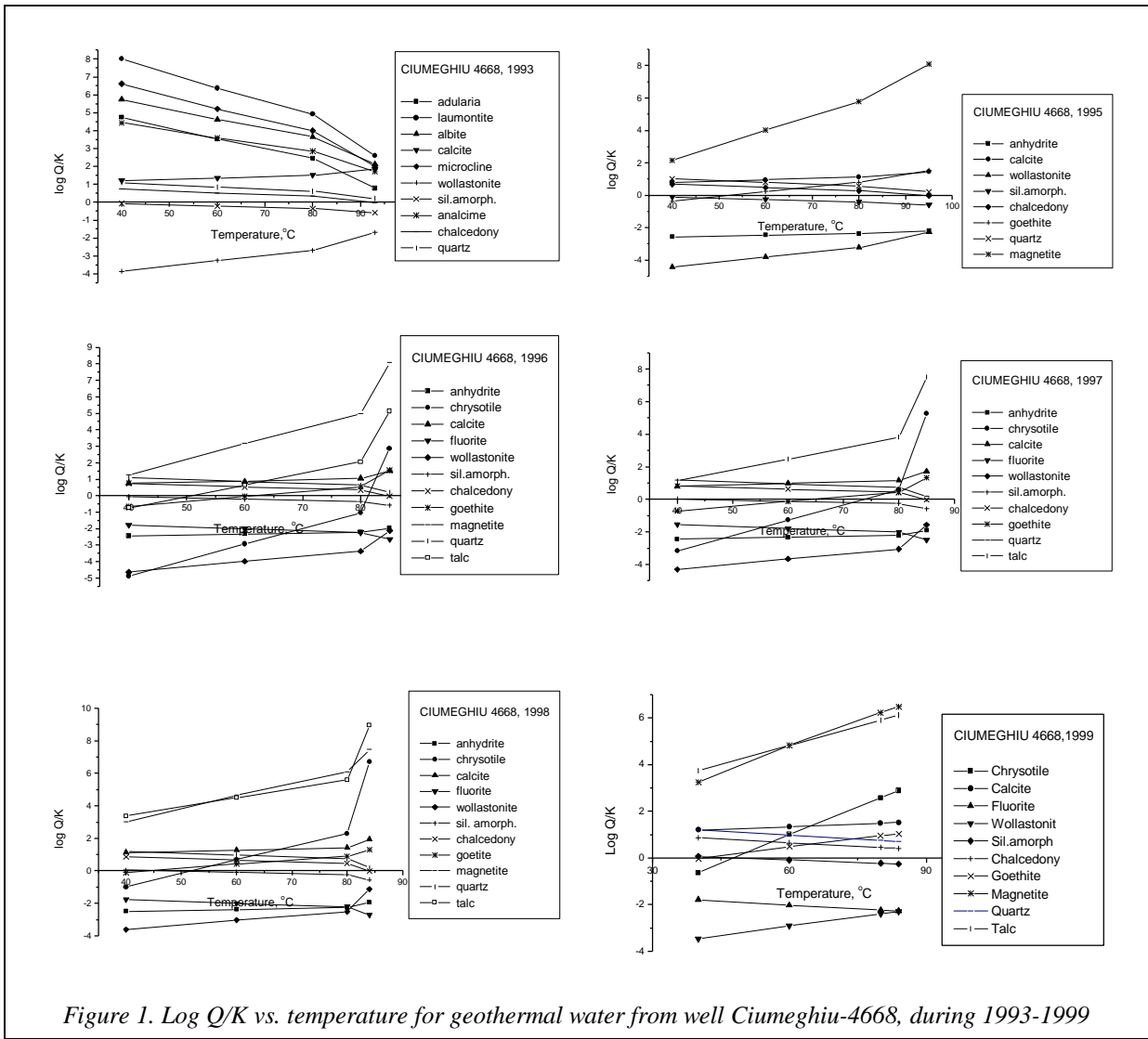


Figure 1. Log Q/K vs. temperature for geothermal water from well Ciumeghiu-4668, during 1993-1999

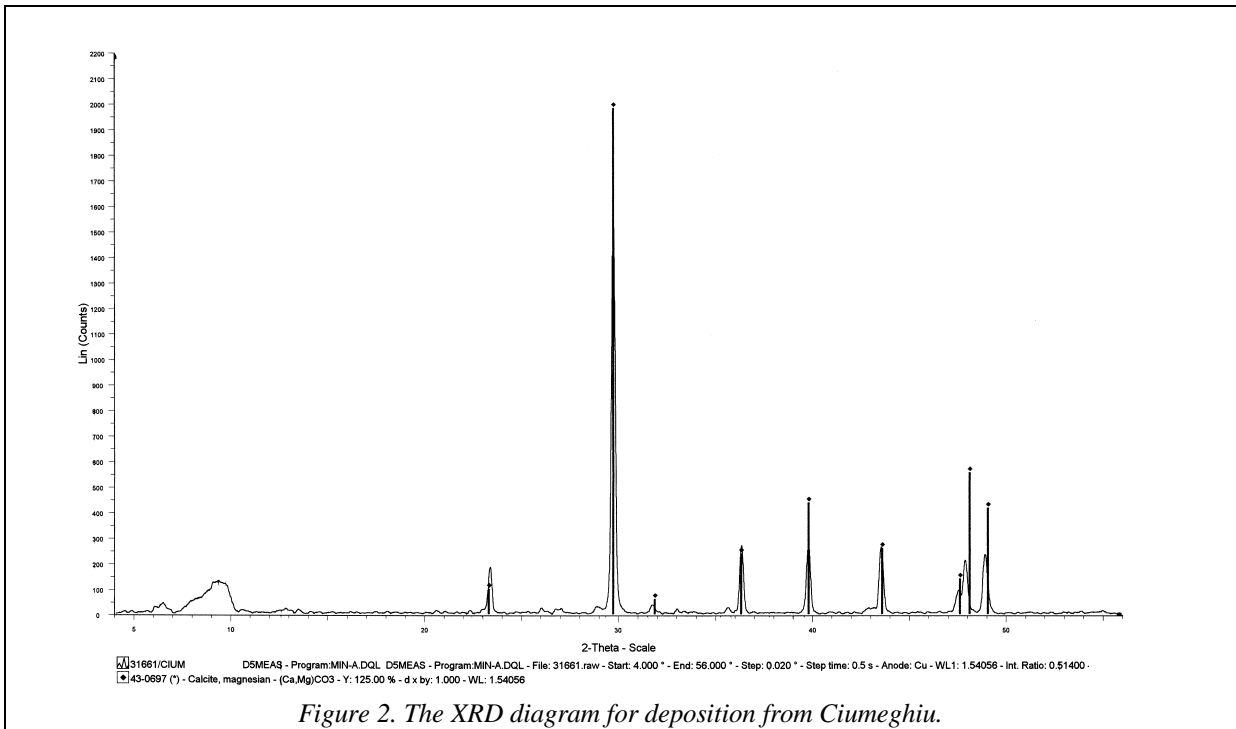


Figure 2. The XRD diagram for deposition from Ciumeghiu.

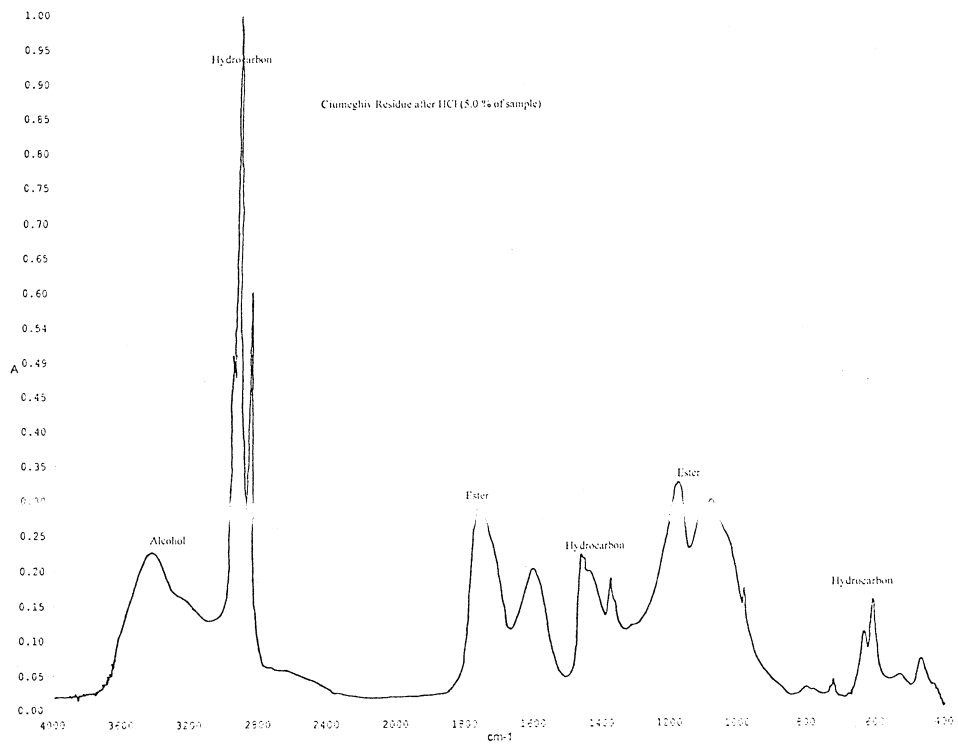
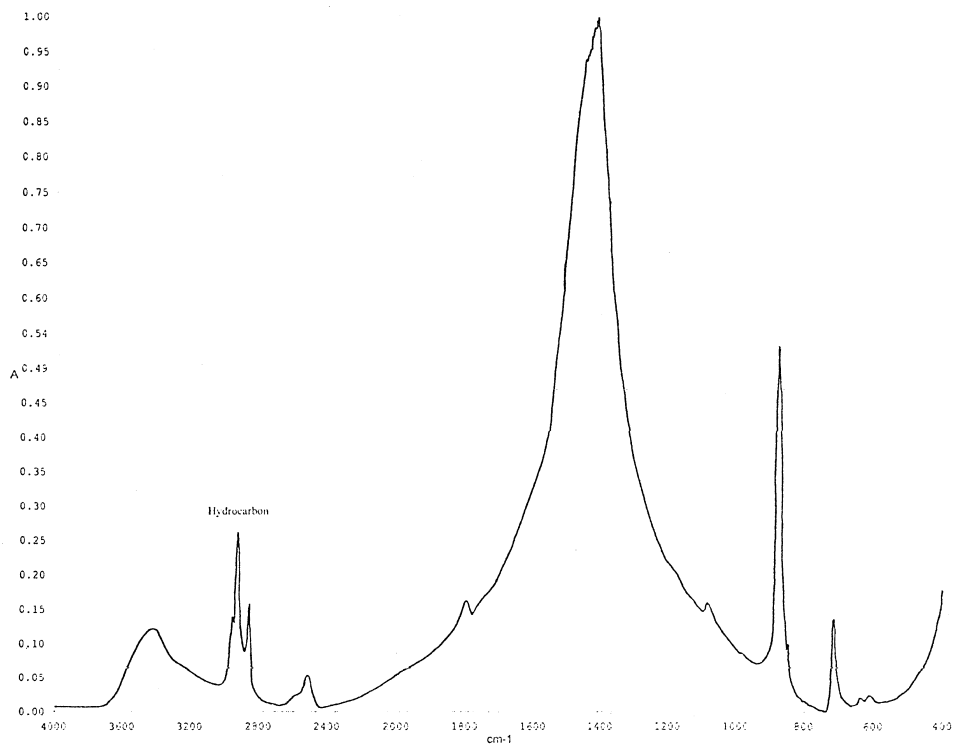


Figure 3. The infrared analyses of solid depositions from Ciuneghiu.

