

Geochemical Studies about the Well 4175 from Tășnad - Romania

Radu Sebeșan*, Mioara Sebeșan**, Oana Stănășel**

* University of Oradea, Faculty of Electrical Engineering and Information Technology,

1, University Street, 411087, Oradea, Romania

** University of Oradea, Faculty of Sciences, Department of Chemistry, Oradea, Universitatii 1, Romania

E-mail address <rsebesan@uoradea.ro>

Keywords: well 4175, chemical geothermometers, ternary diagram.

ABSTRACT

Due to its economical importance, well 4175 from Tășnad was studied. The chemical composition of geothermal waters from this well was established using standard methods of analysis.

Classification of these waters was carried out, taking into account the major anions and cations, using ternary diagrams. The temperature of the geothermal reservoir was assessed and scaling problems were predicted during the well utilization, based on the chemical composition and the use of computer simulation programs. Solid depositions were collected and analyzed and the results were compared to those estimated by the simulation program.

1. INTRODUCTION

Well 4175 in Tășnad is situated in the county Satu – Mare. The geothermal energy from Tășnad is utilized for heating military units, to heating of greenhouses and to heating of houses. People have been using the geothermal resources from the beginning of civilization for cleaning purposes or as place for agreement. Since the XXth century geothermal energy has been used for heating, for industrial uses and for electricity generation.

This paper studies the production well 4175 from Tasnad. This well has artesian production, the wellhead temperature being in the range of 80-85 C. During the utilization of well 4175 solid depositions were noticed, which formed especially from the wellhead to the degasing system.

2. EXPERIMENTAL

In order to get the chemical composition, geothermal water was sampled. The measured temperature at collection was 85 C. The methods of analysis are presented as follows:

- sodium and potassium were flame photometrically determined at $\lambda=589$ nm and 767 nm, respectively;
- calcium and magnesium – complexometric titration;
- ferrum – spectrophotometric determination at $\lambda=510$ nm, using o-phenantroline;
- boron – spectrophotometric determination at $\lambda=420$ nm; the method is based on the reaction with azomethine in a buffer solution;
- silica – spectrophotometric determination at $\lambda=410$ nm; this method is based on the reaction with molybdates at

pH=1,2-1,5 when is formed a yellow silica-molybdate complex;

- chloride was determined by using the Mohr method;
- sulphate concentration was determined by titration with barium perchlorate; thorin was used as indicator;
- total carbonate was analysed by titration with HCl solution with metilorange as indicator;
- total dissolved solids – gravimetric analysis.

Severe scaling was recorded at well 4175, which made necessary to remove the pipe until the degasing system after each winter. Solid deposits were sampled and analyzed. The deposition sample was then structurally analyzed by the use of X-Ray diffraction with $K\alpha$ Cu radiation.

The thermic and thermo-differential analysis was made by using a derivatograph Q-1500D. The thermic conditions were 20 C/ minute until 1000 C.

2.1. Chemical characterization of geothermal waters

The chemical composition of the analyzed geothermal water is shown in table 1.

These waters present a slight basic pH and a high mineralisation. For an initial classification, in terms of the major anions Cl^- , SO_4^{2-} and HCO_3^- , a triangular diagram was used. On this diagram (Figure 1) geothermal waters from Tasnad plot near to the chlorine corner in the field of peripheral waters.

Table1. Chemical composition of geothermal water, in mg/l

Depth [m]	1500-2000	Anions [mg/l]		Cations [mg/l]	
PH	7,6	Cl^-	4875	Na^+	4210
Mineraliz.	11280	SO_4^{2-}	6	K^+	38,5
		HCO_3^-	1521	Ca^{2+}	52,4
Total dissolved solids	13100	PO_4^{3-}	0,22	Mg^{2+}	30,2
Dissolved gases [mg/l]		O_2	2,90	SiO_2	40
		CO_2	1460	Phenols	0,03

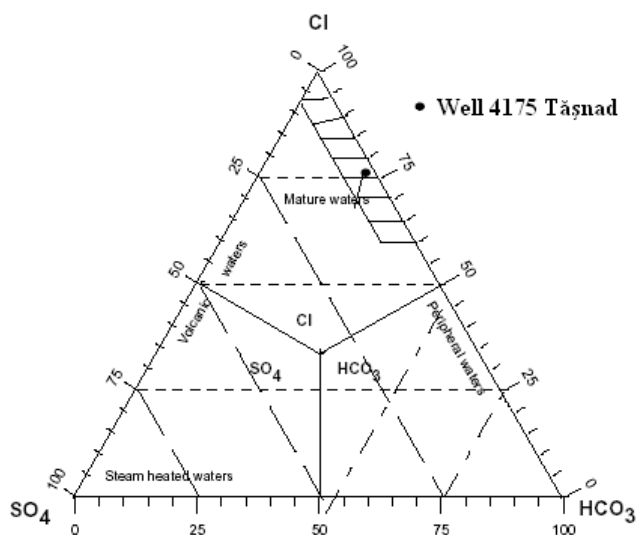
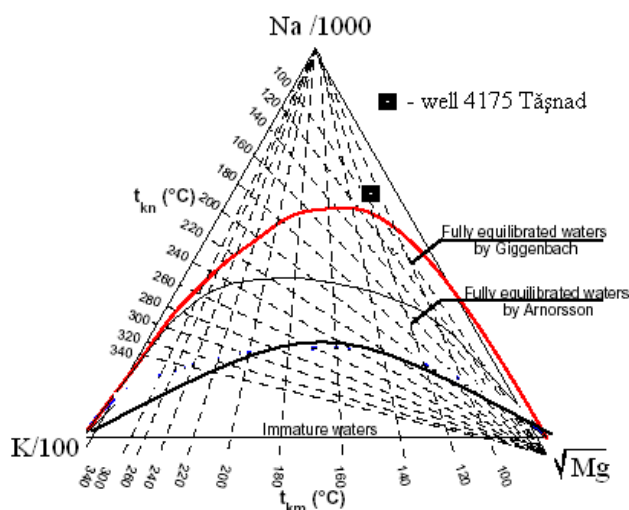
Figure 1: Cl-SO₄-HCO₃ ternary diagram.

Figure 2: Na-K-Mg equilibrium diagram.

Table 2. Temperatures resulted by Watch program calculations.

Well	T (quartz) °C	T (chalcedony) °C	T(Na/K) °C
Tășnad	86,5	96,0	39,8

Table 3: Concentration of SiO₂, based on temperatures and enthalpy of surface for well from, Tășnad.

Well	SiO ₂ (mg/l)	Temperat. to surface, °C	Enthalpy [kJ/kg]
Tășnad 4175	40,1	70 – 74	297,49
Cold water	20	10	42

Table 3: Concentration of SiO₂, based on temperatures and enthalpy of surface for well from, Tășnad.

Well	SiO ₂ (mg/l)	Temperat. to surface, °C	Enthalpy [kJ/kg]
Tășnad 4175	40,1	70 – 74	297,49
Cold water	20	10	42

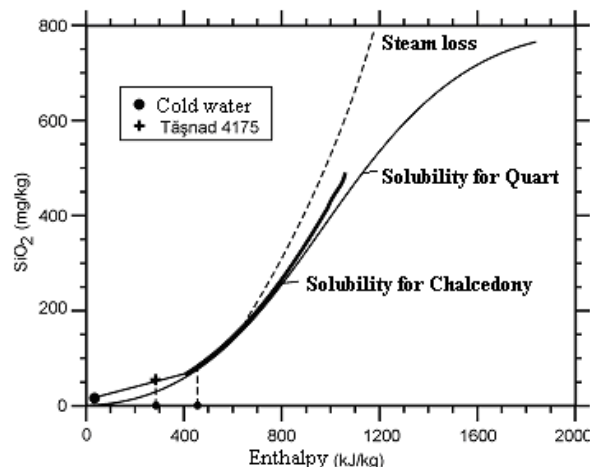


Figure 3 : Dissolved silica-enthalpy diagram.

The Na-K-Mg (Figure2) triangular diagram shows that waters from Tasnad are partially equilibrated according to the Giggenbach and Arnorsson equilibrium curves. This could be a good indicator that the chemical composition of these waters can be used for geothermometer calculations.

2.2. Estimating the deep water temperature

Several indicators were proposed to estimate the deep water temperature. The use of geothermometers is based on the hypothesis that there exists an equilibrium between minerals from the rocks of the reservoir and the fluid from the reservoir. The chemical composition of the surface fluid is controlled mainly by the composition of the minerals from the reservoir and the temperature. Arnorsson and Fournier concluded that the solubility of some components of the geothermal fluid is controlled by the temperature.

The temperatures determined from geothermometers, which were calculated by the Watch program, are presented in table 2.

Notice that temperature calculated by the chalcedony geothermometer is closer to the production temperature of the majority of geothermal waters than the values given by the other geothermometers. Another way to estimate the reservoir temperatures is by using the silica-enthalpy mixing model [2]. This is based on the strength of silica in the geothermal waters and of surface reservoir temperatures which were used to estimate the enthalpy for geothermal fluids. The results are presented in table 3.

It is assumed that the surface geothermal water is the result of mixing of hot geothermal water with cold water. The intersection point with the solubility curve for chalcedony gives the enthalpy of the deep hot water component and its temperature is obtained from steam table, Model silica-enthalpy for well 4175 Tășnad, was presented in Figure 3.

Table 4. Temperatures found by silica-enthalpy model calculations.

Well	SiO ₂ (mg/l)	Enthalpy in reservoir, [kJ/kg]	Hot water temperature in reservoir, °C
Tășnad 4175	40,1	451,01	107,4
Cold water	20	42	10

The reservoir temperature determined with silica-enthalpy model is presented in table 4 .

At Tășnad, well 4175 temperature calculated by mixing model is 107.4°C,. For this geothermal well, the temperatures calculated by the chalcedony geothermometer is 96.0°C. The temperatures calculated by the chalcedony geothermometer is very close to the production temperatures of geothermal waters from Tășnad, well 4175.

The composition and the mineralogical structure of the depositions depends on the chemical composition of geothermal waters, and the temperature and the composition of the material of the distribution systems

The deposition sample was then structurally analyzed by the use of X-ray diffraction with K α Cu radiations. The

thermic and thermo-differential analysis was made by using a derivatograph Q-1500D. The termic conditions were 20°C/minute until 1000°C.

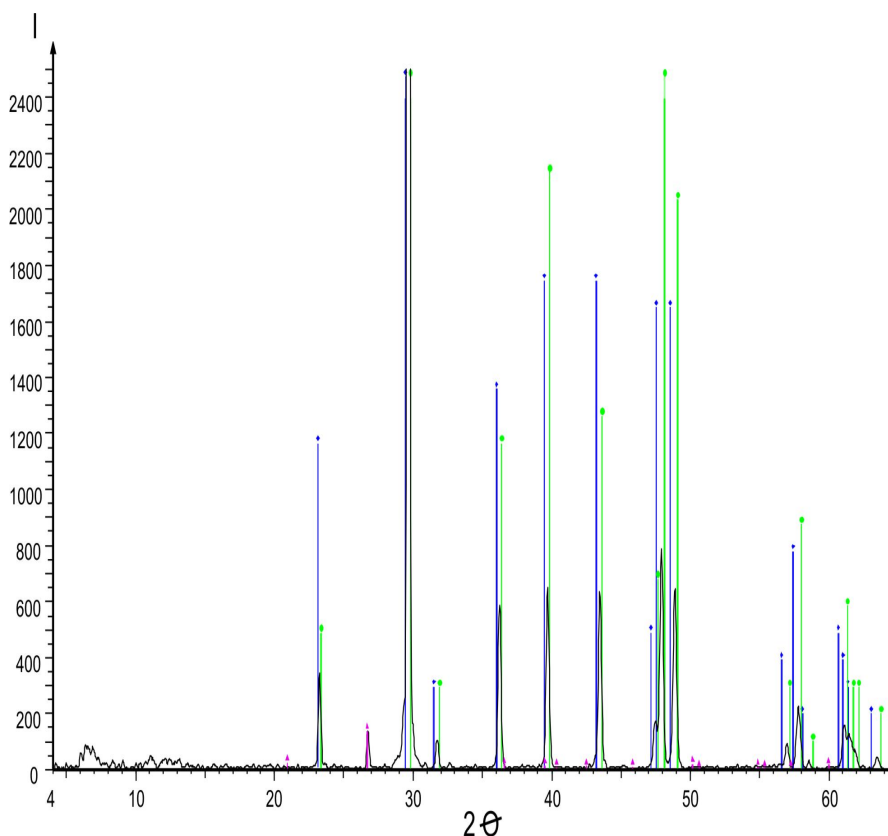
The solid sample was then analysed by X-ray diffraction, Figure 4.

The solid sample was then analysed by X-ray diffraction, having information about the existence of calcite, magnesian crystals and quartz for solid depositions from Tășnad.

For thermic and thermo-differential analysis a derivatograph (Q-1500D) was used. The termic conditions were 20°C/ minute until 1000°C. The sensitivity of the hidrograph was: TG - 500 μ V, DTA - 500 μ V, and DTG – 1 mV.

The speed of advance the paper was 5 mm/minute. The diagram obtained by thermogravimetric analysis is presented in Figure 5.

The diagram obtained by thermogravimetric analysis (Figure 5) indicates an endothermic effect, that starts at 720°C and reaches a maximum at 940-955°C. The mass loss represents 43,58%. This means that the sample consists mainly of carbonates, the residual being carbon dioxide. This is similar to the residual obtained in the chemical analysis.

**Figure 4: The XRD diagram of the solid deposits from well 4175 Tășnad.**

- ▲ -00-046-1045(*)-Quartz, SiO₂ -Y:1.82%;
- ◆ -00-005-0586(*)-Calcite, CaCO₃ -Y:50%;
- -00-043-0697(*)-Calcite,magnesian-(Ca,Mg)CO₃-Y:50%.

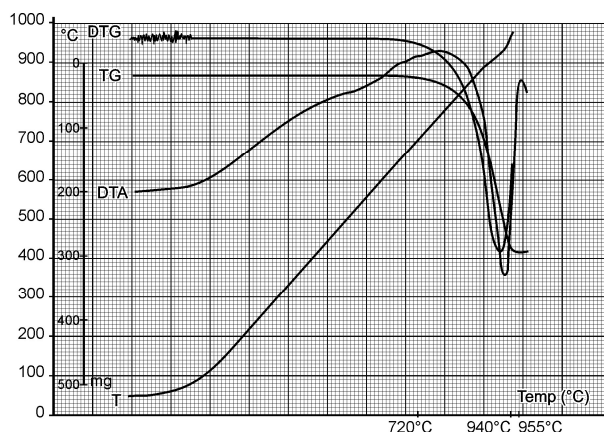


Figure 5: The thermo-differential diagram of the solid deposits from well 4175 Tășnad.

4. Conclusions

Major problems have arisen in heating services due to mineral depositions. Potential scaling problems in geothermal utilization depend on the type of water. The reservoir temperatures indicated by the calculated chalcedony geothermometer is closer to the production temperatures of the water than the values given by the other geothermometers. The reservoir temperature calculated by silica-enthalpy mixing model is rather higher than the temperature given by the chalcedony geothermometer and the wellhead temperature, which indicates a mixing of hot water from the reservoir with the infiltrated cold water in the upper layers. Therefore chemical analysis of the geothermal water was performed in order to predict possible scaling. It is better to avoid scales before they occur. In case of mineral depositions inside the pipes, mechanical removal is not convenient. Geothermal waters with a scaling tendency must be treated by chemical methods in order to prevent the deposits. Simulation programs exist which can be used to estimate the depositions that can be formed at different temperatures reached during geothermal water utilization. The analysis of the solid samples indicated that the depositions consist of calcite and magnesian, CaCO_3 mainly. The calcination loss is CO_2 , that confirms the presence of carbonates in the sample. The scale deposits in the pipeline are more voluminous inside the well towards the surface and at the

degassing entry. This could be due to flow variation, pressure and temperatures changes during exploitation of the well. To control the deposition we shall propose the following methods: prevent deposition alkaline treatment by acid, deposition with balls cleaning, mechanical cleaning, suppressing deposition using inhibitors and choosing material appropriate for the type of water for building metal installations.

REFERENCES

- Fournier R. O.: *Geothermics*, Vol. 5, Pp. 49, (1977), 49.
- Bjarnason J.O.: The speciation program Watch, version 2.1. Orkustofnun, Reykjavik, (1994), . 145.
- Arnorsson, S., J.Volc.*Geotherm.Res.*, Vol. 2.3, 1985), 2749.
- Giggenbach W.F.: *Geochim.Cosmochim.Acta*, Vol. 52, (1988), 2749.
- Keenan, J.H., et.al.: *Steam Tables-Thermodynamic properties of water including vapor, liquid and solid phases*, International Edition-metric units, Wiley, New York, (1969).
- Mackenzie, W.S., Guilford, C.: *Atlas of Rock Forming Minerals in Thin Section*, Longman U.K., (1982).
- Sebeșan M., Stănașel, O., Sebeșan, R.: *Proceedings of the World Geothermal Congress, Atalya-Turkey, (2005), 2040.* Arnorsson S., Stefansson A: *Proceedings of the World Geothermal Congress, Atalya-Turkey, (2005), 870.* ănașel O.: *Monitorizarea chimică a sondelor geotermale de producție*, Ed.Univ. din Oradea, Oradea, (2003). le A., et.al.: *Proceedings of the World Geothermal Congress, Florence, Italy, (1995).*
- Brown K.L., McDowell G.D.: *5th NZ Geothermal Workshop*, University of Auckland, (1983).
- Bothbaum H.P., et.al.: *Geothermics*, 8, (1979).
- Fridleifsson I.B.: *Proceedings of the World Geothermal Congress, Japan, (2000), 789.*
- Evanoff J., et.al.: *Proceedings of the World Geothermal Congress,Florence, Italy, (1995), .2481.*