GEOCHEMICAL STUDY ON THE PERIMETER OF THE GEOTHERMAL FLUIDS FROM SACUIENI

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Abstract – The paper presents the estimation of the geothermal reservoirs temperature using the silica-enthalphy model. The reservoirs temperatures were calculated with chalcedony geothermometers, by Watch simulation program. There were proposed to estimate the deep waters temperatures using the silica-enthalphy model and to compare this temperatures with the temperatures resulting from geothermometers which were calculated by the Watch program.

Keywords: geothermal water, geothermometer, silica-enthalphy model.

1. INTRODUCTION

Using geothermal water in Romania, is based on the quality of drinking water or as needed, directly or indirectly (through heat exchangers) and mixed, water is used for heating, hot water as the greenhouses, swimming pools and technological purposes.

This paper presents the estimations the deep water temperature for geothermal water resulting from: well 4691, 4692, 4696, 1704 from Sacuieni, which are situated at about 80 km from Oradea. The drillings geothermals was presented on the map of figure 1.

Fig. 1.The map of the country Bihor

The geothermal reservoir from Săcuieni was explorated by 7 wells. Four of them were exploited, by the time being just wells 4691 and 4696 is used for heating the greenhouses from Săcuieni area.

The geothermal energy has been used for heating, for industry, and for generation of electricity. This wells has an artesian production, the wellhead temperature being in the range of 80-84^{0}C. Watch program show us the deep waters temperatures, calculated which geothermometer chalcedony, geothermometer quartz and geothermometer Na/K.

The reservoirs temperatures were estimated using the silica- enthalphy model.

In our country the geothermal reservoirs are mainly located in the western part.

2. EXPERIMENTAL DATA

In this paper we utilized Watch program for calculus deep waters temperatures. Based on the chemical composition by the use of simulation computer programs it was assessed the temperature of the geothermal reservoir. The methods of analysis are presented as follows:

Analysis of sodium, potassium, calcium, magnesium and iron was made by atomic absorption spectroscopy,using a spectrophotometer VARIAN SPECTRA AA 110.

Analysis of silica - colorimetric determination- colorimetric methods for determination of silica in water is based on silico-molybdate complex formation and its reduction to molybdenum blue. Phosphorus interference is eliminated by adding oxalic acid.Colorimetric methods used differ by: the form of silica analyzed (total, ionic, colloidal), by concentration and separation process (coprecipitation, ion exchange resins), and investigation of color intensity.Colorimetric method can be applied to a silica content (SiO_2) of 0,5 mg SiO_2/L. Sensitivity of the method is 0.2 mg SiO_2 / l. Water samples with a silica content greater than 10 mg SiO_2/L it will be properly diluted prior to analysis.Soluble silica is formed with ammonium molybdates at pH = 1-1.5 a complex silicate-molybdate yellow. The color intensity is proportional to the concentration of silica. If the sample water contains colloidal silica, for its solubilisation and shift its soluble form reactive to ammonium molybdates, will bring 100 ml sample in a platinum dish, add 0.4 g sodium bicarbonate and is held in a boiling water bath for one hour , then cooled and added slowly and stirring 2.4 ml of H_2SO_4. Make up with distilled water.If the water sample contains silica soluble form it will not chemically treated, but are treated as such. 100 ml of treated or untreated sample is placed in a tube heat successively adding 2 ml of hydrochloric acid, 5 ml of ammonium molybdate and after 5-10 minutes, 2 ml 10% oxalic acid. After each addition of reagents shake. In another heat tube is placed 100 ml sample to be analyzed, then add with microburettes the solution of potassium chromate-sodium borate (0.53 g 5 g potassium chromate and sodium tetraborate dissolved in 1000 ml distilled water) to equalize Work in both tubes. Comparing the color intensity is made after 10 minutes, the addition of oxalic acid solution in the first tube on simultaneously, transparently, from top to bottom, the 2 tubes placed on a white support. 1 ml of potassium chromate-borate introduced in 108 ml of distilled water produced a color intensity corresponding to a content of 1 mg SiO_2 /L.

Analysis of ammonia from ammonium salts was done by colorimetric determination of NH^{4+} ion.

Determination of carbon dioxide was made by titration with hydrochloric acid solution in the presence of metilorange. CO_2 from the carbonates was determined by volumetric titration. The method is based on neutralization of carbonates with hydrochloric acid to bicarbonate step, using phenolphthalein as indicator.

a) Determination of CO_2 (aggressive)

The method is based on the fact, that CO2 free and aggressive, changes carbonate in bicarbonate, which is titrated with a solution of hydrochloric acid in the presence of metilorange.

b) Determining CO_2 (equilibrium).

Carbon dioxide (carbonic acid) found in water, neutralized with a known excess of NaOH solution in presence of phenolphthalein until the persistent pink color.

Excess of NaOH is titrated with hydrochloric acid until water solution discoloration. Treatment sample with excess of NaOH is carried out in presence of salt Seignette, which is a buffer, thus eliminating local acidification and precipitation of ferric hydroxide.

c) Determination of CO_2 from carbonates by titration volume

The method is based on neutralization of carbonates with hydrochloric acid to bicarbonate step, using phenolphthalein as indicator. Analyzed in 100 ml water add several drops of indicator.If the sample turns pink it shows persistent presence of carbonates. Titrated water will be analyzed with a 0.05 N HCl solution until discoloration near the solution (slightly pink).

d) Determination of $C0_2$ from bicarbonate by volumetric titration

Bicarbonate is determined by titration with 0.1 N HCl solution in the presence of methyl orange indicator to passage of color from yellow to yellow-orange.With bicarbonate and carbonate are determined. Therefore the results are corrected by subtracting carbonate determined that the previous method.

- Analysis of chloride [8], was made by titration with silver nitrate in the presence of potassium chromate as indicator (Mohr method).
- Analysis of sulfates and hydrogen sulfide [7] was done by titration with barium perchlorate solution using Thorin as indicator. Determination of hydrogen sulphide was made by titration with mercuric acetate in the presence of dithizone as an indicator.

Experimental data on the chemical composition of geothermal waters, taken in the survey are given in table 1.

Table 1.Chemical composition of geothermal waters from Sacuieni (concentrations of ions, mg/L)

Chemical charact.	Well 4692	Well 1704	Well 4691	Well 4696
pH	7,88	8,6	7,7	8,0
Na^+	1456,75	1178,05	1406,45	1205,0
K^+	193,94	157,32	187,15	136,24
Ca^{2+}	25,7	54	20	45
Mg^{2+}	3,9	0,617	1,236	8,78
Cl^-	828,87	474,27	776,13	410,7
SO_4^{2-}	27,6	14,81	22,63	76,814
HCO_3^-	2596,77	2506,0	2361,88	2508,00
SiO_2	62,5	46,0	44	38,8
Fe^{2+}	0,22	0,13	0,34	0,3
NH_3	-	0,44	-	0,22
CO_2	1998	2010	1890	2000
Mineral.	12208	10560	8900	10140
H_2S	-	-	-	-
Phenols	2,04	-	1,06	-

The Watch program predict possible scaling what occured during the utilization of geothermal water and with geothermometers indicates the reservoirs temperatures.

The use of geothermometers is based on the supposition that there is 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 as main by the composition of the minerals from the reservoir and the temperature. Arnorsson and Fournier [1] concluded that the solubility of some components of the geothermal fluid is controlled by the temperature.

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

Table 2. Temperatures resulted by Watch program calculations for wells from Sacuieni.

Wells	T,°C (quartz)	T,°C (chalcedony)	T,°C (Na/K)
4691	85,5	109,0	104,8
4692	97,5	115,6	88,2
4696	80,9	94,5	106,0
1704	110	89,7	109,9

Is noticed as temperature calculated by chalcedony geothermometer [2] is very close to the production temperature of majority 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]. On the strength of contained of silica from geothermal waters and of surface reservoir temperatures we caused the enthalpy for geothermal fluids.The results are presented in table 3.

Table 3. Concentration SiO_2, temperatures and enthalpy of surface for wells from Sacuieni.

Well	SiO_2 (mg/l)	Temperature to surface, °C	Enthalpy [kj/kg]
4691	44,0	83	348,7
4692	62,5	72	302,4
4696	38,8	84	352,8
1704	46,0	82	344,3
Cold water	20	10	42

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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 tables, Model silica-enthalpy for wells: 4691 Sacuieni, 4692 Sacuieni, 4696 Sacuieni and well 1704 Sacuieni was presented in figures 2, 3, 4 and 5.

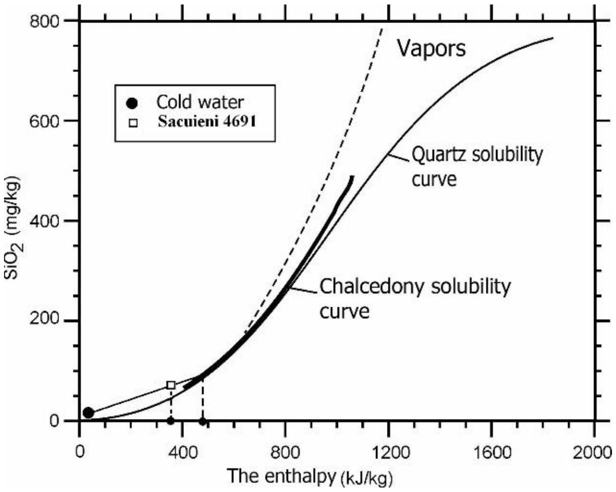

Fig 2. Diagram of dissolve silica-enthalpy for 4691 drilling from Sacuieni.

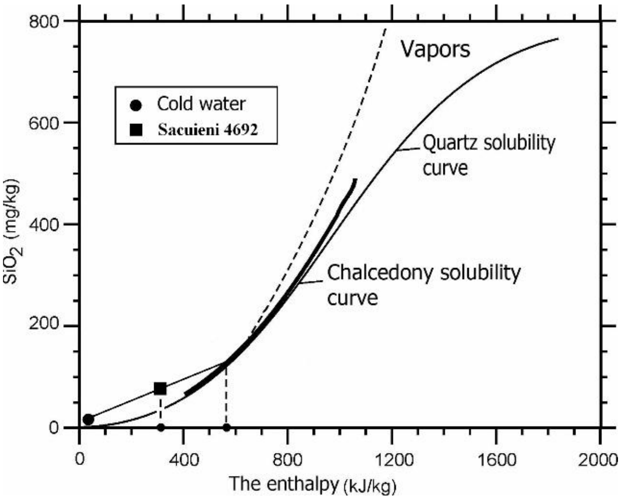

Fig. 3. Diagram of dissolve silica-enthalpy for 4692 drilling from Sacuieni.

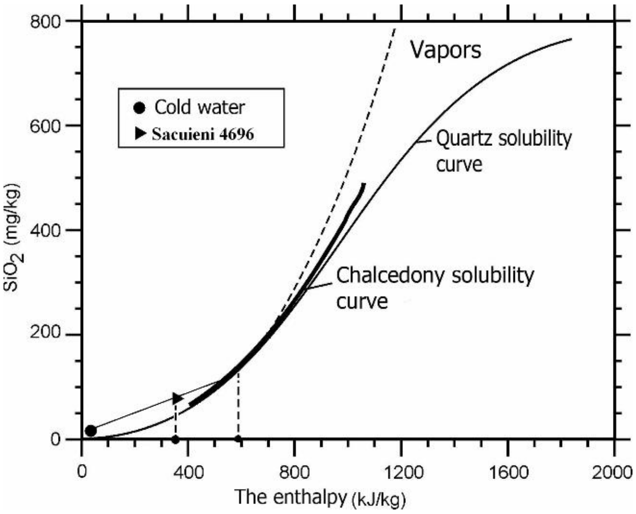

Fig. 4. Diagram of dissolve silica-enthalpy for 4696 drilling from Sacuieni.

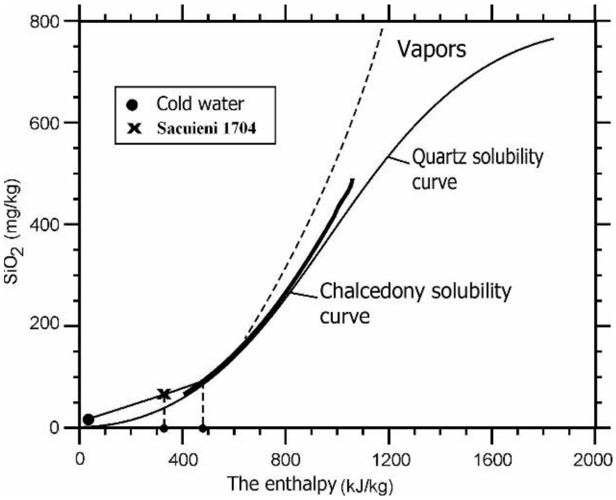

Fig. 5. Diagram of dissolve silica-enthalpy for 1704 drilling from Sacuieni.

3. RESULTS AND DISCUSSIONS

The reservoir temperatures finded out with silica-enthalpy model are presented in table 4 .

Table 4. Temperatures resulted by silica-enthalpy model calculations for wells from Sacuieni.

Well	SiO_2 (mg/l)	Enthalpy in reservoir, [kj/kg]	Hot water temperature in reservoir, °C
4691	44,0	475,8	113,2
4692	62,5	580,5	138,2
4696	38,8	599,7	142,8
1704	46,0	490,2	116,7
Cold water	20	42	10

At Sacuieni, well 4692 the temperature calculated by mixing model is 138,2°C, and for well 4696 of Sacuieni the temperature calculated by mixing model is 142,8°C, therefore differed the temperature calculated by chalcedony geothermometer. The difference compared to the wellhead temperature is assumed to be due to mixing with cold water in the upper layers or due to contact by the cold rocks.

At well 1704 from Sacuieni and at well 4691 from sacuieni this temperature calculated by mixing model is 116,7°C, respectivly 113,2°C. For this geothermal wells, the temperatures calculated by chalcedony geothermometer is 109,9 °C for geothermal water of well 1704 and 104,8 °C for geothermal water of well 4691. The temperatures calculated by chalcedony geothermometer is very close to the production temperatures of geothermal waters of drilling 4691 and from drilling 1704, from Sacuieni.

CONCLUSIONS

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.

The optimum conditions for use a geothermal water is necessary to know their chemical composition.

Exist the simulation programs which to estimate the depositions, which can be formed at different temperatures reached during geothermal water utilization.

REFERENCES

1. Fournier R. O., Geothermics, **5**., 1977, 49.
2. Bjarnason J.O., “The speciation program Watch, version 2.1. Orkustofnun”, Reykjavik, 1994.
3 . Arnorsson, S., J.Volc.Geotherm.Res., Vol**. 2.3,** 1985, 145.
4. Giggenbach W.F., Geochim.Cosmochim.Acta, Vol. **52**, 1988, 2749.
5. 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.
6. Mackenzie, W.S., Guilford, C., “Atlas of rock-forming minerals in thin section”, Longman U.K., 1982.
7. Sebeşan M., Stănăşel, O., Sebeşan, R., Proceedings of the World Geothermal Congress, Atalya-Turkey, 2005, 2040.
8. Arnorsson S., Stefansson A., Proceedings of the World Geothermal Congress, Atalya-Turkey, 2005, 870.
9. Stănăşel O, Sebeşan M., Bota M., Gilău L., Iovi A., Analele Universității din Oradea, Fascicola Chimie **XI,** Oradea, 2004, 46.
10. Stănăşel O.,“Monitorizarea chimică a sondelor geotermale de producție”, Ed.Univ. din Oradea, 2003.
11.Keenan J.H., etal., Steam Tables-Thermodynamic properties of water including vapor, liquid and solid phases, International Edition – metric units, Wiley, New York, 1969.
12. Hauksdottir S., Tulinius, H., Kristjansson, B.R., Proceedings of the World Geothermal Congress, Atalya-Turkey, 2005, 1718.