Interpretation of Exploration Geochemical Data by Modelling Study and Physico - Chemical Investigations

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This paper describes a research study of production characteristics of geothermal waters supplied by well 4797 from Oradea, which has been used for direct heating of blocks of flats. Due to its economic importance, it was considered a necessity to monitor continuously this well. The results represent a part of the researches realised in cooperation with the University of Akureyri from Iceland and University of Oradea, Romania. The chemical composition of the fluid discharged is dependent on the geochemistry of the reservoir. The sampling methods were done according to specific methodology for geothermal fluids and the analysis were done by accurate standard methods, so the chemical results could be used for interpretation. Based on the chemical composition it was made a classification of these waters, it was possible to calculate the deep temperature of the reservoir and were estimated any scaling problems which can appear during well production. The high performance equipment used, made possible to determine the concentrations of trace elements as heavy metals, which may affect people health and the environment. This would be important, because the geothermal water after utilization is reinjected and is good to know if could be any negative impact on the environment. Compared to the maximum recommended values on chemical elements, the heavy metals were found in limits for very low and low probability of effects. Based on the water-rock interaction processes taking place in geothermal reservoir, the temperature of the hot deep water component was calculated by silica geothermometers and compared with the results of silica mixing model. The scaling prediction was realised by using a simulation program which computes the chemical analysis of the extracted waters. It was possible to forecast the behaviour of minerals which could start to precipitate both at the wellhead temperature and at lower temperatures, reached during utilization. One of the predicted deposition was confirmed by structural analysis of the solid sample taken from the exploitation equipment. The utilization of scale additives is a practical method for fighting scaling problems. A technique method to record the efficiency of the additive was successful realised.

Keywords: geothermal waters, blocks of flats, heavy metals, structural analysis

Oradea geothermal reservoir, located in fractured Triassic limestones and dolomites has been exploited by several wells, used mainly for space heating, greenhouses, industrial uses and swimming pool [1-2]. Within these wells, a special economic importance presents well no. 4797, having a beneficial direct use for heating flats in Nufarul side of the town. A two years project (2001-2002) „A comparative study and production characteristics of geothermal waters in Romania and Iceland” was initiated by Research Geothermal Centre from Reykyavik in collaboration with the University of Oradea. The research work for well 4797 has been continuing later and was extended with the University of Akureyri. The purpose of present paper was to create a database of chemical composition of waters sampled from geothermal well 4797 and to interpret the geochemical exploration data by applying the methodology outlined in next section. Most computations were performed by simulation programs of [3-8] and it was approached a new technique to solve the scaling problems appeared at exploitation.

Experimental part

Treatment of water samples and the used analytical methods

In order to make a chemical analysis of waters from well 4797, samples were taken and stabilised according to inhouse practice at University of Oradea and at University of Akureyri, but based on internationally acknowledged methodology for sampling for geochemical analysis [2, 9]. The water temperature was measured at the wellhead.

Samples for pH and volatiles were collected untreated in airtight dark glass bottles. Samples for analysis of cations (main and trace elements) were filtered, collected in plastic bottles and acidified by concentrated superclean HNO₃, added on site. Samples for anions analysis were filtered, but not treated and collected in plastic bottles [2].

Hydrogen sulphide was measured on site, in an alkaline solution by titration with mercury acetate, using dithizone as indicator. Colour changed from yellow to pink in the presence of hydrogen sulphide [2].

Total carbonate and pH were measured in the lab at the University of Oradea, right away after sampling. pH was measured electrometric and total carbonate was measured by titration of water sample with solution of HCl until pH=3.8 followed by backtitration with NaOH solution after flushing the CO₂ out of the acidified sample, by nitrogen gas [2, 9].

The filtered and no treated water samples were used for anion determination. Chloride, fluoride, phosphate, bromide, sulphate, nitrate and nitrite were analysed by a Ion Chromatograph, type DIONEX CX-500 [10].

The filtered and acidified water samples were analysed in 2002 and 2006 by the following methods: Atomic Absorption Spectroscopy (AAS: Perkin Elmer 1100 B),
direct acetylene flame for sodium, potassium, magnesium, calcium (absorption read at 589.6 nm, at 766.5 nm, at 285.2 nm, respectively at 422.7 nm) and with graphite furnace for aluminium and iron, the purge gas was Ar; Spectrophotometry (Hitachi 200 Spectrometer) for silica, absorption was determined at 410 nm and for boron absorption was determined at 420 nm [11-14].

The results from 2008 of: sodium, potassium, calcium, magnesium, iron, silica, boron, aluminium were obtained from filtered acidified samples by Inductively Coupled Plasma Optical Emission Spectroscopy (Activa S equipment) based on standard methods. The concentration of trace components: As, Ba, Cd, Co, Cr, Cu, Hg, Zn, Pb, Ni, Mn, Li were also measured by ICP techniques [15, 16].

Classification of thermal waters

The results of analysis of main components in the water samples from well 4797, in mg/L are shown in table 1. There are also presented the concentrations of trace elements in the water sample from 2008 (table 2), some of them in good limits being nutrient components for soil, as well as trace of heavy metals.

For an initial classification, the Schoeller diagram utilizes the concentrations of sulphate, bicarbonate, carbonate, chloride, magnesium, calcium and the sum of alkalii ions, sodium and potassium. Each water sample is represented on the diagram by a line water samples belonging to the same or similar water groups, which follow the same pattern on the diagram. Crossing lines on the diagram represent water types of unrelated origin [3].

For a classification in terms of the major anions Cl-, SO_4^- and bicarbonate, a triangular diagram was used [4]. The position of a data point in this diagram is obtained by evaluating the percentage of Cl-, SO_4^- and HCO_3^- relative to the sum of the concentrations (in mg/L) of all three constituents.

Giggenbach and Arnorsson suggested that a triangular diagram with Na/1000, K/100 and $\sqrt{Mg}$ can be used to divide waters into fully equilibrated with rock at a given temperature, partially equilibrated and immature water, that means dissolution of rocks is not followed by equilibration [5, 6].

Geothermometers

The chemical geothermometers constitute the most important geochimical tool for exploration and development of geothermal resources. During the exploitation phase, geothermometers are used to estimate subsurface temperatures, below the zone of cooling, expected to be encountered by drilling, using the chemical composition of wellhead waters. When applying geothermometers it is assumed that no changes in water composition occur in conjunction with conductive cooling and that temperature-dependent mineral solution equilibria prevail in the geothermal reservoir. Temperature, time and fluid composition all affect different crystalline forms of silica. Therefore, waters being in contact with rocks at a given temperature, in some places quartz or chalcedony may control dissolved silica [7]. In the range of 0-250°C, in the condition of no steam loss, chalcedony geothermometer or quartz geothermometer could be calculated. Cation geothermometers, like Na-K geothermometer, are based on the temperature dependence of ion exchange or partitioning of alkalis between solutions and solid phases [5].

The results of the chemical analyses of the water samples, obtained in this study (Table 1) were used to calculate deep temperatures based on these geothermometers using the WATCH aqueous speciation program [8].

The silica-enthalpy mixing model

Mixing model has been developed to allow the estimation of a hot component mixed in waters in springs or discharge from shallow drillholes [7]. The diagram plots silica versus the enthalpy of water, giving the temperature of the deep hot water component. It fits well when a mass flowrate is high enough to allow for a little conductive cooling. The cold water point was assumed to represent the hypothetical cold ground water (temperature: 10°C and SiO_2: 20ppm) in the study area. The intersection point of the “cold water-geothermal water” line with the solubility of chalcedony curve gives the silica content and the enthalpy of the deep hot water component, and its temperature is obtained from the steam tables [17].

Solution-mineral equilibrium

The study of fluid-mineral equilibria is a very useful tool providing practical applications for the assessment of equilibrium/dis-equilibrium conditions for geothermal fluids, on which almost all the reservoir processes depend. Such applications are useful in prediction of scaling and corrosion tendencies in a particular geothermal system. Here, the computer program WATCH has been used to calculate the saturation indexes for particular mineral phases believed to occur in the reservoir of Nufarul field [8]. The program uses the results of chemical analysis of waters at wellhead temperature and recalculates the aqueous speciation of the various components at several predetermined temperature values, to obtain the saturation index log Q/K versus temperature relationship for each mineral. Q is obtained by analytical data, while K is the solubility constant for a mineral and is derived from chemical thermodynamic data.

Analysis of scale

A severe scale formation was removed in may 2008 from the pipe inside well 4797 after the production was stopped. The solid deposition sample was finely ground in an agate mortar and transferred to an aluminium sample holder with glass backing. There samples were identified using a Philips PW1710 Diffractometer. They were used K-alpha Cu radiation. The data from the samples were handled using a software, patterns being evaluated and compared using the Powder Diffraction File PDF-2 Database Sets 1-46 from the International Centre for Diffraction Data. In order to get the morphology of deposits, the solid sample was also analysed by Scanning Electron Microscope (model Philips CM30T).
other dosages of this additive. The same experiments were done with a polyacrilate additive produced by NALCO firm. The greater the time reaching that change in pressure, the best the additive.

Results and discussions
Classification of studied geothermal waters over their chemical properties
Fluid geochemistry is an important tool during all stages of geothermal development and production. In the paper, the analytical results are presented in tables 1 and 2, classified and interpreted.

As seen from table 1 waters can be classified as calcium-sulphate, with an almost neutral pH. The sodium concentration in sample from 2008 does not fit well with its previously concentration and there is a lack of cations relative to anions in this sample. The TDS of the last year is lower compared with the results from other years. The iron concentration in 2008 is high, maybe because sampling was done at the beginning of well production, when it is possible to be an instability because of the perturbances.

Apart from the ecological impact of using geothermal water from this well, from table 2 it seems that the discharge would not be of any concern for health and environment [18, 19].

For presentation of water chemistry of well 4797, the concentration of the most important water constituents for each studied year was plotted in a Schoeller diagram (fig. 1). All the water samples show the same pattern, they have a similar origin, suggesting that the ground water comes from local precipitation and has passed through similar rock types.

A triangular diagram (fig. 2) on the relative concentrations of the three major anions, Cl, SO₄²⁻ and HCO₃⁻ was used for the classification and characterization of the waters. The data points for the geothermal waters from Nufarul, well 4797 plot in the field of steam heated waters, within the field of more than 65% sulphate and less than 30% bicarbonate. The higher pH of sample suggest more steam effects and its sulphate concentration is also higher.

The plot for the well 4797 data is presented in the Na-K-Mg ternary diagram (fig. 3). From figure 3 you can notice that none of the waters from well 4797 in the three selected years reach the fully equilibrated water curve. Waters from 2006 and 2008 plot at the boundary between immature and partially equilibrated waters. Waters from well 4797 have a high percentage of Mg, so they plot in the immature region. Since this implies that these waters have not attained equilibrium with the reservoir rocks it would be inaccurate to use them to get the Na/K geothermometer temperature.

Estimation of reservoir temperature
For temperature calculations, WATCH program uses the functions for quartz, chalcedony and Na/K ratio geothermometers. The results are summarized in table 3. The temperatures of the reservoir indicated by the calculated chalcedony geothermometer are close to the production temperatures of the waters in the years 2002 and 2006. In 2008 it seems that quartz geothermometer control better the temperature of silica equilibrium in the reservoir. The Na/K geothermometer does not give good results for low-temperature geothermal waters.
The silica-enthalpy mixing model was used in order to estimate the reservoir temperature. Based on this model, a temperature of 97°C was obtained for the deep geothermal water from well 4797 in 2002, 91°C in 2006 and 76°C in 2008 (fig. 4). The temperatures obtained using this method are higher than both those calculated from the chalcedony geothermometer and those measured at the wellhead. These differences of temperature are due to mixing with cold water in the upper layers. Colder water from the shallow feed zones can mix with hotter water from the deeper ones.

Computer simulation of scaling

The diagram for well 4797 (fig. 5a) indicates a supersaturation for calcite at the wellhead temperature, 72°C and at lower temperatures as well. Talc is supersaturated, but this does not create problems. The saturation of microcline increased by decreasing the temperature. Laumontite and quartz presents supersaturation. There is an equilibrium with chalcedony at all temperatures which were used, assuming conductive cooling during utilization. There is undersaturation with respect to the other minerals.

The diagram from 2006 (fig. 5b) shows a possible scaling with respect to calcite at the wellhead temperature. There is also supersaturation for t alc, quartz, microcline and laumontite, and anhydrite is close to the saturation line. There is equilibrium with respect to chalcedony. Most of the minerals tend to be fairly close to saturation at temperatures exceeding 60°C. Most of the lines intersect between 45 and 55°C, with the minerals in equilibrium at different temperatures within this interval.

The geothermal water from well 4797, in 2008 (fig. 5c) is undersaturated in anhydrite, adularia, fluorite, analcime, albite, amorphous silica, laumontite and chrysotile at the wellhead temperature. Microcline and quartz are slightly supersaturated. Calcite is supersaturated at all temperatures. The diagram indicates equilibrium for chalcedony from the measured temperature to lower temperatures, until about 50°C. Most of minerals tend to be in equilibrium within 45-60°C, temperatures reached during geothermal water utilization.

Structural analysis of scale

The XRD analysis of the sample (fig. 6) indicated the presence of calcium carbonate as aragonite and calcite crystals in the solid sample. The SEM analysis (fig. 7) shows prismatic form of calcite crystals, and dendritic formations of aragonite. Small calcite crystals tend to cover the wall of the metallic pipe, forming an adherent layer, on which develop aragonite crystals.

Scale control results

Additives were evaluated for calcium carbonate inhibition. The results are presented in figure 8. The best additive performance is when it has the ability to stop the growth of calcium carbonate crystals, so to maintain calcium ions in solution. The tests show that the additives tested can control calcium carbonate deposition. The additive that demonstrates the best calcium carbonate control is the polyacrilate. It is better to avoid the use of tripolyphosphate, because it tends to cause additional scale in the form of calcium phosphate or mixed scale including phosphate ions, which can adhere to the walls of the pipes.

<table>
<thead>
<tr>
<th>Year</th>
<th>Wellhead temperatures, °C</th>
<th>Chemical geothermometers, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Quartz</td>
</tr>
<tr>
<td>2002</td>
<td>72</td>
<td>93.3</td>
</tr>
<tr>
<td>2006</td>
<td>71</td>
<td>97.7</td>
</tr>
<tr>
<td>2008</td>
<td>70.5</td>
<td>63.7</td>
</tr>
</tbody>
</table>

Table 3
GEOTHERMOMETRY CALCULATIONS
Fig. 5. Mineral equilibrium diagrams for the geothermal water from well 4797

Fig. 6. XRD analysis of deposition sample
Conclusions
An important production well from Oradea was taken in this study. Waters were sampled for analysis using standard methods. The credibility and usefulness of geochemical data depend on the methods used and the care taken in the collection of samples. The results of the laboratory analysis were monitored. In time, the type of water was maintained as calcium-sulphate, as was demonstrated also by Schoeller classification. As seen from the data presented in the tables, there were recorded great differences in sodium and sulphate concentrations in the last year compared to the previous studied years. Sulphate still remain the main dominating anion. Calcium is always high and varies in the range of 200-300 mg/L. The value of total dissolved solids is about 50% lower than the ones recorded earlier. Some of the heavy minerals show rather high concentrations, especially iron, manganese and mercury. The heavy metals concentration are in the limits that are not dangerously for people and environment.

The presence of heavy metals could be one reason why hydrogen sulphide could not be determined any time, maybe due to reacting of heavy metals with ditizone which interfered. The geothermal water from well 4797 appears to be a steam heated water, which suggests that some boiling in the reservoir has occurred with the hydrogen sulphide transformed into sulphate. The high sulphate concentration in the geothermal water supports this interpretation.

The solubility of silica minerals has been shown to be positively related to temperature, chalcedony as main and quartz geothermometers giving good results for temperature at which is attained the equilibrium between the aqueous H$_2$SiO$_4$ species and the respective solids.

The silica mixing model results have been used to infer the location of the major aquifer feeding the well, being higher than the wellhead temperature and than calculated geothermometry temperatures. This means that into the feedzone a cold water with a similar composition as from the production well is discharged, being a mixing of hot water component from the reservoir and the reinjected cold waters from users.

In low-enthalphy wells like the one studied in Oradea, the main scaling problems are due to calcium carbonate precipitation and other minerals predicted by simulation did not make serious problems during production.

As described previously, by computer simulation, all the samples from well 4797 are supersaturated with respect to calcite. The structural analysis of the solid deposition indicated the presence of calcium carbonate, both as calcite and aragonite crystals.

A new approach of calcium carbonate deposition test was made, which implied to record the pressure changes in a capillary tube, when geothermal water with additive goes through. There were selected two additives produced by NALCO firm. It was established the best performance of additive which retard scale. The ability of additives to maintain the pressure depend on the time needed to plug the tube. It was demonstrated that both additives taken in these tests were good for inhibition of calcium carbonate precipitation, but the poliacrylate gave better performance, being necessary in lower concentration and also it can not give secondary precipitation effects.

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