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Analysis of Treatment Possibles of High-Mineralized Geothermal Water (Central Poland - Gostynin Region)

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ABSTRACT

The geological investigation in Gostynin region (central Poland) has shown favourable geothermal conditions in Lower and Middle Jurassic formations. Composition of the Lower Jurassic waters from Gostynin IG-1/1a well (2290-2245m depth) was used for preliminary evaluation of balneological properties and thermodynamical status of these waters. The performed analyses allowed for including them to so-called specific mineral waters. On the basis of thermodynamical calculations possibility of the precipitation of carbonate minerals, and in case of oxygen entering, also iron oxides and iron hydroxides in the heat exchanger elements was indicated.

1. INTRODUCTION

As part of drilling work conducted in 1960s and intended to, among others, recognize a geology structure of the Kujawy Swell and the adjacent zone of the Płock Trough (Gostynin Region), as well as to define Mesozoic bitumen perspectives, a number of exploration wells were drilled. Hydrogeological conditions of the strata being drilled through in succession were determined.

Detailed well tests made in wells Gostynin IG-1/1a, Gostynin IG-3, and Gostynin IG-4 proved that favorable hydro-geothermal conditions are mainly linked to the contact zone of Middle and Lower Jurassic formations, which occurs at a depth of approximately 2,000m in the Gostynin region (Dembowska and Marek, 1985; Bujakowski et al. 2004) It is expected that a water discharge of the Lower and Middle Jurassic aquifer will range from 50 to 100 m^3/h, with a temperature of 60^{o}C, TDS of 100 g/dm^3, and the static water table depth of 25 m b.g.l.

Based on the analysis of well data (Bujakowski et al. 2004), a project of geological works for drilling geothermal well Gostynin GT 1 has been elaborated. Drilling and reporting for the well are currently (i.e. 2008) near completion. The present paper does not include the information related to the work.

2. CHARACTERISTICS OF PHYSICAL-CHEMICAL PROPERTIES OF LOWER AND MIDDLE JURASSIC WATER

Chemical composition of the Lower Jurassic groundwater has been identified to a minor extent up to date, as a result of single tests in Gostynin IG-1/1a, Gostynin IG-4 wells, and jointly with the Middle Jurassic (Aalenian) formations in well Gostynin IG-3. The scope of physical-chemical testing was limited to the determination of: pH, density, and TDS, as well as contents of: calcium, magnesium, Fe_{tot} (total iron), sodium, potassium, chlorides, sulfates, hydrogen carbonates, bromides, iodine and gases (carbon dioxide and nitrogen). Chemical testing of water was done in the Central Laboratory of the Polish Geological Institute. The determination of gas dissolved in water were carried out in the Bitumen Rock Laboratory of the Oil and Gas Geology Section of the Polish Geological Institute (Dembowska and Marek, 1985).

To determine groundwater zoning, a classification used in oil hydrogeology has been employed, i.e. Sulin's classification. The classification system has a genetic character. It is based on hydrogeochemical equivalent relations between ions of sodium, chlorides, sulphates, and magnesium. The salt where the water derives its name from does not have to prevail in quantitative terms over other salts which are contained in the water. However, to illustrate the share of ions in general water mineralization, results of analyses are also shown according to Altowski-Szwiec's classification. According to this classification system, the name of the type of water is arrived at taking into account ions which content exceeds 20% ± 3% mval against total anions and cations in water.

The results of water composition analyses for Gostynin IG-1/1a well confirmed the occurrence of a brine with TDS of 103.2 g/dm^3, the chloride-calcium type of 2 class according to Sulin's classification, and the chloride-sodium type according to Altowski-Szwiec's classification (Table 1) in the Lower Jurassic fine-grained sandstones (Domerian – Sławęcin Beds, 2290-2245 m. b.g.l.). Chemical analysis of water was done in November 1966 once. In the exploration wells of Gostynin IG-4 and Gostynin IG-3, in Ciechocinek and Borucice Beds (depths: 2702.6 – 2661.8 m b.g.l.; 2615 – 2605 m b.g.l.; 2310 – 2096.4 m. b.g.l.), the occurrence of brines with TDS from 99.4 to 110.0 g/dm^3 was also confirmed. They are characterized by low alteration of chemical composition, expressed, e.g. by a genetic indices relationship rNa:rCl = 0.83-0.81 and rCl:rBr = 600.

In the Aalenian and Kujavian formations of the Middle Jurassic in the Gostynin region, water was found in Gostynin IG-1/1a well at a depth of 2070 - 2060 m. b.g.l., while in Gostynin IG-4 at depths: 2487 – 2476, 2392 – 2385, and 2392 – 2385 m b.g.l. The TDS content (ranging from 74 to 107.5 g/dm^3) and chemical composition of water being hosted in the Middle Jurassic formations depend on the depth and location in relation to the Kujawy Swell. The waters accumulated in shallower margin part of the basin reveal very low TDS content of 6.3 g/l, chloride-calcium type, and low alteration of chemical composition. The TDS content in the water increases with increasing depth. The waters have similar chemical compositions at the hydrogeochemical indices of rNa:rCl = 0.82 – 0.85. According to Sulin's classification, the water is of chloride - calcium nature. Increased contents of hydrocarbons have not been found. In the group of biophile elements, only slightly increased quantities of iodine occur.

As shown above, in the Lower and Middle Jurassic sandstone formations in the Gostynin region, groundwater occur at a depth of 2000-2500 m b.g.l.; and it is highly saline with TDS ranging from 74 to 110 g/dm^3 with chlorides and sodium dominating the ion composition. Among microelements, high concentration of iron, bromides, and iodine have been found. In line with Sulin's classification, this type of water is categorized as chloride and calcium water. It is caused by the fact that chloride ions occur in water with concentrations exceeding aggregate total contents of ions Na^+ and Mg^{2+}, as a result of which they must bond with the Ca^{2+} ions. The chloride and calcium type water commonly feature highly mineralized fossil connate water which originates in zones sealed from the inflow of infiltration water.

According to the Altowski-Szwiec's classification, Middle and Lower Jurassic groundwater in the Gostynin region is classified as chloride and sodium water. Percentage share of chloride milligram equivalents against anion totals ranges between 98.7 and 99, whereas sodium totals – between 86.7 and 88.7% mval (milligram equivalents) of cations.

Table 1. Chemical composition of the brine from Gostynin IG-1/1a well (2290-2245 m depth)

Physical properties:		
pH	-	7
density	g/cm^3	1,0737
Chemical properties:		
Cations		
Ca^{2+}	mg/dm^3	2 670
Mg^{2+}	mg/dm^3	640
Fe - total	mg/dm^3	9
Na^+	mg/dm^3	35 000
K^+	mg/dm^3	360
Anions		
Cl^-	mg/dm^3	64 500
SO_4^{2-}	mg/dm^3	830
HCO_3^-	mg/dm^3	238
Br^-	mg/dm^3	110
J^-	mg/dm^3	3
Gases		
CO_2	% obj.	64,5
N_2	% obj.	35,2

3. EVALUATION OF HEALING PROPERTIES OF THE LOWER JURASSIC WATER

The evaluation of healing properties of natural medicinal resources and climate is carried out based on documented research dating back at least 3 years, according to the Ordinance of the Minister for Health, dated 13 April 2006, related to the scope of research necessary to establish healing properties of natural medicinal resources and healing properties of the climate, criteria of their assessment and a template certificate confirming the properties (Journal of Laws dated 2006, issue 80, item 565.) Based on the evaluation of water reaction, its temperature, redox potential, specific electrolytic conductivity, water absorbance, total radioactivity, contents of dissociative and non-dissociative mineral and gas components of: carbon dioxide, hydrogen sulfide and radon; groundwater is classified as follows:

Mineral water – if 1 dm^3 of water contains at least 1,000 mg of the total dissolved solids;

Specific water (low mineralized water) – either it contains at least one or more specific pharmacological components, i.e. 1 mg iodine, 1 mg sulfide, 2 mg fluoride, 10 mg bivalent iron (Fe^{2+}), 70 mg metasilicic acid, 1,000 mg of dissolved natural carbon dioxide, or it reaches an outflow temperature of at least 20^{o}C, or it displays radioactivity of at least 74 Bq/dm^3;

Specific mineral water – i.e. mineral water which contains one or more specific component as listed above.

The analysis of physical and chemical properties of the Lower Jurassic water which occurs in the Gostynin region (recognized during carrying out a single test while the wells were drilled in 1966-1967) proved that in relation to assessment criteria for healing properties of natural medicinal resources (Journal of Laws dated 2006, issue 80 item 565), there are prerequisites which allow for classifying the water as specific mineral water. It is characterized by increased TDS (103 g/dm^3), outflow temperature exceeding 20^{o}C (the temperature recorded was 60^{o}C), as well as the content of iodine ions exceeding 1 mg/dm^3 (namely about 3-4 mg/dm^3.). In case of Gostynin IG-1/1a well, the analysis of brine from depths 2290-2245 m b.g.l. found it being of 10.3% chloride – sodium and iodine thermal water.

The most frequent applications of iodine thermal brines in balneology refers to bath treatment of rheumatic, gynecological, and dermatological ailments, as well as to inhalations in case of respiratory ailments.

4. ANTICIPATED THERMODYNAMIC STATE OF THE LOWER JURASSIC WATER

Thermodynamic groundwater state depends on a series of factors, including among others: the lithology of a rock system within which the flow occurs, quantity of dissolved components contained in water, saturation with gases, temperature, reaction, redox conditions, and the kinetics of reactions between particular system components. The knowledge of the thermodynamic state of groundwater exploited allows for defining of a water saturation index in relation to particular mineral phases, while taking into consideration the impact of temperature variations on the value of parameters calculated (Kępińska, 2001, 2006; Kania, 2003, Bujakowski et al. 2007.)

The accuracy of thermodynamic calculations for most part depends on the range of indices determined in waters tested. The more physical and chemical data are introduced into the system, the more precise information on saturation indices of the solution. The calculation of thermodynamic state of the Lower Jurassic water occurring in the Gostynin region employs the test results of water occurring at the depth of 2290-2245 m b.g.l. in Gostynin IG-1/1a well. Due to scarce quantity of physical and chemical indices determined for the Lower Jurassic water, the thermodynamic modeling results obtained should be treated as approximate values. Nonetheless, they allow for identifying thermodynamic processes which may occur in the geothermal installation, related to scaling. The knowledge of these processes should be used at the stage of concept design of the future geothermal installation.

Calculations of water thermodynamic state were performed for a series of scenarios, taking into account changes in water temperatures using PHREEQC program. Considerations cover 'raw' water found in Gostynin IG-1/1a well, as well as 'concentrated brines' which may be produced by evaporating a part of water in the vacuum evaporator. Introducing an evaporation unit to the technological system could allow for partial recovery of salt NaCl from water. Concentrating brines by way of water evaporation may be conducted in so-called pan evaporator or vacuum evaporator. Pan evaporators are open reservoirs where intensive water evaporation is performed (most frequently, thanks to heating it up until it reaches the boiling point). Vacuum evaporators are closed (hermetic) system where the evaporation process is performed at a lowered pressure. Lowering of pressure in the evaporation zone facilitates an increase in evaporation intensity, whereas the increase in the pressure in the condensation zone enhances the process. The method of producing salt in vacuum evaporator is classified as a thermal method.

In case of calculations performed for 'raw' waters, water temperature at outflow being equal to 75^oC was assumed as the input value. Next, possible changes in the thermodynamic state of water extracted after being cooled down have been modeled, every 5 degrees down to the final temperature of 5^oC. Due to the lack of measurement data recorded for the redox potential of water tested, the reducing nature of the Lower Jurassic water environment was assumed for calculations. The assumptions correspond to conditions found in other geothermal deep wells in the Podhale region and in the Polish Lowlands. The nature of the redox potential adopted in the model is important due to the fact that redox conditions control most processes which take place in groundwater. The redox potential is the measure of ability to oxidize or reduce a system, while determining the chemical form of migration of given ions in water.

The modeling of the thermodynamic state of 'brines concentrated in the vacuum evaporator' was carried out in a subsequent stage. The loss of water mass due to the precipitation of salt (NaCl) as well as a related process of producing universalized water have been accounted for. The analysis assumed a water temperature of 80^oC, i.e. the precipitation temperature of sodium chloride in the vacuum evaporator.

The simulation was performed for those minerals for which supersaturation of a water solution is possible, i.e. carbonate, sulfate, and ferric mineral compounds. They include: aragonite ($CaCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), gypsum ($CaSO_4{\cdot}2H_2O$), anhydrite ($CaSO_4$), geothite (FeOOH), hematite (Fe_2O_3), magnetite (Fe_3O_4), and siderite ($FeCO_3$). The study of the water saturation index in respect of carbonate minerals: aragonite, calcite, dolomite, magnesite, and siderite proved that in the model conditions, the Lower Jurassic waters are supersaturated with regard to calcium and iron carbonates throughout the temperature range analysed (Figure 1). The supersaturation of water with magnesium carbonate (magnesite) was also recorded in temperatures over 30^oC. The supersaturation of the solution with mineral phases listed above signals the possibility of their precipitation. The process of the precipitation will be of a dynamic nature though, hence, we should keep in mind that it will occur in the geothermal system as well as in installation. At the TDS of the Lower Jurassic water examined (about 103 g/dm^3 at a depth of 2290-2245 m b.g.l., recorded in well Gostynin IG-1/1a,) and the excepted outflow water temperature of 75^oC, conditions for the precipitation of about 8 mg of total $CaCO_3$, $CaMg(CO_3)_2$, $MgCO_3$ and $FeCO_3$ from 1 liter of thermal water exist. The quantity of mineral substances possible to be precipitated decreases with declining temperature. At a temperature of 35^oC, it is possible to precipitate approximately 2.6 mg/dm^3 of the above listed mineral forms in total.

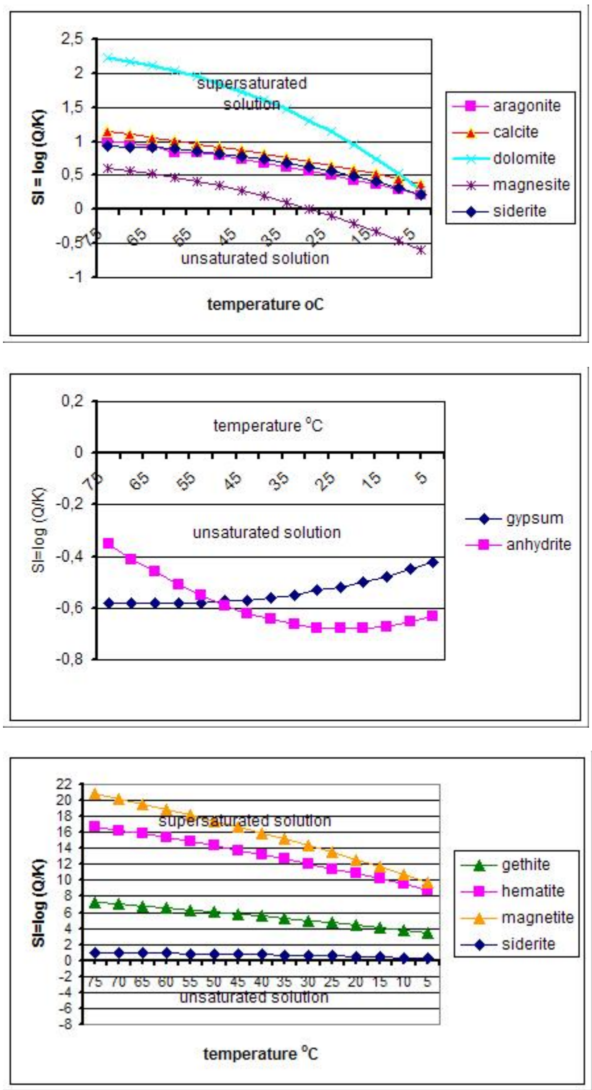

Figure 1. The Gostynin IG-1/1a well (Lower Jurassic). Water-mineral equilibria vs. temperature SI – Saturation Index, Q – ionic product of true concentrations of components participating in dissolution/precipitation reaction with given mineral, K – equilibrium constant

In case of sulfate forms, the simulation was conducted in relation to anhydrite and gypsum. The undersaturation of water with sulfate minerals was concluded, i.e. no indication as to their precipitation from the system under redox conditions tested (Figure 1).

The value of redox potential and pH of the solution determine the iron migration form in water. Minerals which contain trivalent iron Fe^{3+} are not durable in redox conditions, whereas those which contain bivalent iron Fe^{2+} – in oxidizing conditions. Hence, calculations performed while assuming reducing conditions and a Fe^{2+} occurrence in water (characteristic of reducing conditions) indicate that only siderite ($FeCO_3$) discloses favorable conditions for precipitating from solutions among iron minerals. In the expected outflow water temperature of 75°C, conditions for precipitating approximately 0.099 mg $FeCO_3$ out of 1 liter of geothermal water exist, i.e. approximately 12 g/h in case of a water discharge of 120 m^3/h.

Introducing total iron content to the calculations (as given in the chemical composition of water from Gostynin IG-1/1a well), i.e. the total of Fe^{2+} and Fe^{3+} determines the possibility of precipitating geothite, hematite, and magnetite from water, beside siderite (Figure 1). The supersaturating process of the solution with the above stated mineral forms will also take place in oxidizing conditions. The precipitation of iron oxides and hydroxides from water contributes to the occurrence of corrosion and clogging processes in the geothermal system and installation related to.

4. ANTICIPATED THERMODYNAMIC STATE OF THE 'CONCENTRATED BRINE IN AN VACUUM EVAPORATOR"

Modelling of the thermodynamic state of concentrated brines in the vacuum evaporator (figure 2) indicated that at a temperature of 80°C, favorable conditions exist for precipitating the following minerals from the water solution: aragonite, calcite, dolomite, magnesite, and siderite. At TDS of the Lower Jurassic water examined (about 103 g/dm^3 at the depth of 2290-2245 m b.g.l. recorded in Gostynin IG-1/1a well) it is possible to obtain approximately 71.17 g NaCl and about 144 mg of the total of $CaCO_3$, $CaMg(CO_3)_2$, $MgCO_3$ and $FeCO_3$ out of 1 liter of water in the concentration process. In case of a geothermal water discharge being 120 m^3/h, it is possible to precipitate approximately 8.5 Mg NaCl and 16.7 kg of calcium, magnesium, and iron carbonates within an hour. Table 2 displays the quantity of carbonate substances which are possible to be precipitated from the brine analyzed.

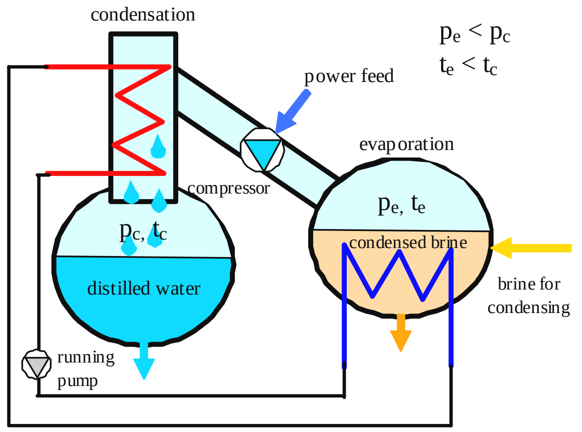

Figure 2. The scheme of evaporation unit

The concentrated brines in the evaporator demonstrate the ability to precipitate the following sulfate forms at a temperature of 80°C: gypsum and anhydrite. It is possible to obtain 1.653 g/dm^3 of $CaSO_4$ out of 1 liter of concentrated water. The total amount of 191.7 kg/h of gypsum and anhydrite is possible to precipitate out of water tested while producing with a yield of 120 m^3/h. In case of a flowrate of 80 m^3/h, possible 125.6 kg/h $CaSO_4$ may be precipitated, while at 40 m^3/h – 59.5 kg/h.

Table 2. The precipitation amount of carbonate minerals from concentrated brine.

Mineral phase	The amount of mineral precipitation [g/h] depending on water exploitation with discharge of:		
	120 [m^3/h]	80 [m^3/h]	40 [m^3/h]
Siderite $FeCO_3$	153,1	100,32	47,52
Aragonite $CaCO_3$ Calcite $CaCO_3$ Dolomite $CaMg(CO_3)_2$	14732	9652	4572
Magnesite $MgCO_3$	1821,2	1193,2	565,2
Total	16706,3	10945,5	5184,72

The analysis of the thermodynamic state of geothermal water, concentrated in the process of concentration in an evaporation installation confirmed the occurrence of favorable conditions for the precipitation of iron oxides. In line with model assumptions based on chemical composition of water found in Gostynin IG 1/1a well, a possibility of precipitating approximately 70.3 g/h of iron oxides in the installation, at a water flowrate of 120 m^3/h has been estimated.

5. SUMMARY

A favorable hydrogeothermal conditions are mainly linked to the contact zone of the Middle Jurassic and Lower Jurassic strata, which occur at a depth of approximately 2,000 m in the Gostynin region. On the basis of one series of the groundwater test (in 1966-1967) it was found that high-mineralized water, from 99.4 to 110.0 g/dm^3, occur in the Lower Jurassic formations. In relation to the valuation criteria of healing properties of the natural resources there is possibility to classify those waters to specific mineral waters.

Considerations presented in the paper related to the thermodynamic state of groundwater which occur in the Lower Jurassic formations in the Gostynin region are for reference. They signal the possibility of the precipitation and deposition of carbonate minerals in the installation units, as well as iron oxides and hydroxides in case of etering oxygen. It should be kept in mind that the thermodynamic state of water and related processes of precipitating mineral substances from the solution are of a dynamic nature, hence corrosion and clogging occur along the entire flow of the water solution from heat exchangers, through the installation, and up to the absorptive zone of the injection well.

In order to confirm the actual role which particular water components or selected forms of chemical elements migration (speciations) in given conditions may perform in the process of corrosion and clogging, it is necessary to specify the composition of water in a number of installation outlets in more detail. First, it is recommended to collect water at the wellhead in order to obtain information on high-level characteristics of thermal water deposit. Next, it is necessary to test waters cooled down at heat exchangers, thanks to which it is possible to identify changes in their chemistry and redox potential. Specific water collection outlets should be determined after the analysis of the technological process related to heat extraction. An analysis of the water thermodynamic state based on a detailed determination of physical-chemical properties of water may provide new information, important from the point of view of system operations; among others, with regard to the evaluation of participation of precipitating siliceous minerals in the process. The information may serve as a prerequisite for considerations on introducing technologies which soften the water and remove excess iron into the geothermal installation system.

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Rozporządzenie Ministra Zdrowia z dnia 13 kwietnia 2006 r. w sprawie zakresu badań niezbędnych do ustalenia właściwości leczniczych naturalnych surowców leczniczych i właściwości leczniczych klimatu, kryteriów ich oceny oraz wzoru świadectwa potwierdzającego te właściwościom (Dz. U. z 2006 r., Nr 80 poz. 565)