

GEOCHEMICAL MODELING OF A HYDROTHERMAL SYSTEM OF THE PAUZHETKA GEOTHERMAL PRODUCTION FIELD

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ABSTRACT

The Pauzhetka geothermal production field in the southern part of the Kamchatka peninsula (Russia) supports an existing geothermal power plant. This geothermal field is a high-temperature, retrograde, low-sulfidation magmatic-hydrothermal system in an active island-arc volcanic setting. We present here a geochemical model for the magmatic-hydrothermal system, involving the following six main regions of the system: primary deep sodium-chloride waters, convective fissure, two-phase geothermal reservoir, aquifers, vadose zone, and surface. Moreover, the model takes fluxes between these regions and also mixing of cool underground water with geothermal fluid and condensed steam into account. The model has been verified using some analytical data of geothermal waters from a drill hole within the Pauzhetka geothermal field. Thermodynamic modeling using a Selektor-C program based upon the Gibbs free energy minimization provides the following results for the system: mineral composition, aqueous species, Eh, pe, pH etc. In this study, quantity of aqueous species of the system under investigation at various temperatures and pressures and also in the presence/absence of atmospheric air has been estimated, implying that chemical analysis of samples from various drill depths is performed under the conditions of an analytical laboratory.

INTRODUCTION

The first geothermal power plant in the former Soviet Union, the Pauzhetka is located in the southern part of the Kamchatka peninsula, 300 km south of the city Petropavlovsk-Kamchatsky, Kamchatka Region, Russia. It was built in 1966 and had 5 MW of active installed capacity. The Pauzhetka geothermal power plant owned currently by the RusHydro Group, one of the largest power generating companies and the leading producer of renewable energy in Russia, has 12 MW of active installed capacity with an average production factor of 57% (6.8 MW). The Pauzhetka field produces a steam-water mixture and has 10 active wells at present. To maintain generation capacity in the face of a productivity decline, a binary cycle block has

to be installed by the end of 2011 (Asaulova et al., 2009; RusHydro Group, website). The decline in well productivity may be due to an overdevelopment of the field by the operator. However it may be associated with an evolution of the geothermal area. Geochemical modeling is an important tool in studies in the area of geothermal resources. It applies to various parts of geothermal area, from the near-surface vadoze zone to deep-seated primary geothermal reservoir. Geochemical model can simulate the chemical and physical processes affecting the distribution of chemical elements between aqueous, gas and solid phases. Therefore, geochemical models are required to gain an understanding of the processes occurring in the subsurface within a geothermal production field.

GEOLOGICAL SETTING

A flat-topped tectonic dome dominates the structure of the southern part of the Kamchatka peninsula. It is approximately 40 km in diameter and rises to an elevation of 2 km in the central part. Two main periods in the building of the tectonic dome are recognized; one, the formation of the dome, during late Miocene or early Pliocene time and a second, the development of a tectonic depression in the center of the dome, in the Lower Quaternary. The tectonic depression, referred to as the Pauzhetka depression, is 20 km wide and 25 km long. The northwestern part of the depression was sunk deeper than other parts, to a depth of 1000 - 1200 meters (Leonov, 1989).

The southernmost volcano on the Kamchatka, 2156-m-high Kambalny stratovolcano, delineates the southern boundary of the tectonic dome zone. His number is 1000-01= according to the Global Volcanism Program of Smithsonian Institution. At its northern end, the Kambalny volcano merges into a short ridge of older destroyed volcanoes. The ridge, termed the Kambalny ridge, is 10 km wide and extends approximately 24 km north from the Kambalny volcano toward a central part of the tectonic dome. A geothermal area, approximately 15-20 km long and 1.5-2.0 km wide, is located in the western part of the Pauzhetka depression. The

Pauzhetka geothermal production field spans an area of around 5-6 km² of the northern part of the geothermal area. It extends northwest between the western flank of the Kambalny ridge and the Pauzhetka river from which the dome, depression, geothermal area and geothermal production field take their name. The Pauzhetka river bed is in line with an axis of a large-scale fault bordering the Pauzhetka tectonic depression on the west. A deep fault system occurs within the geothermal field (Belousov, 1965).

The geothermal reservoir of the Pauzhetka geothermal field is contained in aquiferous volcanic and volcanic-sedimentary rocks of Upper Miocene to Pleistocene age and underlying volcanic-sedimentary rocks of Oligocene to Miocene age. The groundwater system at the Pauzhetka consists of upper and lower aquifers separated by a less permeable aquitard about 70 to 190 meters in thickness. The lower sandy aquifer approximately 150 meters thick exists at depths of about 650 meters below the land surface. The upper aquifer consists of two levels. The first level of the upper aquifer approximately 70-140 meters thick is composed of tuff breccia of andesite and basalt. The second level of the upper aquifer approximately 180-240 meters thick is composed of pschitic tuff of dacite and reaches to a depth of 100 to 340 meters below the land surface. Overlying alluvium about 0 to 20 meters in thickness as well as mudstone rocks about 0 to 100 meters in thickness provide a thermal blanketing effect (Averiev and Belousov, 1965).

Hydrothermal alteration processes involving zeolitization and feldspathization are associated with the second level of the upper aquifer. Lomontite, adularia, albite, quartz, chlorite, montmorillonite, sphene and apatite comprise the secondary minerals. The abundance of lomontite increases with depth and may achieve 50-60%. Adularia decreases in abundance with depth and albite substitutes for it. The abundance of quartz varies within a wide range. Such mineral assemblages as quartz-adularia, wairakite-prehnite-epidote-quartz-adularia and epidote-quartz-adularia indicate a liquid-vapour change zone within the geothermal reservoir. Hydrothermal alteration processes involving kaolinization, argillization and zeolitization are associated with the vadose zone. The main secondary minerals in this zone are kaolinite and hydro-hematite representing red clays as well as kaolinite and pyrite representing blue and grey clays (Naboko, 1965).

METHODS

The geochemical model of the Pauzhetka hydrothermal area has been designed using a program Selektor-C based upon the Gibbs free energy minimization method (Chudnenko, 2010).

In the program, chemical equilibrium for the assessment of phase stability is calculated using an interior point method (Karpov et al., 1997). Standard thermodynamic properties of aqueous species, gases and minerals are recalculated for elevated temperatures and pressures by means of the revised Helgeson-Kirkham-Flowers (HKF) equations of state for aqueous species (Helgeson et al., 1981) and other heat capacity equations. The model can compute pH, Eh, total dissolved solids concentration, aqueous species and quantity of each of species for aqueous solution; gas specification and fugacity of each gas; mineral assemblage and quantity of each mineral.

A sample of hydrothermal fluid from an active well GK-3 within the Pauzhetka geothermal production field was analyzed for major ions in the Analytical center of Institute of Volcanology and Seismology of Far Eastern Branch of RAS (analyst O. V. Schulga) in August 2008. The content of chloride ions in the hydrothermal solution has been determined using the mercurimetric method. The accuracy, expressed as relative standard deviation, of this method is 10%. The concentration of sulphate and ammonium ions has been measured by turbidimetric methods (15% and 10% accuracy, correspondingly). The hydrocarbonate ion content has been evaluated by a potentiometric titration providing 21% of accuracy. The flame photometry method has been used for the determination of potassium ions (18% accuracy) and sodium ions (10% accuracy). A volumetric method has been applied to measure the content of calcium and magnesium ions. The content of silicic acid has been measured using a calorimetric method and the content of boric acid has been determined by a potentiometric method.

GEOCHEMICAL MODEL OF THE PAUZHETKA GEOTHERMAL AREA

Conceptual model

The geothermal area has been divided into 6 conventional zones (Mitchell, Leach, 1991). The first zone is a deep zone of primary hydrothermal fluid dominated by sodium and chloride. It has been assumed that primary hydrothermal fluid sources are magma fluid, subducted marine sediments and meteoric water. A magma chamber roof within the Pauzhetka geothermal area is assumed to lie at a depth of 2.0 to 2.5 km below the land surface (Structure of..., 1993). The temperature near the magma chamber associated with volcanic structure of the Kuril-Kamchatka island arc is assumed to equal from approximately 700 to 500 degrees C (Fedotov et al., 2005).

The second zone is a convective fissure of tectonic origin, located between the deep primary hydrothermal fluid reservoir and the geothermal

reservoir near the land surface. The flow of hydrothermal fluid ascends from the deep reservoir to the land surface along the convective fissure. A part of the flow is assumed to interact with host rocks. The model provides also the mixing of the hydrothermal fluid with a colder groundwater flow.

The third zone is a two-phase zone, or a vapour-dominated reservoir. As deep fluids ascend to the surface, decreasing the pressure will result in a boiling of hydrothermal solution. Water vapour and other gases, including mainly CO₂ and less H₂S, are separated from the fluid. For the Pauzhetka, the vapour-dominated reservoir is assumed to be located at depths of 25 to 125 meters from the surface (Structure of..., 1993). The vapour-dominated reservoir has two inflows: the upward flow of deep hydrothermal fluid from the convective fissure and an inflow of colder meteoric and ground water.

The fourth zone represents aquifers where the vapour is assumed to be condensed and mixed with colder meteoric water. In the proposed model, the second level of the upper aquifer of the Pauzhetka geothermal area is considered. The fifth zone is a vadoze zone, or aeration zone. Here, the condensation of vapour and its mixing with meteoric water occurs exactly in the same way as in the aquifers. The sixth zone represents the land surface. Geothermal fluid reaches the surface in a variety of ways of discharge, such as large boiling springs, boiling mud pools, and hot springs with temperature of 80 to 90 degrees C and below. A schematic of the geothermal study area and the fluid flows is shown in Figure 1.

Input data of the model

The elements comprising the bulk composition of the system under study are Al, Ar, B, Br, C, Ca, Cl, Mn, F, Fe, He, I, K, Mg, N, Na, Ne, P, S, Si, Sr, Ti, H and O. The bulk composition of hydrothermal fluid has been computed on the basis of analytical data from a sample collected from the wellhead GK-3 within the Pauzhetka geothermal production field (Table 1). The sampled water is saline, because its total dissolved solids concentration is 2642 mg/L. The chemical composition of the sampled water is dominated by chloride and sodium and has a pH of 8.05.

Table 1: Bulk composition of hydrothermal fluid.

| Element | Content (mol) |
|---------|---------------|
| B | 2.3000e-06 |
| C | 0.0007754 |
| Ca | 0.0010458 |
| Cl | 0.0326871 |
| K | 0.0018268 |
| Mg | 8.3956e-07 |
| N | 0.0000339 |
| Na | 0.0312659 |
| S | 0.0008163 |
| Si | 5.0000e-06 |
| H | 111.0233380 |
| O | 55.5180182 |

The temperature is assumed to be equal to 500 degrees C and the pressure is 600 bar for the first zone of the model. Table 2 presents the chemical composition of andesitic basalt samples collected from the Kamalny volcano.

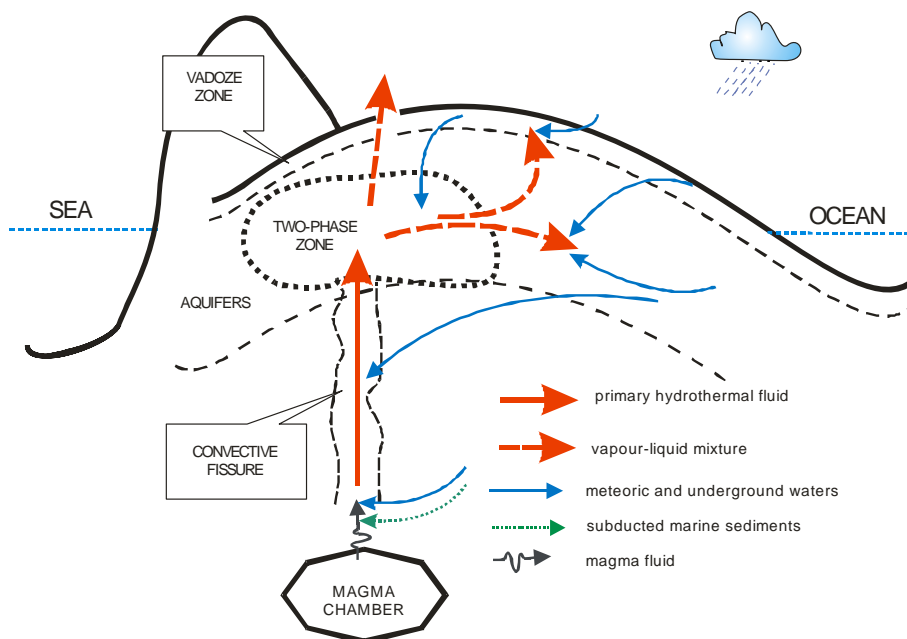


Figure 1: Conceptual model of hydrothermal area of the Pauzhetka geothermal production field.

Table 2: Andesitic basalt composition according to B. V. Ivanov (2008).

| Constituent | Content (mol) |
|--------------------------------|---------------|
| SiO ₂ | 0.92359 |
| TiO ₂ | 0.01030 |
| Al ₂ O ₃ | 0.17569 |
| Fe ₂ O ₃ | 0.01849 |
| FeO | 0.06859 |
| MnO | 0.00239 |
| MgO | 0.09579 |
| CaO | 0.13700 |
| Na ₂ O | 0.05500 |
| K ₂ O | 0.01990 |
| H ₂ O | 0.04329 |
| P ₂ O ₅ | 0.00160 |

The temperature for the second zone (convective fissure) is assumed to be equal to 350 degrees C (Pisareva, 1987). The pressure is 260 bar. A host rock is assumed to be andesitic basalt (Table 2).

The temperature and pressure for the vapour-dominated reservoir are assumed to be equal to 200 degrees C and 38 bar, correspondingly. For the second level of the upper aquifer, the temperature is 200 degrees C (Averiev, 1961; Sugrobov, 1964) and the pressure is 20 bar. The chemical composition of psephitic tuff of dacite sampled from the Pauzhetka geothermal field is shown in Table 3.

Table 3: Chemical composition of psephitic tuff of dacite according to S. I. Naboko et al. (1965).

| Constituent | Content (mol) |
|--------------------------------|---------------|
| SiO ₂ | 1.1314 |
| TiO ₂ | 0.0036 |
| Al ₂ O ₃ | 0.1616 |
| Fe ₂ O ₃ | 0.0236 |
| FeO | 0.0295 |
| MnO | 0.0014 |
| MgO | 0.0337 |
| CaO | 0.0684 |
| Na ₂ O | 0.0293 |
| K ₂ O | 0.0351 |
| P ₂ O ₅ | 0.0008 |
| S | 0.0077 |
| H ₂ O | 0.1882 |

The number of input components, termed dependent components in thermodynamics, in a model must far exceed the number of them resulted from chemical equilibrium calculation using the Gibbs free energy minimization. The list of input dependent components of our model consists of 205 aqueous species, 23 gases and 136 minerals. The standard thermodynamic properties for the dependent components have been taken from various data bases (Table 4).

Table 4: Data bases for dependent components potentially possible in equilibrium.

| Dependent components and their number | Literature |
|---------------------------------------|--|
| Aqueous species, 205 | Johnson et al., 1992 Shock et al., 1997 Sverjensky et al., 1997 |
| Gases, 23 | Reid et al., 1977 |
| Minerals, 136 | Karpov et al., 1976 Robie, Hemingway, 1995 Berman, 1988 Yokokawa, 1988 Holland, Powell, 1998 |

Model results

The model computed that the deep hydrothermal fluid at 500 degrees C and 600 bar has a pH of 8.4 and its total dissolved solids concentration equals 3263.2 mg/L. Aqueous species and amount of each of them will be considered in the following section (Table 10). Table 5 presents a mineral assemblage computed with the model for the first zone.

Table 5: Mineral phases computed for the first zone.

| Mineral phase | Content (g) |
|---------------|-------------|
| albite | 29.6675 |
| anortite | 28.1374 |
| quartz | 12.0396 |
| phlogopite | 11.1852 |
| magnetite | 7.0157 |
| clinopyroxene | 5.7261 |
| K-feldspar | 2.2615 |
| sphene | 1.3681 |
| ilmenite | 0.8656 |
| apatite | 0.5358 |

For the convective fissure at 350 degrees C and 260 bar, the model computed a hydrothermal fluid with a pH of 6.7 and total dissolved solids concentration equal to 3310.2 mg/L. The equilibrium mineral assemblage is the following: plagioclase – amphibole – biotite – quartz – ilmenite – sphene – apatite – calcite. In the vapor-dominated reservoir, a computed pH of hydrothermal fluid is equal to 5.5 and total dissolved solids concentration equals 102571.8 mg/L. The model calculated the equilibrium assemblage shown in Table 6.

Table 6: Mineral phases computed for the third zone.

| Mineral phase | Content (g) |
|---------------|-------------|
| K-feldspar | 43.6390 |
| wairakite | 30.0981 |
| quartz | 22.3330 |
| ilmenite | 6.3160 |

The vapor leaves the vapour-dominated reservoir and condenses. It may occur in the upper aquifer hosted in psephitic tuff of dacite. The model computed the composition and main hydrological features of such a condensate (pH=6.9 and TDS = 2034.9 mg/L) at temperature 200 degrees C and pressure 16 bar. The calculated mineral composition of hydrothermally altered host rock is presented in Table 7. Varying temperature and pressure within the upper aquifer, various mineral assemblages can be computed. For example, at 150 degrees C and 20 bar the equilibrium mineral assemblage is montmorillonite – quartz – Na-amphibole – K-feldspar – calcite – phlogopite – ilmenite – pyrite – apatite.

Table 7: Mineral phases computed for the fourth zone at temperature 200 degrees C and pressure 16 bar.

| Mineral phase | Content (g) |
|-----------------|-------------|
| lomontite | 31.3935 |
| Na-amphibole | 21.5547 |
| quartz | 18.3602 |
| montmorillonite | 17.0982 |
| K-feldspar | 17.0699 |
| ilmenite | 0.6973 |
| pyrite | 0.4301 |
| sphene | 0.2197 |

The vapour may also condense in the vadoze zone. In this case, the equilibrium mineral assemblage is kaolinite – lomontite – illite – quartz – clinocllore – ilmenite – rutile. A vapour condensate, computed by the model, has a pH of 7.2 and its total dissolved solids concentration equals 535.1 mg/L.

AQUEOUS SPECIES OF HYDROTHERMAL FLUID AT VARIOUS THERMODYNAMIC SETTINGS

The aim of this part of the study is to compare amounts of aqueous species for a hydrothermal fluid of one and the same chemical composition under various thermodynamic conditions of interest. We have chosen the deep primary hydrothermal fluid at the temperature 450 degrees C and the pressure 600 bar which corresponds to a depth of 2.5 km; the upper aquifer of the Pauzhetka

geothermal field at the temperature 200 degrees C and pressure 16 bar; a discharge of the hydrothermal fluid at the temperature 95 degrees C and pressure 1 bar (the land surface); a chemical laboratory where a sample of hydrothermal fluid is studied at the temperature 25 degrees C and pressure 1 bar.

Atmospheric air is inevitably present in some parts of the geothermal system under study: a fault or fracture plane at moderate depths, near-surface conditions of the aeration zone and a discharge of hydrothermal fluid. The study of a sample of hydrothermal fluid in a chemical laboratory implies the presence of atmospheric air in many cases. The bulk composition of the modeled hydrothermal fluid has been taken from Table 1. We have recalculated the bulk composition taking into account 0.1 mol of atmospheric air (Table 8).

Table 8: Bulk composition of hydrothermal fluid in the presence of 0.1 mol of atmospheric air.

| Element | Content (mol) |
|---------|---------------|
| Ar | 0.0320900 |
| B | 2.3000e-06 |
| C | 0.0018114 |
| Ca | 0.0010458 |
| Cl | 0.0326871 |
| K | 0.0018268 |
| Mg | 8.3956e-07 |
| N | 5.3948139 |
| Na | 0.0312659 |
| Ne | 0.0000616 |
| S | 0.0008163 |
| Si | 5.0000e-06 |
| H | 111.023338 |
| O | 56.9664902 |

Some important parameters of the system computed with the model are presented in Table 9. The calculated data reveal no appreciable trend of pH values between the thermodynamic conditions under study. The redox potential, referred to as Eh, increases constantly from the deep hydrothermal fluid zone to the land surface.

Table 9: Parameters and phase composition of the system at various temperatures and pressures in the presence or absence of atmospheric air

| Temperature | 450°C | 200°C | | 95°C | | 25°C | |
|--------------------------|----------|----------|----------|----------|----------|----------|----------|
| Pressure | 600 bar | 16 bar | | 1 bar | | 1 bar | |
| Air | No air | No air | Air | No air | Air | No air | Air |
| pH | 7.96 | 7.01 | 7.35 | 7.65 | 8.09 | 8.56 | 8.22 |
| Eh, V | 0.0050 | 0.5446 | 0.5338 | 0.6566 | 0.6149 | 0.7155 | 0.7309 |
| TDS (mg/L) | 2079.1 | 2074.7 | 2074.7 | 2107.7 | 2076.4 | 2111.2 | 2121.5 |
| Phase composition (wt.%) | | | | | | | |
| water | 99.99995 | 99.99739 | 90.93707 | 99.99923 | 90.92012 | 99.99943 | 90.92498 |
| gas | 0.00005 | | 9.06058 | | 9.07758 | | 9.07502 |
| calcite | | 0.00261 | 0.00234 | 0.00077 | 0.00230 | 0.00057 | |

The total dissolved solids concentration increases slightly with decreasing pressure and temperature. The precipitation of calcite has been calculated for the conditions of the upper aquifer and discharge of hydrothermal fluid. The amount of precipitated calcite is not dependent on the presence of atmospheric air in the thermodynamic conditions of the upper aquifer. The amount of it increases 3 times in the presence of air, when the hydrothermal fluid discharges at 95 degrees C and 1 bar. In a

chemical laboratory, calcite does not precipitate in the presence of air and precipitates in the absence of air.

Table 10 presents computed amounts of aqueous species of the hydrothermal fluid at thermodynamic conditions discussed above and in the presence or absence of the atmospheric air.

Table 10: Amount of aqueous species of hydrothermal fluid (mg/L) at various temperatures and pressures in the presence or absence of atmospheric air

| Temperature Pressure | 450°C 600 bar | 200°C 16 bar | | 95°C 1 bar | | 25°C 1 bar | |
|------------------------------------|------------------|-----------------|-----------|---------------|-----------|---------------|-----------|
| Air | No air | No air | Air | No air | Air | No air | Air |
| Na ⁺ | 354.86 | 700.96 | 701.31 | 712.89 | 712.52 | 713.83 | 713.84 |
| NaOH ⁰ | 2.1546 | 7.1148e-2 | 0.15550 | 1.5353e-2 | 4.3499e-2 | 2.3745e-3 | 1.0975e-3 |
| NaCl ⁰ | 916.96 | 42.718 | 41.769 | 12.617 | 13.268 | 7.1526 | 7.1577 |
| NaHSiO ₃ ⁰ | 1.5466e-3 | 1.8337e-3 | 3.9381e-3 | 9.5806e-3 | 2.3722e-2 | 6.6323e-2 | 3.4768e-2 |
| NaSO ₄ ⁻ | 10.196 | 5.0755 | 4.9431 | 4.7543 | 5.2398 | 10.978 | 10.967 |
| K ⁺ | 39.988 | 69.883 | 69.915 | 71.055 | 71.018 | 71.224 | 71.225 |
| KOH ⁰ | 0.42269 | 8.2894e-3 | 1.8118e-2 | 1.2247e-3 | 3.4720e-3 | 1.1379e-4 | 5.2321e-5 |
| KSO ₄ ⁻ | 53.577 | 4.5366 | 4.4176 | 1.1762 | 1.2953 | 0.66719 | 0.66656 |
| KHSO ₄ ⁰ | 0.22563 | 6.1607e-6 | 2.6846e-6 | 3.2454e-9 | 1.3303e-9 | 6.627e-12 | 1.437e-11 |
| KCl ⁰ | 29.702 | 0.42200 | 0.41266 | 4.8891e-2 | 5.1444e-2 | 9.2847e-3 | 9.2908e-3 |
| Mg ⁺² | 1.4821e-4 | 1.5566e-2 | 1.3410e-2 | 1.9674e-2 | 1.9494e-2 | 1.9982e-2 | 2.0012e-2 |
| MgOH ⁺ | 3.2523e-2 | 4.8144e-3 | 9.1991e-3 | 2.4102e-4 | 6.6438e-4 | 1.5291e-5 | 7.0380e-6 |
| MgCl ⁺ | 2.7480e-3 | 4.1214e-3 | 3.5362e-3 | 9.7301e-4 | 9.9511e-4 | 5.9845e-4 | 5.9875e-4 |
| MgCO ₃ ⁰ | 5.4139e-8 | 4.2378e-5 | 3.7355e-5 | 1.7470e-4 | 2.1369e-4 | 3.3078e-4 | 1.8372e-4 |
| Mg(HCO ₃) ⁺ | 1.6521e-5 | 1.1187e-3 | 4.6772e-4 | 5.0151e-4 | 2.1680e-4 | 2.6606e-4 | 3.2138e-4 |
| Ca ⁺² | 0.55068 | 21.081 | 20.785 | 35.832 | 28.974 | 37.859 | 40.210 |
| CaOH ⁺ | 26.797 | 1.6542 | 3.4825 | 6.3789e-2 | 0.15420 | 1.7159e-3 | 8.4226e-4 |
| CaSO ₄ ⁰ | 16.758 | 15.400 | 14.090 | 5.2590 | 5.1914 | 3.0253 | 3.1706 |
| CaCO ₃ ⁰ | 7.5340e-3 | 0.29620 | 0.29578 | 0.87310 | 0.87759 | 0.99285 | 0.58657 |
| CaCl ⁺ | 27.410 | 7.6856 | 7.2396 | 1.4605 | 1.3090 | 0.60734 | 0.64434 |
| CaCl ₂ ⁰ | 8.4077 | 9.0563e-2 | 8.3380e-2 | 1.1512e-2 | 1.0828e-2 | 9.4430e-3 | 9.9657e-3 |
| CaHSiO ₃ ⁺ | 3.9201e-4 | 3.7070e-4 | 7.5966e-4 | 2.6274e-4 | 5.6187e-4 | 2.5186e-4 | 1.3948e-4 |
| Ca(HCO ₃) ⁺ | 8.3343e-2 | 1.1017 | 0.50355 | 0.63218 | 0.22390 | 0.37223 | 0.47694 |
| B(OH) ₃ ⁰ | 0.10092 | 0.13420 | 0.12554 | 0.11321 | 8.4092e-2 | 5.6051e-2 | 8.3181e-2 |
| BO ₂ ⁻ | 1.0431e-3 | 2.0173e-3 | 4.2067e-3 | 6.1436e-3 | 1.2326e-2 | 8.9855e-3 | 6.1573e-3 |
| NaB(OH) ₄ ⁰ | 6.1272e-2 | 1.1328e-3 | 2.3068e-3 | 8.0629e-4 | 1.7023e-3 | 9.4043e-4 | 6.4308e-4 |
| B(OH) ₄ ⁻ | 3.2824e-3 | 5.6241e-3 | 1.1724e-2 | 2.5045e-2 | 5.0086e-2 | 9.2582e-2 | 6.3428e-2 |
| HCO ₃ ⁻ | 0.12678 | 13.982 | 6.7931 | 39.724 | 15.689 | 41.622 | 50.257 |
| CO ₃ ⁻² | 2.3322e-5 | 1.0361e-2 | 1.1541e-2 | 0.26334 | 0.26399 | 1.1349 | 0.62841 |
| CO ₂ ⁰ | 33.993 | 11.922 | 2.5870 | 1.2055 | 0.17746 | 0.15496 | 0.40484 |
| NO ₃ ⁻ | 2.1153e-7 | 1.5193e-3 | 0.48001 | 3.1877e-2 | 5.4289e-2 | 0.10074 | 0.10737 |
| NO ₂ ⁻ | 1.5692e-5 | 1.7020e-3 | 0.18704 | 3.4425e-3 | 1.0718e-2 | 1.1937e-3 | 1.8152e-3 |
| SO ₄ ⁻² | 15.761 | 60.145 | 61.305 | 70.028 | 69.599 | 66.944 | 66.852 |
| HSO ₄ ⁻ | 4.4067 | 8.1103e-2 | 3.6068e-2 | 7.3818e-4 | 2.8752e-4 | 1.0848e-5 | 2.3532e-5 |
| Cl ⁻ | 570.20 | 1129 | 1129.8 | 1150.5 | 1150.1 | 1154.2 | 1154.2 |
| HCl ⁰ | 9.9605e-3 | 6.8453e-5 | 3.0614e-5 | 2.6914e-6 | 1.0020e-6 | 3.5457e-7 | 7.7073e-7 |
| HSiO ₃ ⁻ | 1.7115e-3 | 7.2698e-3 | 1.5980e-2 | 2.0247e-2 | 4.7690e-2 | 3.3402e-2 | 1.7472e-2 |
| SiO ₂ ⁰ | 0.29795 | 0.29345 | 0.28520 | 0.27874 | 0.24871 | 0.23443 | 0.26585 |
| Ar ⁰ | | | 8.8602 | | 0.31794 | | 0.51428 |
| N ₂ ⁰ | 0.47535 | 0.47449 | 48.214 | 0.46707 | 3.8368 | 0.45223 | 14.285 |
| Ne ⁰ | | | 7.3087e-3 | | 1.7701e-4 | | 1.6216e-4 |
| O ₂ ⁰ | 17.385 | 17.383 | 143.29 | 17.362 | 5.2081 | 17.319 | 8.5072 |
| OH ⁻ | 6.4344 | 1.1414 | 2.5533 | 0.42122 | 1.1337 | 0.07224 | 0.033317 |
| H ⁺ | 2.0570e-5 | 1.2783e-4 | 5.8399e-5 | 2.7848e-5 | 9.8450e-6 | 3.3398e-6 | 7.2637e-6 |

The concentration of sodium and potassium ions increases by a factor of 2 between the deep hydrothermal fluid zone and other thermodynamic conditions under study. In contrary to the sodium and potassium ions behavior, the model demonstrates how significant the increase in NaCl is with depth. As compared with the circumstances of a chemical laboratory, the content of NaCl in the hydrothermal solution is doubled at the conditions of hydrothermal fluid discharge. It increases 6 times at the conditions of the upper aquifer and 130 times at a depth of 2.5 km. The concentration of KCl also increases rapidly with depth.

In the conditions of the hydrothermal fluid discharge and the upper aquifer, the amount of NaSO_4^- decreases 2 times as compared with a chemical laboratory and the deep hydrothermal fluid zone. The content of KSO_4^- goes up with depth. It increases by one order of magnitude in the upper aquifer and by two orders of magnitude at a depth of 2.5 km.

The behavior of calcium ions is quite opposite to the sodium and potassium ions behavior. The amount of calcium ions decreases by two orders of magnitude at a depth of 2.5 km. The increase in calcium species is also observed with depth. So, between the conditions of a chemical laboratory and the deep hydrothermal fluid zone, the concentration of CaOH^+ increases by 5 orders of magnitude, the concentration of CaSO_4^0 increases 5 times, the concentration of CaCl^+ increases 45 times, the concentration of CaCl_2^0 increases by 3 orders of magnitude.

At a depth of 2.5 km, the amount of Cl^- decreases 2 times, whereas the content of HCl^0 increases by 4 orders of magnitude as compared with the conditions of a chemical laboratory.

CONCLUSION

In 1957, the Institute of Volcanology of Siberian branch of AS USSR began a cooperative study with an exploration company to evaluate sources of superheated steam within the Pauzhetka geothermal area for generation of renewable energy. The past half-century since its exploitation began, the Pauzhetka geothermal field is still studied by geologists, hydro-geologists and geophysicists. Although a geochemical model is not unique and cannot be always validated, geochemical modeling can elucidate dominant ways in the evolution of the geothermal system and can give insights into how the near-surface and deep parts of the system are related.

There are some reasons for believing that our model, which incorporates surface, vadoze zone, aquifers, conductive fissure and deep-seated primary geothermal reservoir, can be considered a

reasonable representation of the geothermal area. The mineral assemblages computed with the model fit in broadly with observations. Our model provides a sufficiently close match between computed and measured values of a pH and total dissolved solids concentration for hydrothermal fluid. Modeling in this report focuses on the hydrothermal fluid flow ascending from the deep-seated primary hydrothermal-fluid reservoir along the convective fissure to the land surface. On this way, the hydrothermal flow gets the zone where the water boils due to decreasing pressure. Then the steam-liquid mixture condenses within an aquifer or the vadoze zone. The model provides the mixing of hydrothermal fluid flow and its condensate with colder meteoric or underground water flows.

We have made computations of a hydrothermal fluid of one and the same bulk composition under several thermodynamic conditions. The purpose of this study is to provide additional information regarding amount of aqueous species at temperatures and pressures of various environments within the geothermal area. Amount of aqueous species, measured in a chemical laboratory, can differ significantly from if it may be measured in the circumstances of the primary geothermal-fluid reservoir. For example, at a depth of 2.5 km and 450 degrees C, the content of NaCl increases 130 times against the conditions of a chemical laboratory. We have shown further that the presence of atmospheric air influences amount of some aqueous species under some thermodynamic conditions. We concluded that even if the modeling scenarios are limited by lack of measurements in the deep parts of the geothermal area, the geochemical model allows a better understanding of chemical processes in the geothermal area.

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REFERENCES

- Asaulova, N. P., Vorozheikina, L.A., Manukhin, Yu. F. and Obora, N.V. (2009) "Results of long-term exploitation of the Pauzhetka geothermal field", *Gorny vestnik Kamchatki*, issue 2 (8), 47-56. (in Russian)
- Averiev, V. V. (1961) "Conditions of discharge of Pauzhetka hydrothermal fluid in the south of Kamchatka," Proceedings of Laboratory of Volcanology of AN SSSR, issue 19. (in Russian)
- Averiev, V. V. and Belousov, V. I. (1965), "Geological essay of the field," in book: *The Pauzhetka hot waters on Kamchatka*, Moscow, Nauka Press, 8-22. (in Russian)

- Belousov V. I. (1965) "Geological structure of the Pauzhetka field of high-temperature waters," in book: *The Pauzhetka hot waters on Kamchatka*, Moscow, Nauka Press, 23-30. (in Russian)
- Berman, R.G. (1988) "Internally - consistent thermodynamic data for mineral in the system $\text{Na}_2\text{O-K}_2\text{O-CaO-MgO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2\text{-H}_2\text{O-CO}_2$," *J. Petrol.*, **29**, 455-522.
- Chudnenko, K. V. (2010) "Thermodynamic modeling in geochemistry: theory, algorithms, software, and applications," Novosibirsk, Academic publishing house "Geo," 287 p. (in Russian)
- Fedotov, S. A., Delemen, I. F., Utkin, I. S. and Utkina, L.I. (2005) "Dynamics of growth and development of ductal magma chambers for the Mutnovskii-Gorelovskii group volcanoes; their heat fields and underground heat accumulated," *Geothermal and Mineral Resources of Modern Volcanism Areas*, Proceedings of the International Kuril-Kamchatka Field Workshop, Petropavlovsk-Kamchatsky, Russia, July 16 – August 6, 141-152. (in Russian)
- Helgeson, H.C., Kirkham, D.H. and Flowers, G.C. (1981) "Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb," *Amer. J. Sci.*, **281**, 1249-1516.
- Holland, T.J.B. and Powell, R. (1998) "An internally-consistent thermodynamic dataset for phases of petrological interest," *Journal of Metamorphic Geology*, **16**, 309-344.
- Ivanov, B. V. (2008) "Andesites of Kamchatka," Moscow, Nauka Press. (in Russian)
- Johnson, J.W., Oelkers, E.H. and Helgeson, H.C. (1992) "SUPCRT92: software package for calculating the standard molal thermodynamic properties of mineral, gases, aqueous species, and reactions from 1 to 5000 bars and 0° to 1000°C," *Computers Geosci.*, **18**, 899-947.
- Karpov, I.K., Kiselev, A.I. and Letnikov, F.A. (1976) "Modeling of natural mineral formation using a computer," Moscow, Nedra Press., 255 p. (in Russian)
- Karpov, I.K., Chudnenko, K.V. and Kulik, D.A. (1997) "Modeling chemical mass-transfer in geochemical processes: Thermodynamic relations, conditions of equilibria and numerical algorithms," *Amer. J. Sci.*, **297**, 767-806.
- Leonov V. L. (1989) "Structural conditions of localization of high-temperature hydrothermal waters," Moscow, Nauka Press. (in Russian)
- Mitchell, A.H.G. and Leach, T.M. (1991) "Epithermal gold in the Philippines; island arc metallogenesis, geothermal systems and geology," London, Academic Press, 457 p.
- Naboko, S. I., Karpov, G. A. and Rosnikova, A. P. (1965) "Hydrothermal metamorphism of rocks and the formation of minerals," in book: *The Pauzhetka hot waters on Kamchatka*, Moscow, Nauka Press, 76-119. (in Russian)
- Pisareva, M. V. (1987) "Zone of nature steam within the Nizhnekoschelevskii geothermal field," *Volcanology and Seismology*, No. 2, 52-63. (in Russian)
- Reid, R.C., Prausnitz, J.M. and Sherwood, T.K. (1977) "The properties of gases and liquids," New York, McGraw-Hill Book Company.
- Robie, R.A. and Hemingway, B.S. (1995) "Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures," *U. S. Geol. Survey Bull.*, **2131**, 1-461.
- RusHydro Group. Available from: <http://www.pauzhet.rushydro.ru/company/history>
- Shock, E.L., Sassani, D.C., Willis, M. and Sverjensky, D.A. (1997) "Inorganic species in geologic fluids: Correlation among standard molal thermodynamic properties of aqueous ions and hydroxide complexes," *Geochimica et Cosmochimica Acta*, **61**, 907-950.
- Structure of hydrothermal system (1993) Moscow, Nauka press. (in Russian)
- Sugrobov, V. M. (1964) "Pauzhetka hydrothermal fluids of Kamchatka as an example of high-temperature water-pressure system," in book: *Hydrogeothermal conditions of the upper part of earth's crust*, Moscow, Nauka Press. (in Russian)
- Sverjensky, D.A., Shock, E.L. and Helgeson, H.C. (1997) "Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5kb," *Geochimica et Cosmochimica Acta*, **61**, 1359-1412.
- Yokokawa, H. (1988) "Tables of thermodynamic properties of inorganic compounds," *Journal of the National Chemical Laboratory for Industry*, **83**, 27-121.