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Mineral Extraction from Brines and Geothermal Resources Complex Use in Russia

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ABSTRACT

Geothermal energy use is the perspective way to clean sustainable development of the world. Russia has rich high and low temperature geothermal resources and makes good steps in their use.

The most perspective direction of usage of low temperature geothermal resources is the use of heat pumps. This way is optimal for many regions of Russia - in its European part, on Ural and others.

The electricity is generated by some geothermal power plants (GeoPP) only in the Kamchatka Peninsula and Kuril Islands.

There are two possible forms of utilization of geothermal resources depending on structure and properties of thermal waters: heat/power and mineral extraction.

The mineral-extraction direction is basic for geothermal waters, containing valuable components in industrial quantities. The most significant deposits of thermal waters represent the brines containing from 35 up to 400 and more g/l of salts. They are mineral raw materials for many chemical elements.

1. INTRODUCTION

Thermal waters are used for many purposes - for development of the electric power, for central heating and cooling, for hot water supply, in agriculture, animal industries, fish culture, in the food, chemical and oil-extracting industry, in balneology and spa, in the recreational purposes.

In Russia the geothermal resources are used predominantly for heat supply both heating of several cities and settlements on Northern Caucasus and Kamchatka. Besides in some regions of country the deep heat is used for greenhouses. Most active the hydrothermal resources are used in Krasnodar territory, Dagestan and on Kamchatka.

At the same time the problem of the most effective utilization of a natural source of raw materials is put forward in the category of actual tasks, including thermomineral waters and brines. Involving of these waters in economic activities can promote the decision of some social - economic and environmental problems.

2. GEOTHERMAL ENERGY USE

In Russia the geothermal resources are used predominantly for heat supply both heating of several cities and settlements on Northern Caucasus and Kamchatka with a total number of the population 500000. Besides in some regions of country the deep heat is used for greenhouses of common area 465000 м^2. Most active the hydrothermal resources are used in Krasnodar territory, Dagestan and on Kamchatka. (Gadzhiev *et al*. (1980), Kononov *et al.* (2000), Svalova (1998-2008)). The approximately half of extracted resources is applied for heat supply of habitation and industrial puttings, third - to a heating of greenhouses, and about 13 % - for industrial processes. Besides the thermal waters are used approximately on 150 health resorts and 40 factories on bottling mineral water. Quantity of electrical energy developed by geothermal stations of Russia, per 1999 almost twice has increased as contrasted to by former level. Nevertheless, it remains extremely minor, making some 0,01 of percent from common development of the electric power in the country.

The Western Siberian plate is another promising region for direct use applications. The aquifers located down to 3 km in this region have a high hydrostatic pressure, temperatures of up to 75°C, and are capable of producing about 180 m^3/s. These waters are used to heat dwellings in some small settlements and, on a small scale, assist in the recovery of oil, the extraction of iodine and bromide, and for fish farming. The region is rich in natural gas, which has limited geothermal development.

The most perspective direction of usage of low temperature geothermal resources is the use of heat pumps. This way is optimal for many regions of Russia - in its European part, on Ural and others.

Heat pumps are at an early stage of development in Russia. An experimental facility was set up in early 1999 in the Philippovo settlement of Yaroslavl district. The source supplies 5-6°C to eight heat pumps that heat the water to 60°C for a 160-pupil school building. There are some buildings with supply of heated water, using heat pumps, in Moscow (Fig. 1,2).

Figure 1: Moscow, Anokhina Str.,50.House for pilot heat-pump installation.(Photo of Svalova V.)

Figure2: Moscow, Anokhina Str., 62. House with heat-pump supply. (Photo of Svalova V.)

The electricity is generated by some geothermal power plants (GeoPP) only in the Kamchatka Peninsula and Kuril Islands. At present three stations work in Kamchatka: Pauzhetka GeoPP (11MW $_e$ installed capacity) and two Severo-Mutnovka GeoPP (12 and 50 MW_e). Moreover, another GeoPP of 100 MV_e is now under preparation in the same place. Two small GeoPP are in operation in Kuril's Kunashir Isl, and Iturup Isl, with installed capacity of 2,б MW_e and 6 MW_e respectively.

Russia has considerable geothermal resources and the available capacity is far larger than the current application. This resource is far from adequately developed in the country. In the former Soviet Union, geological exploration was well supported for minerals and oil and gas. Such expansive activities did not aim to discover geothermal reservoirs even in a corollary manner; geothermal waters were not considered among energy resources. Still, the results of drilling thousands of "dry wells" (in oil industry parlance), bring a secondary benefit to geothermal research. These are the abandoned wells themselves, and the data on the subsurface geology, water-bearing horizons, temperature profiles, etc., that were collected during exploration. Not all currently operating companies are willing to disclose their well data, still, in face of the cost of maintaining shut-in wells, it is cheaper to turn them over to others for new purposes.

Development and implementation of geothermal power technology is facilitated by social, scientific, economical and environmental aspects.

Social aspects reflect public opinion and willingness to reject old, traditional power generating methods and implement new, non-traditional, environmentally friendly geothermal power technology.

Nowadays the scientific and technical level of geothermal technology is very high in Russia. Unique geothermal power equipment has been developed domestically and for the first time in the world two environmentally friendly power plants were constructed in Kamchatka, In 1999 the

Figure 3: Verkhne-Mutnovsky GeoPP. First ecologically clean GeoPP(Photo of Svalova V.).

Figure 4: Verkhne-Mutnovsky GeoPP (Photo of Svalova V.)

unique pilot Verkhne-Mutnovsky GeoPP (V-MGeoPP) of 12 (3x4) MW was constructed (Fig. 3, 4).

It has been operating in extremely severe climatic conditions on the site located near 1000 m above sea level. High level of environmental protection is provided due to isolating the geothermal fluid from the environment by using both air condensers and a system of full re-injection of the waste geothermal fluid back into reservoir. The major problem of protecting the GeoPP equipment from corrosion and salt depositions was solved by using a special technology of film-forming amine additives. Over the last years the V-MGeoPP has proved sustained reliability in generating reasonably priced electricity of about 1.5 cents/kWh (Nikolski, Parshin, and Bezotechestvo (2003)). The experience gained while constructing and operating the V-MGeoPP was used for construction of the 50 MW Mutnovsky GeoPP – a completely automated power plant with a satellite-based communication and control system (Fig. 5, 6, 7).

The economic impact from geothermal power plants is especially high in remote locations. As there is practically no detrimental gases emission, modern GeoPPs can be considered as practically absolutely environmentally friendly (Tomarov, Bubon, and Martynova (2003)).

Figure 5: Mutnovsky GeoPP (Photo of Svalova V.).

Figure 6: Mutnovsky GeoPP. Primary separators provide MGeoPP with the high-quality steam (Photo of Svalova V.).

Figure 7: Mutnovsky GeoPP. The main entrance(Photo of Svalova V.).

3. THERMAL WATERS COMPLEX USE

Thermal waters are used for many purposes - for development of the electric power, for central heating and cooling, for hot water supply, in agriculture, animal industries, fish culture, in the food, chemical and oil-extracting industry, in balneology and spa, in the recreational purposes.

Thermal waters, it is especial chloride brines, contain in the structure a huge complex of metal and nonmetallic microcomponents. The saturation of brines microcomponents is in close dependence both on genetic essence of brines, and on lithological-structural and geothermal features of containing breeds.

Interest to geothermal waters and brines as mineral raw material is connected to a number of advantages of this kind of raw material in comparison with firm sources of rare elements, metals and mineral salts.

Industrial underground waters are characterized by wide regional distribution and big geological and exploitation stocks. They are polycomponental raw material and simultaneously can be used in balneology and power system. Extraction of this raw material demands realization concerning small capital works and is carried out by boreholes methods, allowing to take hydro mineral raw material from the big depths.

Geothermal waters and brines are characterized by the big variety of mineralization, a chemical compound, the contents of useful components and their quantitative ratio, and also gas structure and temperatures. The most widespread types of hydro mineral raw material are: thermal brines of intercontinental rift zones; thermal waters and brines of island arches and areas of Alpine folds; waters and brines of artesian pools; brines of modern evaporate pools of a sea or oceanic origin and continental lakes; sea waters (Table 1).

Profitability of industrial reception of those or other components from hydro mineral raw material is determined not only by their concentration, but also by depth of underground waters and operational chinks, filtration properties of rocks, flow rate of operational stocks etc. On economic parameters of operation the way of dump of the fulfilled waters that defines expenses for protection of the natural environment essentially influences.

Proceeding from the general conditions and laws of distribution of underground geothermal waters and the brines containing rare elements, and also in view of experience of use of such waters as hydro mineral raw material in Russia and abroad the following limits of concentration of elements at which waters represent industrial interest are established (mg / l): iodine - 10, lithium - 10, cesium - 0.5, germanium - 0.5, bromine - 200, rubidium - 3, strontium - 300. (Bondarenko (1999)).

Even before the Second World War abroad, in particular, in USA, the technology of extraction from hydro mineral raw material of one of its components - lithium was developed. In 70th years about 85 % of world extraction of this metal was carried out in such a way. (Kogan and Nazvanova (1974)).

In Japan from geothermal underground brines are commercially extracted I, Br, B, Li, As, Ge, W and a number of mineral salts. In Israel from brines of the Dead sea the carnallite, bromine, chlorides of magnesium and calcium, and also raw material for manufacture of medical products and perfumery are produced. In 80th years from hydro mineral raw material it was received 30 % of world extraction of lithium, 31 % - cesium, 8 % - a boron, 5 % - rubidium, and also in significant scales Ca, Mg, Na, K, S, Cl, U, Ra, Cu. (Bondarenko (1999)). (Table 2, 3).

Huge stocks of rare-metal raw material are in geothermal underground waters and brines on territories of Russia and the CIS. They contain over 55 % of the common stocks of lithium, 40 % of rubidium and 35 % of cesium. (Kremenetsky et al.(1999))

Thermal waters with a high mineralization are located in the greater territory of Russia and the former USSR. They are known almost in all areas. Brines with mineralization higher than 200 g/l are known in Perm and Kujbishev areas, Tatarstan, Moscow, Ryazan and other central areas. In Moscow, for example, on depth of 1650 m are met chloride brines with mineralization of 274 g/l. In Western and Eastern Siberia there are large deposits of brines with high temperature. Some deposits have mineralization of 400-600 g/l. There are many thermal brines in Central Asia, Kazakhstan, on Ukraine, Kamchatka, Kuriles, Sakhalin. (Shcherbakov (1985), Resources … (1985), Kurbanov(2001)).

There are chemical elements which are possible for taking only from underground waters. So iodine is extracted from brines since iodine is good dissoluble and in breeds iodine does not collect. Iodine concentrates in sea seaweed but to extract this seaweed as industrial raw material is effectively only at their big congestion. Bromine can be extracted from some salts and seaweed, but traditionally bromine also is extracted from superstrong chloride brines. (Antipov et al., (1998)). (Table 4).

The significant part of deposits of thermal waters represents the brines containing from 35 up to 400 and more g/l of salts. They are mineral raw material on many chemical elements. Many brines which are taking place on the big depth, can become deposits of the most valuable chemical elements: cesium, boron, strontium, tantalum, magnesium, calcium, tungsten etc. (Table 5,6,7).

Under the cheap technological circuit from natural solutions basically it is possible to take iodine, bromine, boron, chloride salts of ammonium, potassium, sodium, calcium, magnesium. Extraction of other chemical elements is complicated because of dearness of technology. A perspective method is use of ion-exchange pitches for selective extraction of the certain components from natural waters. In a basis of a method there is the principle of selective sorption of ions of useful elements or their complexes in solutions with special compounds.

Works of some scientific institutes in Russia allow to create the processes of chemical processing of hydromineral raw material and to expand spheres of its economic application. Many laboratory and natural tests on extraction of valuable components from thermal waters confirm the necessity and an opportunity of complex use of this nonconventional raw material.

It is planned to recover I, Br, KCl, CaCl, NaCl from brines in Yaroslavl area. New methods of mineral and valuable elements extraction from industrial solutions are developed on the basis of biosorbent use.

4. CONCLUSION

Depending on structure and properties of thermal waters it is possible to allocate two basic directions of use of geothermal resources: heat power and mineral-raw materials.

The heat power direction is the basic for fresh and low mineralized waters when valuable components in industrial concentration practically are absent, and the general mineralization does not interfere with normal operation of system. When high potential waters are characterized by the raised mineralization and propensity to scaling, the recycling of mineral components should be considered as the passing process promoting the effective heat supply.

The mineral-raw direction is the basic for geothermal waters, containing valuable components in industrial quantities. Thus the substantiation of industrial concentration is caused by a level of technologies. For such waters the heat is a passing product which use can raise efficiency of process of reception of basic production and even to save fuel.

Designing such systems the process of allocation of valuable components should be dominant at. Calculations show, that complex use of thermal waters in a mineral-raw direction economically is more effective, than in heat power. The choice of a direction of complex use of thermal waters should be defined not only by their structure and properties, but also by the level of development of complex technological processes of extraction and processing of hydromineral raw material and by technology of heat power processes. But for all that the presence of consumers and needs for thermal water play the main role.

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Table 1. The main types of hydromineral raw material

TYPE	VALUABLE ELEMENTS	EXAMPLES
Thermal brines of intercontinental rift zones	$CaCl_2$, CO_2, (NaCl, Zn, Pb, Cu, Fe, Ag, Li, Br)	Atlantis-II (Red Sea) Salton Sea (California, USA)
Thermal waters and brines of island arches and areas of Alpine folds	B, NH_4, CO_2, (Li, Cs, As, Ge, W)	Japan, Iceland, New Zealand, Toscana (Italy), Russia
Waters and brines of artesian pools	NaCl, KCl, CH_4, Mg, Br, I, Rb, CsO	San-Kristobal (Mexico), Danison-Trof (Australia), Michigan (USA), Niigata (Japan), Russia
Brines of modern evaporate pools	NaCl, Na_2CO_3, K, Li, Br, B, (W, Rb) NaCl, KCl, K_2SO_4, Na_2SO_4, Mg, Br, Li, B NaCl, $CaCl_2$, Mg, K, Li, (Sr, Rb)	Searles Lake, Great Salt Lake (USA), Kara-Bogas-Gol (Turkmenistan)
Sea waters	NaCl, $CaSO_4$, Mg, Br, K, (U, Li, B, D_2O)	USA, Japan, Germany
Man-caused waters:		
I-Br plants	NaCl, Br, Sr	Russia
Oil-gas fields	Br, I	USA (Oklahoma), Japan
Heat-and-power engineering	$CaCl_2$, (NaCl, Zn, Pb, Fe, Ag, Li, B, As)	Salton Sea (USA), B. Pauzhetka (Russia)
Salt-mines and K-plants	NaCl, Br	Germany, France, Russia, Japan
Water-desalinating plants	NaCl	Poland, Russia

Table 2. Extraction of rare elements and mineral salts from hydromineral raw material (during a year)

PRODUCTION	COMMON (thousand tons)	FROM HYDROMINERAL RAW MATERIAL/ % - part of common
NaCl	120000	36000/30
KCl	16000	1400/9
soda	35000	3500/10
Na_2SO_4	4600	1400/30
$CaCl_2$	2700	600/22
B_2O_3	1000	250/25
Br	350	320/90
Mg	200	50/25
Li	40	17/30
I	15	13/85

Table 3. The elements under development by industry for extraction from hydromineral raw material

	COMMON EXTRACTION (tons)	FROM HYDROMINERAL RAW MATERIAL
Fe	$4.1x10^8$	+
Cu	$6.0x10^6$	++
Zn	$5.0x10^6$	++
Pb	$2.3x10^6$	+
U	$3.8x10^4$	++
W	$4.3x10^4$	++
Sr	$5.8x10^4$	+
Ag	$1.0x10^4$	++
Hg	$4.3x10^3$	
Ge	$1.0x10^2$	
Cs	n x 10	
Rb	n x 10	
D_2O	-	

+ Technological testing

++ Projects of extractions

Table 4. The limits of minimal industrial concentrations of i and br(mg/l)for mineral water deposits in Russia

TYPE	I	Br
I	16-44	-
Br	-	492-4700
I+Br	10-40	350-1650

Table 5. Concentrations of some rare elements in brines of Russian platform (mg/l)

WATER TYPE	MINERALIZATION (g/l)	Cs	Rb	Sr	B
Cl-Ca-Na	35-75	0.1-0.4	0.1-0.5	50-150	5-30
	75-150	0.2-0.4	0.3-1.5	100-400	10-40
Cl-Na-Ca	150-340	0.2-1.0	1.0-3.0	100-300	5-30
	340-430	1.0-2.0	3.0-20.0	900-3000	90-100

Table 6. Middle concentrations of rare elements in water-bearing complexes of Azov-Kuban and Eastern Pre-Caucasus basins (mg/l)

Water-bearing complex	Rare metals	I	B	Br	Sr
Azov-Kuban Basin					
The Jura	19	19 (max 68)	29	122	158
Low Cretaceous	5	13	32	60	81
Eastern Pre-Caucasus Basin					
The Jura	43	12	5	54	500
Low Cretaceous	30	14	91	173	33

Table 7. Composition of valuable components in industrial waters of large artesian basins

Typical basins of underground industrial waters	ELEMENTS
Volga-Pre-Caucasus	I, Br, Sr, Cs, B, Rb
Volga-Kama	I, Br, Sr, B, Rb
Tungus	Br, Sr, B, Rb, Cs
Angara-Lena, Mangishlak-Ustyurt, Pechora, Dnepr-Donetzk	Br, Sr, B, Rb
Moscow	Br, Sr
Pre-Baltic	Br, Sr
Western-Turkmenistan, Kurinsko-Apsheronsky	I, Br, Sr
Western-Siberian, Sakhalin	I, Br