Possibility of application of peat from Mitoginskoye deposit of Kamchatka Krai for purification of waste geothermal heat carrier mediums from toxic compounds

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Abstract. On the basis of literature review and patent investigations methods of cleaning natural and technical waters of toxic compounds are surveyed. The possibility of applying peat from Mitoginskoye deposit of Kamchatka krai for cleaning up spent geothermal heat carrier mediums, which are formed on the geothermal deposits in exploitation, of toxic compounds with the purpose of decreasing environmental impact is assessed.

Key words: peat, geothermal heat carrier mediums, clean-up, toxic compounds, sorption.

1. Introduction
In the majority of technological schemes of geothermal resources exploitation there is a geothermal solution used at Geothermal Power Stations as a heat carrier medium of the first contour or disposed at the Geothermal Power Station as a separated liquid. Geothermal deposits are used for producing thermal and electric power, extracting mineral raw materials, implementing balneology purposes and so on [1, 2, 3]. The chemical analysis of the composition of waters from various deposits that are discharged to the surface water courses shows the increased concentration of some components in the water in comparison with maximum permissible concentrations established for water bodies of commercial fishing importance [4, 5, 6]. Geothermal waters contain chemical compounds which, upon definite concentration and environmental conditions are toxic for live organisms, they may be of organic (phenols, naphthenic acids, aromatic hydrocarbons and others) and inorganic (boron, arsenic, strontium, bromine, copper, lead, zinc and others) origin. Ions of some metals and semi-metals contained in geothermal water belong to widespread pollutants. In case of exceeding the maximum permissible concentration values for the discharge to the surface water bodies and sewerage network geothermal waters must be subject to clean-up after their utilization.

The results of investigating the chemical composition of the geothermal heat carrier medium taken from the wells of Pauzhetskoye and Paratunskiye geothermal deposits which were obtained by RGC FEB RAS in 2015 show that the concentrations of As, Li, F, Cu, B compounds considerably exceed maximum permissible concentrations established for water bodies of commercial fishing importance [7, 8, 9].
2. Purification of the used geothermal heater carrier

Nowadays various methods are used for the purification of water mediums and removal of toxic compounds from them among which sorption is of great interest. Sorption is quite effective and in case of multiple stage organization it can provide purification to any required extent. The sorption-based purification of water generally refers to the sorption (concentration) of substances on the surface or within the scope of pores of solid material. Anybody in space is limited by the surface, and, consequently, its substance is a potential sorbent. However, in water purification practice only sorbents with a full-fledged or specific surface are used the application of which is much more effective. Finely dispersed and porous sorbents have the largest specific surface area. The pores of sorbents are divided into: micropores \( r_{\text{eff}} < 0.7 \text{ nm} \), supermicropores \( 0.7 \text{ nm} < r_{\text{eff}} < 1.5 \text{ nm} \), mesopores \( 1.5 \text{ nm} < r_{\text{eff}} < 100 \text{ nm} \) and macropores \( r_{\text{eff}} < 100 \text{ nm} \) [10].

For the purification of natural waters in most cases synthetic sorption materials are used which are highly efficient and can be re-used. However, to solve geothermal problems it is necessary to use sorbents that satisfy additional requirements: they should be relatively inexpensive, accessible (preferably taken from the regional deposits of natural materials), easily recycled and subject to biodegradation.

Sorbents obtained by means of modifying natural materials with the purpose of increasing their sorption properties meet such requirements. One of the most promising natural materials for the creation of sorbents is peat which is widely used for purification of various liquid mediums even in its non-modified form. [11]. Complex polydisperse multicomponent structure of peat and its chemical composition determine its sorption capability. The role of ion-exchange properties of peat is especially great when it is used for cleaning up foul runoffs [12]. Peat consists of organic mass, mineral additions and water. The organic mass contains humic acids, bitumens, water-soluble and highly hydrolyzable substances, cellulose and non-hydrolyzable remaining residue. Peat has high porosity. Ash elements contained in peat make considerable influence on the sorption properties of peat. Ash content value (total content of inorganic part, \%) is determined by water-mineral regime of peat formation and depends on the type of peat and the degree of its decomposition. The average ash content for peats of lowland type amounts to 6-18\%, for transient peats - 46\%, for highmoor peats - 2-4\%; the degree of decomposition \( B \) of lowland peat is 15-55\%, of transient peat - 5-50\%, of highmoor peat - 2-55\%.

With low degree of decomposition the structure of peat is less damaged, it has higher porosity, specific surface, more well-developed structure in comparison with peat of high decomposition degree. Thus, a decrease in the ash content and decomposition degree of peat leads to the improvement of its sorption properties in regard to, for example, oil, oil-products and so on, therefore most researchers offer to use highmoor peat of low decomposition degree in order to obtain sorbents [13].

The paper [14] describes some experiments aimed at studying the sorb properties of natural sorbents in relation to the ions of copper (II); marl, gaize, peat were used as sorbents. Balance and kinetic parameters of sorption were defined. It was found out that peat and gaize have the best sorption properties in regard to copper kathions. With such characteristics of peat applied for sorption as decomposition degree 83.3\%\pm2.3\%, moisture content 2.62\%\pm0.1\%, ash content 24.02\%\pm0.12\%, exchangeable acidity 6.8\%\pm0.1 \text{ pH}, movable compounds of phosphor 60.2\%\pm1.2 \text{ mg/kg}, movable compounds of calcium 2.00\%\pm0.07 \text{ mg/kg}, of magnesium 1.47\%\pm0.02 \text{ mg/kg}, potassium 90.2\%\pm6.9 \text{ mg/kg}, movable sulfur 98.5\%\pm3.8 \text{ mg/kg}, organic substance 75.34\%, total nitrogen content 1.62\%\pm0.05\%, it took 30 minutes to achieve 80-85\% extraction of copper by means of peat, with the original concentration of copper in the solution – 10 \text{ mg/dm}^3. One of crucial factors influencing the process of sorption is the pH value of the solution. Maximum sorption of copper on the basis of gaize, marl, and peat occurred with the pH level of 7.0-8.0 [14].

The area of Zapadniy in Mitoginskoye peat deposit (Kamchatka Krai) was thoroughly explored by Yelizovo geophysical expedition of the “Kamchategologiya” enterprise in 1989–1992. The volume of peat deposit of the area without organic and mineral sediments amounts to 41 447 thousand m\(^3\), total supplies are 6 951 thousand tonnes, the balance ones – 6877 thousand tonnes with 40\% conditional moisture [15]. Peat from Mitoginskoye deposit (Kamchatka Krai) has the ash-content of 13\% on
average, with the decomposition degree of 25% [15, 16], that proves its high sorption and an opportunity to apply the peat of Mitoginsky deposit (Kamchatka Krai) for purifying a waste geothermal heat carrier medium from heavy metals and semi-metals with toxic properties.

Preparation of effective sorption material on the basis of peat with increased porosity is connected with its modification, which, as a rule, results from thermal destruction. The alternative way of peat modification is providing thermal destruction by means of microwave (UHF) impact in the oxygen-eliminating regime that allows us to prepare analogous highly porous hydrophobic material but in a more energy-efficient way [17]. The modification of peat is also carried out by means of mechanic processing – granulation, chemical activation, thermochemical processing. The phasic process of peat processing determines the efficiency of the resulting sorbent. The efficiency of natural moss peat usage as an absorbent of hazardous technology-related compounds of lead, mercury, cadmium, chromium, oil is higher than of those made of cellulose material. The application of this kind of peat is efficient with low speeds of runoff filtration. Actually, the use of granulated peat allows us to enlarge the range of peat sorbent functioning due to the higher permeability of the flow of filtering liquid. The results of the investigations accomplished during the work [18] confirm the principal possibility of applying peat for purification of mine drainage waters containing ions of heavy metals.

There is an approach to the purification of highly mineralized waste geothermal waters based on biochemical processes with the use of adapted cultures of microorganisms. The researchers [19] found out that it was rather difficult to purify waste geothermal water with the help of aerobic biochemical treatment. In case of relatively low concentration of the initial contamination by both volatile phenols and other organic substances it requires long biochemical treatment with the period of aeration of one step of treatment not less than 4-6 hours in order to achieve allowable BOD (biological oxygen demand) and phenols values. Therefore it is advisable to purify waste geothermal water by means of two-stage biochemical method, as well as to involve other physical and chemical methods of purification (ozonization, reverse osmosis, sorption) [19]. Thus, it is possible to combine biochemical and sorption ways of purifying geothermal waters, including the application of peat as one of the most accessible natural sorbents.

The paper [20] presents the survey of methods of extracting lithium and boron from natural and technogenic solutions. The researchers of RGC FEB RAS performed a series of experiments aimed at the extraction of lithium from a geothermal heat carrier medium with the application of organic sorbents and studying the kinetics of ion exchange of lithium from simulated solutions in static conditions [21]. They studied the sorption properties of industrial cation exchangers TOKEM–160, AMBERLITE IR-120 and the possibility of their application for the extraction of lithium from geothermal solutions of Paratunskoye, Pauzhetskoye, and Malkinskoye deposits (Kamchatka krai). The researchers revealed a number of limitations in the available methods of lithium and boron extraction from natural heat carrier mediums, such as: application of expensive sorbents, difficulties related to regeneration, use of toxic reactive chemicals, problem of sorbent disposal, hence a conclusion should be drawn that it is necessary to improve and develop new methods and means of extracting lithium and boron from heat carrier mediums of geothermal deposits.

The outlined above review of scientific works concerning purification of various water solutions with the application of peat as a sorbent showed its efficiency, in this respect we suggest the possibility of applying peat of Mitoginsky deposit (Kamchatka krai) for the purification of waste geothermal heat carrier mediums from toxic substances taking into account the experience presented in the review. Thus, complex technological schemes including renewable energy sources with the purpose of increasing the completeness of exploitation of Kamchatka geothermal and raw material resources are implemented [22,23].

3. Conclusions
The accomplished review shows that peat is widely used for sorption purification of various natural and technogenic solutions. The existing experience of geothermal solutions purification from heavy metals and semimetals confirms good prospects of applying sorption methods of decreasing the
chemical compounds concentration in the solution to the level of maximum permissible concentrations with the purpose of reducing the toxic impact of waste geothermal solutions discharge on the environment. Taking into consideration the availability of considerable supplies of peat in Kamchatka, the availability of transport infrastructure in the area of Mitoginskoye peat deposit, it is possible to apply this natural sorbent for solving ecological problems in the geothermal power production industry of Kamchatka. It is necessary to define optimal parameters of geothermal solutions purification from toxic compounds and technical and economical assessment of the results.

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