Purification of the used geothermal heater carrier from arsenic compounds

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Abstract. Based on the literature search and patent studies, an overview of the purification methods of natural and technical waters from arsenic compounds was made. Promising methods to reduce arsenic concentration in geothermal heat carriers in Kamchatka deposits have been identified with a view to decrease the toxic discharging effect of exhausted solutions on the environment.

Key words: geothermal resources, arsenic, purification, maximum permissible concentrations, environment.

Introduction

Geothermal fields are complex resources used for generating thermal energy and electric power, for the production of mineral raw materials, for balneology purposes and so on [1, 2]. One of the directions of industrial development of Kamchatka and the Kuril Islands geothermal resources is the creation of geothermal power technology systems.

All over the world there is an increase in the share of producing heat and electric power generating from non-conventional and renewable energy sources, including geothermal systems. A geothermal solution is found in the most of technological schemes of the geothermal resources use. This solution is used at geothermal power stations as the transfer medium of the primary circuit or utilized at the geothermal power plant by separation.

The geochemical analysis of the composition of geothermal waters discharged into the surface stream waters of various geothermal fields in Kamchatka shows that the threshold limit value (TLV) estimated for fishery-related water bodies is exceeded. For example, the exceedance multiplicity of TLV in waste waters at the Pauzhetsky geothermal deposit is Li - 37, H3BO3 - 54, As - 70 [3].

Arsenic is assigned to the irritation category 2 – highly hazardous substances. The threshold limit (TLV) value in fishery-related water bodies is 0.05 mg/dm3, in domestic and recreation water bodies it should not exceed 0.05 mg / dm3.

The micro component analysis of the coolants of the production wells in the Pauzhetsky geothermal deposit shows it contains As from 3 to 3.7 mg/dm3. The results are obtained by a mass-spectral method with inductively coupled plasma and an atomic-emission method with inductively coupled plasma using the NSAM technique No. 480-X. The analysis of the coolants of the production wells of the Paratunsky geothermal deposit indicates an average As content of about 0.8 mg/dm3.

Currently, considerable attention is given to the introduction of modern environmental protection technologies for industrial waste water treatment. Waste water from the spent coolants, formed during
the exploitation of geothermal deposits, have a complex composition. Discharging untreated wastes into water bodies and to relief significantly increases harmful impacts on water bodies by pollutants. These factors urge the development of effective flow sheets for the purification of spent geothermal waters which will bring the level of purification to the standard ratios [4, 5].

**The methods of natural and industrial water purification of arsenic (an overview)**

Worldwide there is an extensive search for both effective and inexpensive ways to remove arsenic from water. On the recommendation of the World Health Organization, the arsenic content in potable water should not exceed 0.01 mg / dm³, this amount of substance can be consumed daily over an entire lifetime without appreciable risk to health. Elevated levels of arsenic compounds are toxic for animals and humans: they inhibit oxidative processes, damage the supply of oxygen to organs and tissues.

Many authors’ studies have shown that it is appropriate to consider the waste-water treatment technologies that ensure the maximum transfer of arsenic to hazard categories 3 and 4 waste, that is in the form of the most stable (less soluble) and convenient for disposal or utilization. This approach is more environmentally sound and takes into account economic dimensions of the technological process [6,7,8].

Arsenic can exist in natural water in two forms – trivalent (As³⁺) and pentavalent (As⁵⁺). There are some methods of removing both of these arsenic forms from water – adsorption, membrane technology, ion exchange. The concentration of arsenic in a colloidal state can be reduced by the set of traditional methods of water purification – coagulation, flocculation, sedimentation and filtration.

According to the results of the made overview the methods of reduction arsenic concentration and its extraction from aqueous solutions could be combined into the mentioned groups of methods.

Iron-folate, manganese, aluminum, titanium, a phosphorus compound are recommended to be used for transferring arsenic from soluble forms to less soluble. For the obtaining of relatively stable, slightly soluble arsenates and their complexes a number of reagents – oxidizers and catalysts should be used.

Oxidation of trivalent As to pentavalent precedes many technical schemes of water purification from arsenic. Ozone, hydrogen peroxide in the presence of catalyst Fe²⁺ or coagulant with Fe³⁺, air oxygen at elevated pressure (up to 9 bar) in the saturation mode are used as oxidizers.

Coagulation is used for the purification of water from arsenic after solutions treatment with oxidants, ferrous polydysulfate, water-soluble salts of trivalent iron or aluminium with metal concentration g / dm³: 2-10 and 5-15 [9]. Coagulation can be used together with flotation of a dispersed arsenic phase, followed by filtration of the precipitate through a mixture of anthracite chips and quartz sand, a drum filter, etc. [10].

Precipitation of arsenic from the solution is a widely spread technological method, which makes it possible reduce seriously its initial concentration. The deposition on the surface of metals and precipitation in the form of sulfide and arsenates (calcium, iron, magnesium and aluminum) are applied. For example, iron chloride or ferrous sulphate are quite inexpensive, and the methods with their application are effective enough [8, 11]. In order to reduce the concentration of arsenic in natural water with the help of Fe₂(SO₄)₃ up to TLV standards (TLV) the ratio Fe³⁺/As⁵⁺ = 7 is sufficient. Arsenic also precipitates with iron hydroxide Fe(OH)₃. Iron precipitation with the use of other compounds – for example, additional introduction of calcium ions into the process – allows to achieve a higher purity level [12]. Calcium silicates can be also used for the precipitation of silica and arsenic from geothermal wastewater [13]. When silica precipitates from a geothermal solution, an accumulation of arsenic takes place, the removal of it can be carried out with the use of inorganic sorbents [14].

Some combined methods can be presented as well. Sequential transmission of water through tanks filled with iron-floating activated carbon allows to reduce in the arsenic concentration from 10 to 1 µg/dm³ [15].
Membrane methods are usually used after reagent treatment of water. The advantages of nanofiltration are described in a number of studies: compounds containing pentavalent form much larger complexes that are effectively retained by membranes. Whereas the trivalent arsenic purification index is much lower, but it is growing with the increasing pH of the solution and the content of organic compounds in water [16].

The processes of natural water purification from arsenic by means of microfiltration, ultrafiltration and reverse osmosis have been studied. The research shows it is possible to reduce arsenic concentration from 10 to 1 mg/dm³ by using tubular ceramic membranes with pore sizes of 20-50 nm [17].

The experiments on extraction of arsenic compounds using nanofiltration and reverse osmosis polyamide filters and polyethersulfone showed a recovery of 89-99% [5,18,19].

Adsorption of arsenic in various substrates is one of the most widely used natural waters and solutions treatment techniques [8]. Granular materials, which are used for these techniques, are not washed away as compared with powdered reactants. These are mainly oxyhydroxides and hydroxides of metals, for example, iron, aluminum, magnesium, tin [8,20]. Such natural minerals as siderite, hematite, goethite, magnetite, pyrite, zeolite are also used. Using activated carbon in the form of a loading a multilayer filter, arsenates and arsenites are removed from the solutions by an ion-exchange process that gives the possibility of subsequent adsorbent regeneration [21].

Coprecipitation and adsorption capture by the developed surface are used for arsenic sorption carried out with the help of substances of organic and inorganic nature. Synthesized polymers with predominantly ion-exchange interaction, organic natural sorbents, cellulose and activated sludge can be used for the process as well. Organomineral and inorganic sorbents remove not only arsenic, but also heavy metals from solutions. The sorbents-anion exchangers AB-16GS, AN-2FN and cation exchanger KU-2-8 are used in the case.

Arsenic extraction from technological solutions and wastewater is carried out by neutral organophosphorus compounds and organophosphorus acids, carboxylic acids, amine salts.

Solutions with a high arsenic level are purified in electrochemical reactors of various designs. The cathodes made of Fe, Cu, C, Pb, Ni, Cd, Al, Ti and the stainless steel anodes are used for As⁵⁺ and As³⁺ removal from acidic and alkaline solutions by electrochemical remediation. Iron, aluminum, copper, titanium anodes are applied for electrocoagulation. Under the action of the current, the metal dissolves and its cations pass into the aqueous phase. The cations and hydroxyl groups form metal hydroxides in the form of flakes, followed by coagulation and precipitation. A number of researches focus on the possibility of applying electroflotation and electrodialysis for solutions purification from arsenic compounds [8].

For reducing the concentration of arsenic in spent geothermal solutions the author proposes a combined method with the use of tubular membrane filters with a pore diameter of 0.1-0.2 μm and a pre-coat layer of colloidal silicon dioxide obtained by ultrafiltration or nanofiltration on the membrane surface. A geothermal solution containing 10-20 g / dm³ of silica (a particle size up to 0.3 μm) is passed through the membrane filter. A helium layer is formed on the surface of the tubes as a result of concentration polarization. When a geothermal solution, containing an increased concentration of arsenic compounds, passes through a filter, on the surface of the colloidal silica particles, constituting the helium layer, the sorption of arsenic takes place and the concentration of arsenic compounds reduces in the filtrate.

Conclusions
The review presents a wide range of methods of arsenic removal from the water – adsorption, ion exchange, coagulation, flocculation, sedimentation and filtration. The existing technological solutions are developing and therefore improve the economic parameters of the process. The combination of fine treatment methods (ion exchange, sorption, nanofiltration) seems to be the most promising ways of reducing the arsenic concentration to the level of TLV. It allows reducing the toxic effect of spent geothermal solutions on the surrounding environment. The choice of the treatment scheme for
individual and depends on the physicochemical characteristics of the solution, the concentration of arsenic, the availability of generated electrical energy and the available natural material, the sorbent. A series of experimental studies and subsequent technical and economic evaluation of the results are necessary for establishing the optimal parameters of purification of geothermal solutions from arsenic compounds.

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