Perspectives and Tasks of Mineral Substances Extraction from Ukrainian Geothermal Brines. Project of Experimental-Industry Elaboration of North-Sivash Iodine Thermal Field (the Crimean Peninsula)

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The potential of geothermal resources of Ukraine for mineral substances extraction has been analysed within this article. There have been offered complex use of power, mineral and water constituents of geothermal transmitters. As for the deposits located on the Crimean peninsula the technology of iodine extraction from geothermal waters has been suggested. This technology combines adsorption and diaphragm methods. Sorbent series have been researched and based on modified silica gel sorbents efficiency use has been showed.

Ukrainian deposits of geothermal waters contain considerable power potential (thermal energy as well as dissolved combustible gas) and mineral constituents. They are concentrated in four artesian basins: Zakarpatsky, Prikarpatsky, Dneprovsko-Donetsky and Prichernomorsky. The confirmed resources of geothermal waters make up more than 27 million m^3 per day with a temperature about 70° C.

Mineral composition of Ukrainian geothermal waters (mean values of general mineralization within the limits of 30-350 g/dm^3) is represented mainly by the ordinary set of sulphates, chlorides and carbonate metals. Deposits of geothermal waters containing iodine (25-35 mg/dm^3), bromine (85-90 mg/dm^3), boron (60-65 mg/dm^3), strontium (300-350 mg/dm^3), rubidium (to 5 mg/dm^3) and lithium (to 10 mg/dm^3) are perspective and promising for industrial production.

The main task for industrial production organization of the above listed substances is the development of technologies and technical projects aimed at complex use of the whole spectrum of geothermal carrier constituents. Above all the projects provide for power support of technological cycle due to own geothermal water thermal energy and dissolved gas use.

The presence of significant amount of dissolved natural gas (mainly methane with gas factor not less than 1 m^3 per 1 m^3 water) in thermal water makes the development of various types of heat- and electric- utilizing technologies economically expedient. One of the variants of such technology can be the plant containing a separator with gravitational division of liquid and gas phases.

After gas component being isolated, thermal water moves into heat-power driven block, which consists of consistently connected hydro cyclone, geothermal heat exchanger and force-pump. The isolated natural gas moves on the electromechanical block with electrical generator for further electric energy production.

The technologies of complex utilization geothermal water power- and gas- components are characterized by high technical and economic parameters.

Along with the utilization of geothermal water heat and gas components the parallel development of technologies for valuable mineral components isolation promotes to increase the economic efficiency. The technologies for utilization geothermal water components such as iodine, bromine, rare, rare-ground metals (lithium, strontium, rubidium and others) have been developed.

It is well known that depending on extraction form – either elemental iodine (J_2) or iodide ion – there are two groups of methods for iodine extraction. Among first group methods (adsorptive, flotation, membrane and method of air desorption) the most promising from economical and environmental point of view are membrane method and a series of adsorptive technologies based on such adsorbents as activated carbon, zeolites and ion-exchange tar. The second group includes technologies for iodine extraction without iodide oxidation in the form of insoluble compounds with a number of metal (Cu, Ag, Hg). There have been developed a complex two-stage method for a series elements extraction from geothermal solutions. It combines the advantages of adsorptive and membrane technologies [1].

The problem of choosing the most optimal and economically feasible technology for iodine industrial production could be solved when having researched stability of different iodine forms in mineralised geothermal waters. Considering data on outer electron shell the most stable iodine forms are iodide and iodate. In neutral environment (pH=7) these forms coexist but a mixture of solutions (iodate with surplus amount of iodide) is a very stable system and when adding some acid makes up iodine amount equivalent to iodate one [2].

Performed detailed chemical analysis of geothermal water samples in the wells series in Prichernomorsky artesian basin (Crimean peninsula) has shown that predominant iodine amount exists in the form of iodide and average element concentration makes up $24{,}5 + 1{,}2$ mg/dm^3.

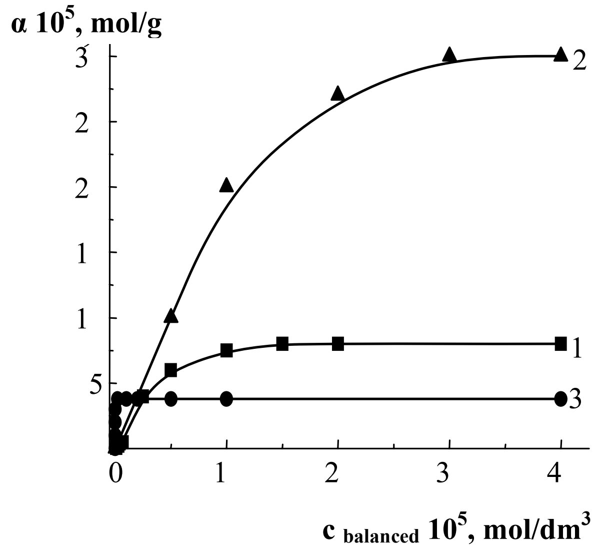
There have been also studied the possibility of sorbents series utilization for iodine extraction from geothermal waters, particularly two types of modified silica gel and activated carbon (see table).

Table. Sorbent characteristics for geothermal waters iodine extraction.

No	Sorbent type	Iodine extraction level	Adsorptive capacity, dm^3/mol	Sorption constant, dm^3/mol
1	Silica gel modified with silver chloride	0.85 – 0.90	$8.0 \cdot 10^{-5}$	$0.5 \cdot 10^{-5}$
2	Silica gel modified with tetra-alkyl-ammonium	0.90 – 0.95	$30.1 \cdot 10^{-5}$	$0.3 \cdot 10^{-5}$
3	Activated carbon	0.95 – 0.98	$3.8 \cdot 10^{-5}$	$0.4 \cdot 10^{-5}$

The presented figure shows corresponding adsorption isotherms, obtained from model solution. For modified silica gel samples (relations1, 2) isotherms form corresponds to Langmuir equation, as for activated carbon – Henry equation (relation 3).

Figure. Sorption isotherms of iodide on silica gel modified with AgCl (1), tetra-alkyl-ammonium groups (2) and elemental iodine on activated carbon (3). T=283 K.



Modified with AgCl and used as a sorbent for industrial volumes utilization silica gel has got some lacks, namely, high price for argentum salts and considerable time period for gaining adsorption balance. As for activated carbon is concerned, the last also has got a defect – iodide should be transferred into elemental iodine. The most perspective sorbent for iodine extraction in the form of iodide (as marginally soluble compounds) is silica gel modified with tetra-alkyl-ammonium groups.

This is the main basis used for project development of experimentally industrial unit for crystalline iodine production from geothermal waters located in North-Sivash deposit (Prichernomorsky artesian basin, the Crimean peninsula).

Total amount of drilled and studied wells 1500-1900 m deep is over 20 only on Predmostny part of this deposit, approved thermal waters resources amount to not less than 33.6 thousand m^3 per 24 hours. Calculated operation life of the deposit is defined by the length of the area of worked-out geothermal water travel from injection to operational well (over 3000 m) and amounts to not less than 25 years.

Basing on approved operational geothermal water resources, average output about 2700-3000 m^3/24 hours and average iodine concentration of 25mg/dm^3 iodine production is estimated as 27-28 t annually.

Literature

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