Development of a Non-Reagent Method For Extraction of Iodine from Reservoir Waters of Oil and Gas Deposits

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Abstract. Currently, two methods of extracting iodine are mainly used: air-desorption and ion-exchange. Common to these methods is the use of chemical reagents such as sulfuric acid and chlorine in the stages of acidification and oxidation, which are the main sources of costs in the production of iodine and environmental pollution. Therefore, the development of technology for the processing of reservoir waters in oil production with the goal of isolating such elements as iodine for further use is an urgent task of rational nature management. A new method for extraction of iodine from the geothermal reservoir water and oil and gas fields in Western Siberia, which eliminates the use of chemicals in the technological scheme, which reduces the environmental burden on the environment. This technology was tested in a pilot plant and can be used in the preparation of iodine-bromine water Cherkashinskoye field Tyumen Oblast of the Russian Federation.

1. Introduction

Geothermal Cenomanian waters of oil and gas fields in Western Siberia are fairly perspective natural source of iodine raw materials.

In connection with it we researched the use of geothermal waters as the feedstock for the contraction of the iodine, which disclosed that the latter can effectively enough be separated from the amount of cationites alkaline elements and anions of the chlorine, bromine with the use of anionite AB-17×8 in the OH form. Ion-exchange technological scheme of processing thermal waters containing the iodine is shown in Fig.1.

The suggested technology allows not only to use thermal drilling waters, separate the amount of alkaline metals and iodine from admixtures but also to extract each by selective sorption, e.g. rubidium on the nickel ferrocyanide, lithium by selective cationite ISM-1. The reality of processing Western Siberia Cenomanian waters by means of the sorption technology is proved by our experimental data (Fig.1) [1].

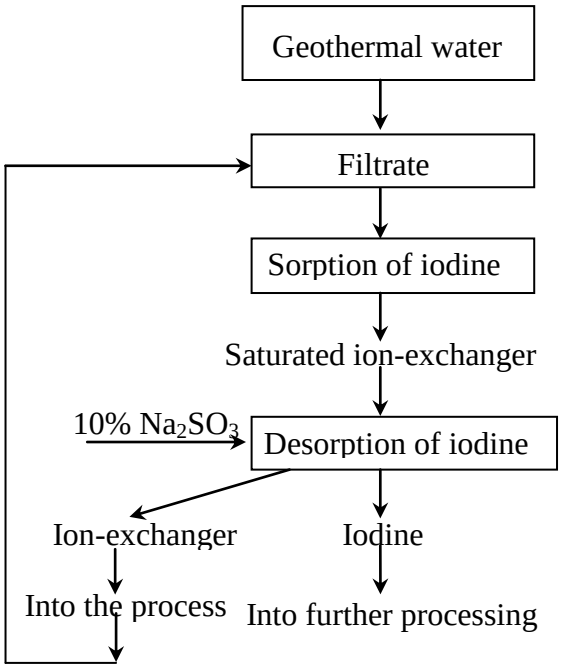

Figure 1. The technological scheme of processing Cenomanian thermal waters containing iodine.

Table 1. The extraction of iodine from drilling waters of the borehole №512 of Surgutskoye oilfield by means of the anionite AB -17×8 (100 gr.).

Ion-exchanger	The volume of the drilling water and containing elements in it		The volume of the commercial fraction and containing elements in it		% of of extraction
Anionite AB-17×8 in the OH form	V, l	I, mg/l	V, millilitre	I, mg/l	
	20000,0	14,0	1000,0	162	57,8

2. Materials and methods

Techniques of the iodine extraction from natural brines and solutions are covered in the study of Ksenzenko [2], in which the efficiency of sorption iodine extraction from solutions depends on the transition of the ion iodide to the molecular iodine by such oxidants as chlorine or hydro-chlorite or potassium is shown. The use of the mentioned oxidants complicates the technological scheme process; follow-up actions are required to recover chlorine and its derivatives. Taking it into account, to extract iodine we suggest a reagentless technology of its oxidation by preliminary electrotreatment (electrodialysis) of the inflowing solution to the anionite AB-17×8 in the CT form. For that purpose laboratory trials on electrolytic oxidation of iodine were conducted in the natural water of Yalutorovskoye field (table 2) [3].

Table 2. Chemical composition of the thermal natural water of the borehole №10p of Yalutorovskoye field, Tyumen region, the RF.

Field	The date of sampling	pH	Content, mg/ l				
			Σ of salt	Br^-	J^-	Cl^-	Li+
Yalutorovskoye (Pamyatnoye settlement)	27.11.2007	7,3	14283	51,6	9,1	8510	0,14

So, 0,7 gr. of the swollen resin AB-17 was put into the electrolyzer with 50 milliliters of the natural water brought up to concentration I^- to 19,1 mg/l and acidulous up to pH=3,2. The analysis of iodine was performed by sample extraction of the chloroform solution with the consequent titration of the coloured solution by the sodium thiosulfate. The electrodes were the graphite anode and cathode. The solution was subjected to mechanical mixing and electric current with 6 volt voltage and 200 milliampere current intensity was run through it. Along with this, experiments were carried out with the hypochlorite iodine oxidation 0,14н KOCI to complete oxidation of ion iodides. The outcomes of experiments are given in Table 3.

Table 3. Experimental data of the iodide sorption with the limited volume from the thermal water pH=3,2 with the preliminary oxidation.

Oxidation methods	V, ml	C_i, mg/l	t, min	Ionite	Number of experiments	Eh beg., mV	Eh end., mV	% of extraction	measure of inaccuracy, S_x
Electrolytic	50	19,1	9	AB-17 in Cl^- form	5	595	511	95	1,29
Hypochlorite	50	19,1	9	AB-17 in Cl^- form	5	595	550	85	1,27

According to Table 3 one can see that the percentage of the iodine extraction by electrolytic oxidation is higher (95%) than under the hypochlorite one (85%).

The dependence of iodine sorbing on the time of the anionite AB-17 in CL form contact with the solution is given in Fig.2.

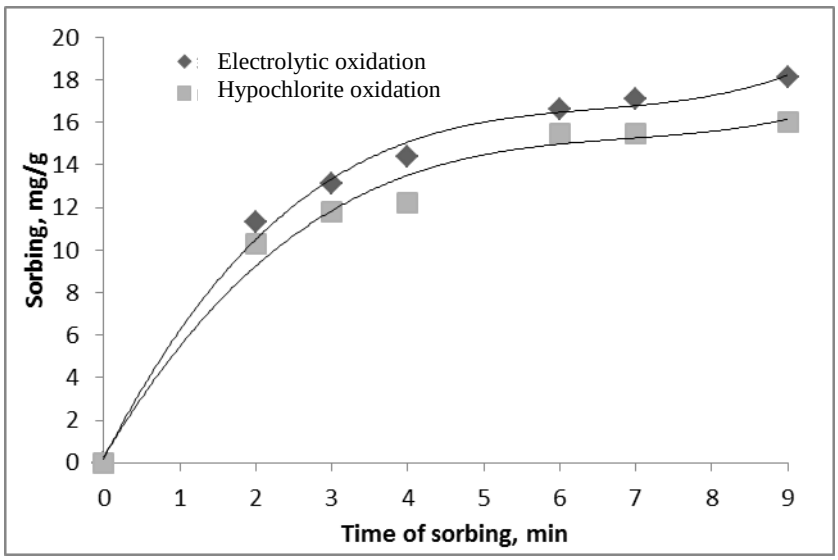

Figure 2. Outcome curves of the iodide sorption in the limited amount of the natural water at pH=3,2 with the preliminary oxidation.

Experiment results show that with the preliminary electrooxidation the iodide sorption is 10% higher than at the hypochlorite oxidation.

3. Results and discussion

At the same time as the result of many-year researches and industrial resting now in the world practice two methods are accepted and widely used everywhere by leading iodide producers (Japan, the USA, Chile): air-desorbing and ion-exchange methods [5-9]. The first one is effectively applied in hot waters at the temperature no less than 40 °C. The second one is acceptable as for cold as for hot waters. In general all methods concentrate on the idea that the iodide is separated by the chemical oxidising agent from natural alkaline underground waters or from acid, acidified by the sulfuric acid; then the separated iodide is absorbed by an adsorbent, coal or an ion-exchanger or is blown out by air. From the adsorbent the iodide is separated by the deoxidizing agent in the form of iodide-ion. Further the concentrate is subjected to standard chemical treatment. Application of this or that method implies the addition of chemical agents at different processing stages that results in the product cost appreciation and possible environmental pollution.

We suggest a new method to extract the iodide; it differs from all the above mentioned by the fact that electro-chemical oxidation and acidifying of iodide-ions take place in the anode space of the flow-through electrolysis unit without any reagents being added with the simultaneous process of the iodide sorbation by the selected coal of a high degree adsorbing capacity [3]. As the cathode copper was used. Recovery and washing out of the iodide from the coal happen as the result of the electrodes polarity change. In the received iodide concentrates the iodide content exceeds 1000 times the initial concentration. All iodide extraction stages are in one chemical reactor - the sorbation tower. Then, from iodide concentrates with adding oxidising agents raw-iodide is separated. Raw-iodide or technical iodide is a by-product which is necessary to purify from different dirts up to the product corresponding to GOST 4159-79 iodide of the reactive line Ч. Research results are presented in Table 5, the main technological scheme of our experimental iodide extraction unit is shown in Fig.3, the experimental iodide extraction unit itself is shown in Fig.4.

Table 4.

Indicators	Units of measurement	The known method	The suggested method
Static exchange capacity for iodine	mg\g	180	600
Reagent consumption per 1 kg of the iodide			
H_2SO_4	kg	4,1	-
Cl_2	kg		-
Na_2SO_3	kg		-
Electroenergy consumption per 1 kg of the iodide	KWt\h	-	5.7
Yield of the iodide into the filtrate	%	89	97

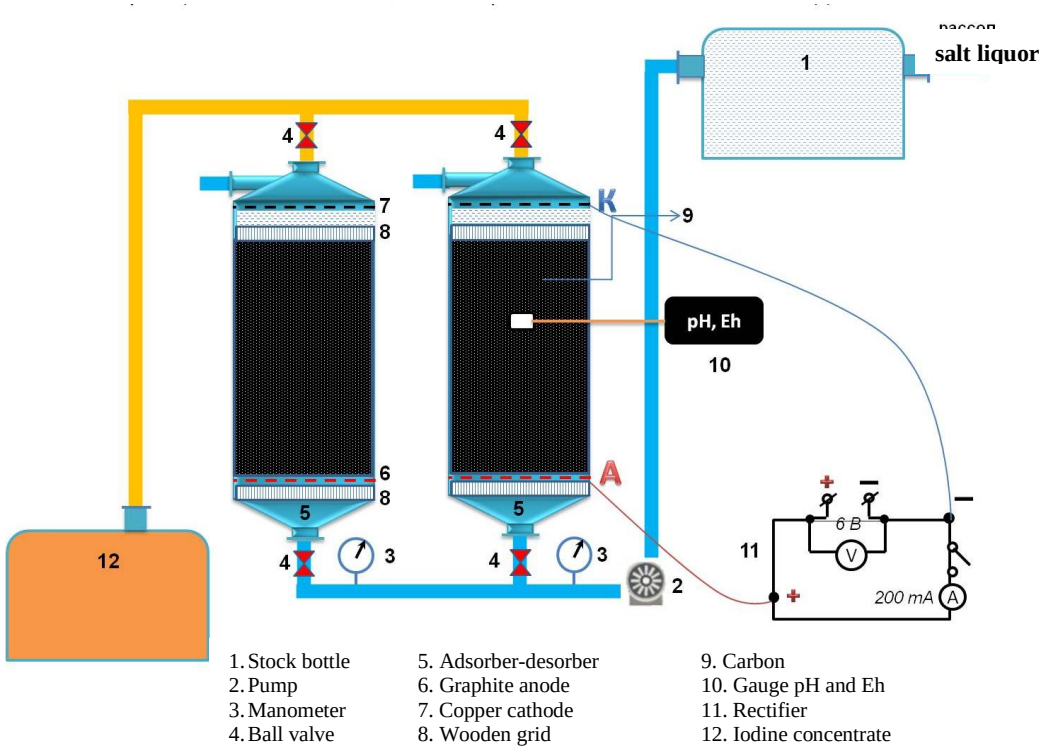

Figure 3. The main technological scheme of the iodide extraction unit.

(A) (B)

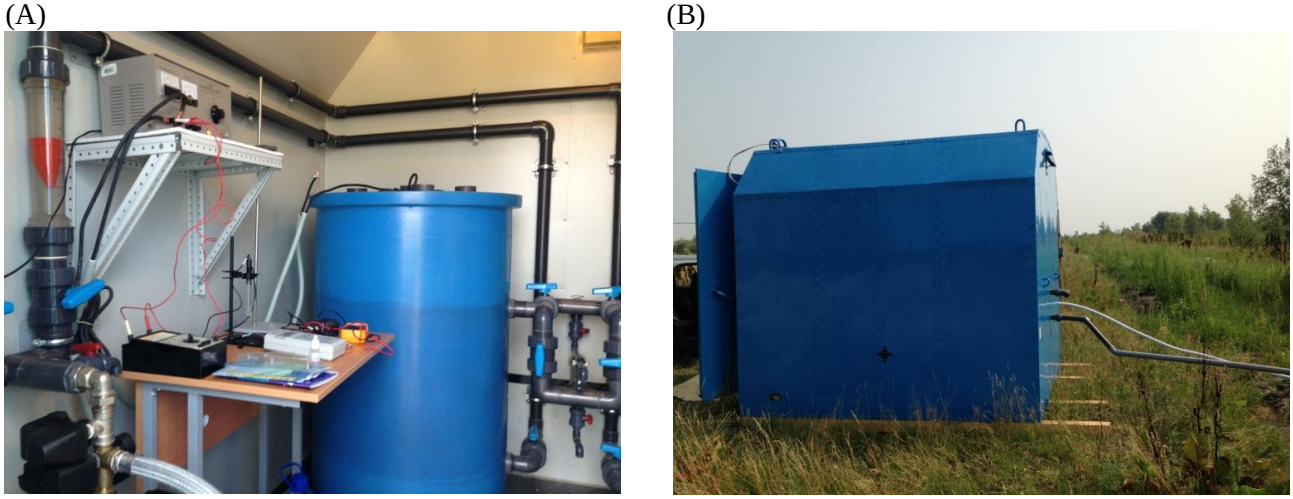

Figure 4. The experimental iodide extraction plant. (A) inside and (B) outside.

In Russia earlier and at present the iodide is produced only from underground industrial waters. Now in the Russian Federation there is only one working Troitsk iodide plant in Krasnodar krai with the production capacity 180 tons of iodide per year. Current demand of the iodide is evaluated as not less than 1200-1500 tons per year and in the nearest future it can rise 2-3 times because of the expected expansion of its usage in new spheres of engineering, technologies and in agriculture.

The main source of the iodide producing is underground industrial waters (hydromineral raw materials). For example, the explored dynamic resources of iodide waters of Cherkashinskoye field (Tyumenregion) are 92 thousand cubic meters per 24 hours and 870 tons of the iodide per year. The

presence of such a sufficient iodide field stipulates the reasons to create the iodide production just here. Despite of the iodide stores Russia remains the importing country.

4. Conclusions

Taking into account everything the above said, we can conclude as follows:

1. To organize the production of the iodide from underground waters, e.g. Cherkashinskoye field, there should be applied the original combined reagentless method having in comparison with other methods a number of sufficient advantages: lower expenses for reagents, not so strict demands as to the quality of initial raw materials; decrease in the number of production stages, decrease in environment dangers.
2. Development of the field implies the exploitation of 20 wells with the average yield 900 m3 per 24 hours with connecting each well with the mobile (module) iodide extraction unit. The unit can process up to 1000 m^3 of water per 24 hours. The concentration of the unit allows keeping the production 24/7 without standing time with the high iodide output (85%). The calculated cost of the product can be 577,6 thousand of rubles for the ton of the iodide at the general plant production 100 tons per year. The net profit can be 67 mln. of rubles per year.

5. References

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