Redox processes in extracting iodine from underground water

N.M. Korchyk, N.M. Budenkova, O.A. Prorok, O.I. Musina
The National University of Water and Environmental Engineering, Ukraine.
E-mail: budenkovanm@ukr.net

Aim: Researching iodide oxidation by hydrogen peroxide in acidic medium with extracting iodine from drilling waters for compiling technological schedule.

Methods: Redox processes in the technology of removing iodine from underground waters was determined by the method of potentiometric titration and chemical sedimentation in the periodic action reactor with the intensive mixing of reacting substances, here was determined the concentration of J- and J2+, the molar interrelationship of components, pH, redox potential (Eh), index rH2 of the system. The research was carried out on the basis of real waters of Pripyat depression with iodine content up to 100 mg/dm^3.

Results: A series of theoretical and practical studies was carried out to the result of which the method was substantiated of removing iodine from underground waters using hydrogen peroxide and lactic acid on the basis of which a technological scheme was proposed.

Scientific novelty. Optimal physics-chemical parameters (pH, Eh, rH2) were suggested for each stage of the technological process of removing iodine from underground waters which decreases the cost price of final product.

Practical value: The results of the work permitted to substantially cut down expenditures of H_2SO_4, to provide for excluding side processes. The results of the work were introduced into research-industrial equipment for extracting iodine from underground brines of the boring hole 504 in Borisov deposit of hydromineral products. The mass part of iodine in the final product constitutes 99.4-99.6%.

Keywords: Iodine extraction; brines; hydrogen index; redox potential; potentiometric titration; redox properties of system

Problem statement

The requirement for iodine in Ukraine is 30-40 t/year. The development is urgent of methods of extracting iodine from underground waters, from accompanying waters of oil deposits, from waste waters of industrial enterprises. This water is highly mineralized and may lead to the environment detriment. The most perspective direction is to be considered of the reception of halogens and their derivatives from underground brines.

## Analysis of latest researches and publications

As the iodine content in drilling waters of oil deposits and in other mineral aqueous systems is small (0.001-0.005%), which is less than its solubility in water, to obtain iodine from such solutions in the crystal form or sediments of little dissolved salts by the action of oxidizers or other reagents is impossible. Therefore, the extraction of iodine is preceded by obtainment of its saturated water systems - technological solutions (TS), from which later on the desired product is gotten. Technological schemes of iodine extraction include the following stages: preliminary purification from admixtures (naphthene acids, ferrum, hardness salts etc.); the extraction from natural waters by alkalization; obtaining concentrates of a ready-made product by oxidizing iodides (Rogov & Korchyk, 2007). There are known three main ways of getting iodine from drilling waters - air-desorption, coal-desorption and extraction by ion-exchange resins (Korchyk, Budenkova & Turchenyuk, 2004). The stage of oxidizing iodides to the elementary iodine is common for all three ways. The selective oxidizer for iodides is nitrate sodium:

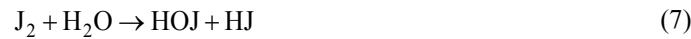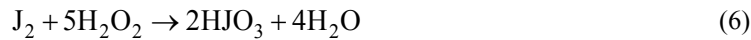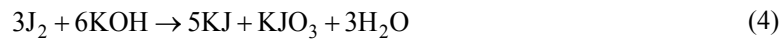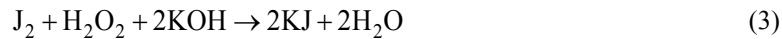$$2NaJ + 2NaNO_2 + 2H_2SO_4 \rightarrow 2Na_2SO_4 + J_2 + 2NO + 2H_2O \qquad (1)$$
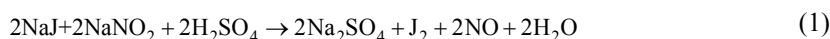
Iodine which was singled out is adsorbed by active carbon. The desorption by air is done in towers with injector. The content of free iodine in the air which exits the desorber fluctuates from 0.05 to 0.25 mg/dm^3. But for air-desorption method $NaNO_2$ is not suitable because nitrogen oxides which are formed during the reaction are blown off by air and pollute the finished product. In extracting iodine by the said methods expenditures of H_2O_2 amount to 130%, of sulfuric acid - 600% of stoichiometric calculations. Under such conditions overdosage of oxidizer causes the overoxidation of raw material (Korchyk, Budenkova & Romanenko, 2001).

Formulation of work aims

To get iodine from alkaline technological solutions we used as an oxidizer hydrogen peroxide:

$$H_2O_2 + 2KJ + H_2SO_4 \rightarrow J_2 + K_2SO_4 + 2H_2O \qquad (2)$$
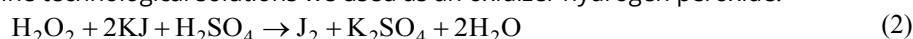
One of conditions for the successful reaction running (2) is the creation of the medium where side reactions were reduced to the minimum:

$$J_2 + H_2O_2 + 2KOH \rightarrow 2KJ + 2H_2O \qquad\qquad (3)$$

$$3J_2 + 6KOH \rightarrow 5KJ + KJO_3 + 3H_2O \qquad\qquad (4)$$

$$J_2 + 2KOH \rightarrow KOJ + KJ + H_2O \qquad\qquad (5)$$

$$J_2 + 5H_2O_2 \rightarrow 2HJO_3 + 4H_2O \qquad\qquad (6)$$

$$J_2 + H_2O \rightarrow HOJ + HJ \qquad\qquad (7)$$

$$J_2 + J^- \rightarrow J_3^- \qquad\qquad (8)$$

$$H_2O_2 + 2KJ \rightarrow J_2 + 2KOH \qquad\qquad (9)$$

The aim of researches was the determination of redox properties of alkaline TR for obtaining iodine from underground waters with the subsequent introduction of received results into technological schedule.

Exposition of main material

For investigation we used highly mineralized water of Pripyat depression.

Table 1. Composition of highly mineralized natural aqueous systems for removing valuable components.

No.	Indices	Measurement units	Value
1	Density	g/m^3	1.23-1.27
2	pH		2.4-6.85
3	Eh	mV	195-490
4	rH_2		11.5-30.6
5	Salt content	g/dm^3	239-412
6	Calcium	mg/dm^3	32000-75630
7	Magnesium	mg/dm^3	6906-12920
8	Ferrum	mg/dm^3	7100-8600
10	Sodium	mg/dm^3	33870-43510
11	Potassium	mg/dm^3	3000-9420
12	Sulphates	mg/dm^3	71-200
13	Iodides	mg/dm^3	5.92-59.2

The technological process chosen by us of extracting iodine from highly mineralized waters includes in itself:
a) oxidation of iodide-ine to free iodine in the presence of sulfuric acid H_2SO_4 by hydrogen peroxide H_2O_2 which acts as an oxidizer:
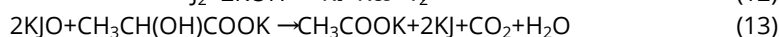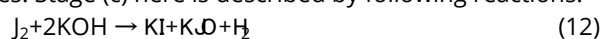
$$2I^- \rightarrow I_2; \qquad\qquad (10)$$

b) distillation of obtained iodine I_2;
c) dissolution of iodine in the mixture of Potassium hydroxide KOH and hydrogen peroxide H_2O_2 which under these conditions acts as a reductant:

$$I_2 \rightarrow 2I^-; \qquad\qquad (11)$$

d) repeated oxidation of iodide-ion to free iodine by hydrogen peroxide with the presence of sulfuric acid and its extraction in the form of finished product.
H_2O_2-is an unstable reagent: in the acidic medium there is possible oxidation decomposition $H_2O_2 > H_2O + O$, in alkaline one-restored $H_2O_2 > O_2 + 2H+$, therefore perspective is the use of lactic acid which is stable and depending on conditions reveals either restoring or oxidizing properties. Stage (c) here is described by following reactions:

$$J_2 + 2KOH \rightarrow KI + K_2JO + H_2 \qquad\qquad (12)$$
$$2KJO + CH_3CH(OH)COOK \rightarrow CH_3COOK + 2KJ + CO_2 + H_2O \qquad\qquad (13)$$

With molar interrelationship J_2: KOH: lactic acid 1:1.1:1,1 takes place the drop of pH from 10.4 to 6.2, change of Eh from -234 to +318 mV.

For stage d) chemical process may be presented in such a way:

$$CH_3CH(OH)COOH+2KJ+H^+ \rightarrow CH_3CH_2COOK+J_2+H_2O+K^+ \qquad (14)$$
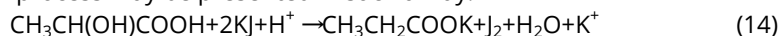
The change of parameters in system pH=6.2 → 1.5; Eh = +318 mV →+468 mV. As an intermediate product the solution is formed of Lughole KJ_3 which disappears under low values of pH.

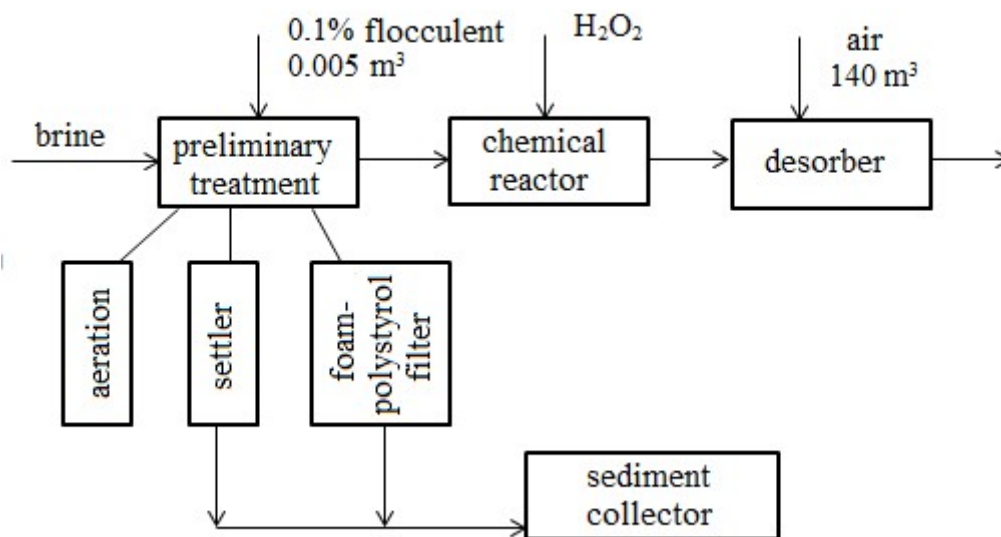Further on are presented technological models of obtaining iodine (Figures 1 and 2):

Figure 1. Main subsystem of technological process of obtaining iodine.
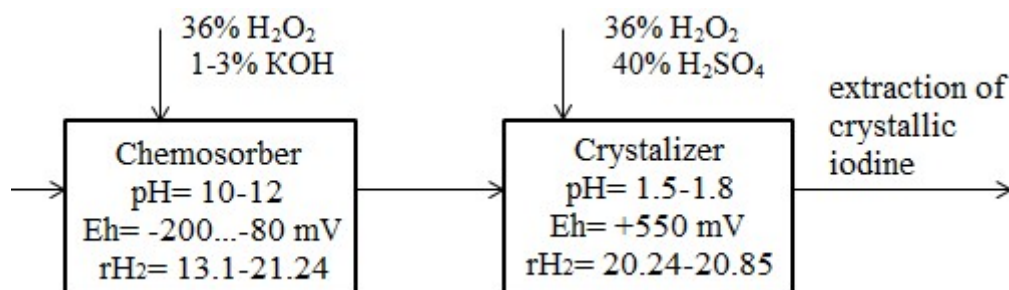

Figure 2. Additional subsystem of technological process of obtaining iodine.

The hydrolysis of iodine in alkaline medium which is used for obtaining concentrated solutions (leaching) is presented by reactions (3) and (4). However, salts which are created - iodides and others have lesser solubility and form sediment in the process of saturating the solution. To prevent this undesirable phenomenon and for increasing the efficiency of iodine absorption by alkaline solution we recommend to conduct the process in the presence of a restorer - hydrogen peroxide (2). For removing iodine in free state, the interaction is used of KJ with acidified solution H_2O_2 in reaction (5), and under pH=2 takes place further interaction of JO_3 with hydrogen peroxide:

$$2HJO_3 + 5H_2O_2 \rightarrow J_2 + 5O_2 + 6H_2O \qquad (15)$$
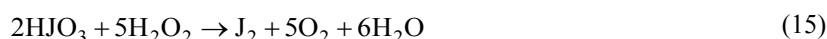
H_2O_2 depending on the medium (pH and rH_2) may be both oxidizer and restorer. This is, on the one hand, simplifies technological process, and, on the other hand, requires the strict control over these parameters at each stage of the process. Researches were carried out to find optimal conditions of the main process (reaction 1) with the aim of decreasing expenditures of acid and get the product with high output at the expense of excluding side reactions. On the basis of curves of potentiometric titration Eh=f(pH) TR with the restorer it is established that this oxidation is done with pH 0.5-2. The minimum quantity is calculated of H_2SO_4 for supporting the said pH during the reaction. Under the concentration J-60 mg/dm^3 is taking into account the decrease of pH from 12 to 2.0; 1.5; 1.0; 0.5 is 1.10-2; 0.85.10-1; 0.55.10-1; 0.35.10-1 mole/dm^3.

For reaction (1) by Nernst reaction:

$$\varphi = \varphi^0 + 0,059 \cdot \lg[H_2O_2] - 0,059 \, pH \qquad (16)$$

With pH: 0,5; 1,0; 1,5; correspondingly φ=1,72; 1,69; 1,67; 1,63.

Taking into account $\varphi 0$ of redox systems (1-8) the theoretically calculated excess of H2O2 is 32,55. Research results show that with adding acid in lesser quantities from calculated ones is not guaranteed the optimum value of pH during the whole process. Here during 20 minutes (period of oxidation and crystallization of iodine) pH increases to 6-7, the product output is only 70%. In adding acid to pH<2 the reaction takes place by way (1) with the output of 94%. With the aim of increasing the output of the final product main parameters are determined of redox systems: pH, Eh, rH2; molar interrelationship of reagents at each stage of technological process (table 1, 2, 3). It is established that the evaluation of oxidation-reduction balance of the system of highly mineralized waters in technologies of removing iodine by Eh value may be carried out only under same values of pH (Rogov & Korchyk, 2007; Korchyk & Budenkova, 2014).

On the basis of researching results of potentiometric titration and their interpretation was determined of substances depending on values pK of acidic-main forms. It is possible to state that iodine transformation takes place in sequence:

$$J_2 \rightarrow J^- \rightarrow J_2 \qquad (17)$$
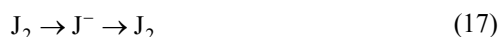
Table 2. Characteristics of state of redox balance in aqueous systems at separate stages of processing.

Place of sample selection	pH	Eh	rH$_2$
Boring hole	4.7	-100	13.0
Branch of clean water	4.5	100	19.5
Mixer	4.5	100	19.5
Desorber	4	400	28.9
Chemosorber	9.5	-200	19.2
Crystallizer	1.8	550	29.6

Table 3. Technological parameters of process of iodine extraction (restoration).

		Chemosorber 1			
C(I$^-$)	pH	Eh	rH$_2$	dC(I$^-$)	drH$_2$(I$^-$)
1.6	12	260	32.79	1.1	8.16
2.7	11.47	50	24.63	0.04	-2.23
2.74	11.4	120	26.86	-0.14	-6.76
2.6	11.4	320	33.62	0.9	7.58
3.5	11.5	90	26.04	0.51	-1.61
4.01	11.8	120	27.66	0.33	-0.15
4.34	11.2	160	27.81	0.58	-6.69
4.92	11.5	340	34.49	0.4	1.08
5.32	11.3	320	33.42	0.98	-0.68
6.3	11.3	340	34.09	0.4	0.88
6.7	11.2	320	33.22	0	0.68
6.7	11.2	300	32.54	0.5	0.00
7.2	11.2	300	32.54	-0.2	0.20
7	11.1	300	32.34	0.7	1.69
7.7	11.1	250	30.65	0	-2.37
7.7	11.1	320	33.02	1	0.00
8.7	11.1	320	33.02	0.1	0.20
8.8	11	320	32.82	0	32.82

Thermodynamic calculations were carried out for obtaining the optimum interrelationship of initial substances by formulas:

$$\Delta G = -RT\ln K_P \qquad (18)$$

$$\Delta G = \Delta H - T\Delta S \qquad (19)$$

With temperature 298K:

$$\Delta Gp0 = -255.6 \text{ kJ/mole·K} \qquad (20)$$

$$KP = 6 . 1044. \qquad (21)$$

Reaction takes place into the direction of forming reaction products.

Under the bonds of reagents

$J_2:H_2O_2:KJ=1:0.13:0.53$ g/dm^3:

$$K_p = \frac{[KJ]^2}{[H_2O_2].[KOH]^2} = 0.1857 \qquad (22)$$

$$\Delta G = RT·\ln·Kp = 4170.5 \text{ kJ/mole·K - reaction is impossible.} \qquad (23)$$

with KP=0.66, then mass interrelationship between KOH and H_2O_2 must be = 5.6:1

Having carried out the correlation analysis of dependence of iodine concentration on parameters of pH, Eh, rH2 we obtained coefficients of variation which testify to the absence of distinct linear dependence of product output on the sum of these parameters. However, a substantial growth is clearly seen of product output in certain boundaries of values of pH and rH2. The regulation of parameters of the system by values of Eh and pH is complicated. This is connected with the fact that the value of Eh itself depends on the value of pH and calls for carrying out the process in a manual regime (alternate addition of reagents) (Ananieva, Trokhymenko & Hvorov, 2007).

Table 4. Technological parameters of process of extracting iodine (oxidation).

Chemosorber 2

C(I⁻)	pH	Eh	rH$_2$	dC(I⁻)	drH$_2$(I⁻)
0	13.4	-100	23419	0.2	-0.476
0.2	13.5	-120	22943	0.12	0.690
0.32	13	-70	23634	1.38	1057
1.7	11.5	50	24690	-0.3	1014
1.4	11.5	80	25705	-0.4	9266
1	11.4	360	34970	0.5	-7837
1.5	11.2	140	27133	0.6	-0.276
2.1	11.4	120	26857	0.1	0.276
2.2	11.2	140	27133	0.44	-1876
2.64	10.6	120	25257	0.34	7661
2.98	11.05	320	32918	1	0.914
3.98	11	350	33832	0.32	-0.338
4.3	11	340	33494	0	-8790
4.3	11	80	24705	0.3	7914
4.6	10.9	320	32618	-1.1	-3618
3.7	11.7	200	30161	0	-3781
3.7	11.5	100	26381	0.2	5409
3.9	11.5	260	31790	0	2766

We suggested for regulating the technological process to use independent from one another indices of the state of system pH and rH2, here the regulation of pH is done by adding KOH, and rH2 - by dosing the solution H2O2 (lactic acid), which permits to introduce the system of automatic regulation of the process with the help of a special computer program. The range of optimum values of pH and rH2 for each stage of the process is taken into account in compiling technological schedule.
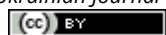
Conclusions

Discussed are redox properties of aqueous systems, separate stages of obtaining iodine from highly mineralized underground waters. Parameters are determined of pH, Eh, rH_2 for each stage of the process. Theoretical calculations are done to calculate the quantity of H_2SO_4 necessary for supporting such acidity of medium which diminishes the possibility of running side reactions. At the expense of proposed technologies production is returning about 0.35 \$/m^3 from wastes taking into account all expenditures for reagents and electric power.

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