Obtaining Bromine from the Brines of the Siberian Platform by Means of Non-Diaphragm Electrolysis

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Abstract

A technology of electrochemical oxidation of bromide and chloride ions present in the brines of calcium chloride type involving an electrolyzer without a diaphragm is proposed. This technology allows one to obtain active chlorine from the initial raw material and to exclude transportation of liquid chlorine to consumption sites. It is proposed to use an excess of chlorine formed during electrolysis to oxidize bromide ions in the fresh portions of brine.

INTRODUCTION

Natural bromine-containing brines are a valuable raw material for obtaining elemental bromine. Bromide ion content in them can reach $1.6–2.0$ kg/m^3 and more, while the minimal concentration in hydromineral media used for industrial recovery of bromine is ≥ 0.17 kg/m^3, according to the data of [1]; most frequently used raw material contains bromide at the level of $0.7–0.8$ kg/m^3.

Highly mineralized bromine-containing brines of calcium and magnesium chloride type (with a sum of magnesium and calcium chloride up to 450 kg/m^3) are very widespread over the territory of East Siberia. These brines contain $9–11$ kg/m^3 of bromide ions, which is tens times higher than the industrial concentrations. Nevertheless, the brines of the Siberian platform have not been used in industry up to present because the brine deposits are situated far from the industrial complexes, the depth of brine occurrence is large and climatic conditions are inclement. However, an actual possibility to use the brines of this type as a valuable raw material for obtaining bromine

has appeared in connection with the development of large oil and gas deposits in East Siberia; these deposits are usually accompanied by salt water flows.

The most profitable method of extracting bromine from the brines of this type is vapour desorption of the target component after the oxidation of bromide ions with chlorine [1]. The indicated method is well investigated, reliable and simple for implementation. A classical version of the technology is widely used by the known bromine manufacturers: Great Lakes, Ethyl Corp. (USA), Dead Sea Bromine (Israel). However, the necessity to transport and store large amounts of liquid chlorine makes these works ecologically dangerous.

At the same time, there are indications in literature that gaseous electrolysis chlorine can be used for this purpose without its liquefaction. Because of this, a very urgent problem is electrochemical production of chlorine which is necessary for bromide ion oxidation; chlorine is to be obtained directly from the same brine. High efficiency of bromine obtaining from brine in electrolyzer is also provided by the direct electrochemical oxidation of bro-

TABLE 1

Overall table of the parameters of electrochemical oxidation of chloride and bromide ions in the brine (V_{br} = 1 dm³, Q = 65 ml/min, concentration of Br⁻ ion 9.7 g/dm³, chamber thickness 9 mm)

Experiment No.	Conditions			Residual Br⁻ concentration, g/dm³	Oxidation degree of Br⁻, %	Amount of Cl₂, mol			Excess of chlorine E_{exc} = E_{ev}/E_{theor}
	j, A/dm³	S, dm²	U, V			evolved in the electrolyzer	consumed for the oxidation of Br⁻	remained in the gas and liquid phases	
1	10.0	0.8	5.7	3.9	59.4	0.075	0.072	0.003	0.62
2	12.5	1.6	7.6	1.1	88.7	0.186	0.0107	0.079	1.53
3	12.5	2.4	7.8	0.2	98.0	0.280	0.118	0.162	2.31
4	12.5	3.2	8.4	0.03	99.7	0.373	0.120	0.253	3.08
5	12.5	4.0	8.8	0.03	99.7	0.470	0.120	0.350	3.88

mide ions to elemental bromine. The proposed process will allow avoiding the difficulties connected with transportation and consumption of liquid chloride; in addition, it is attractive as a reagent-free and ecologically safe procedure.

The authors of [3] propose to obtain bromine from natural water, for example from lake water or stratal petroleum water, by electrochemical oxidation of bromide and chloride ions in water using an electrolyzer without a diaphragm (with the distance between electrodes 5−15 mm). Free chlorine very rapidly appears in the acidified brine, which is due to close potential of chlorine and bromine evolution under the prevailing chloride ion content (Cl⁻/Br⁻ = 280−315). Since an evident excess of gaseous chlorine is formed, the authors of [3] propose to mix the brine, after passing through the electrolyzer, with fresh bromine-containing brine in order to oxidize Br⁻ ion with excess chlorine. In the case when calcium ions are present in the initial brine, it is recommended to acidify it with sulphuric acid to exclude precipitation in electrolyzer followed by the isolation of calcium sulphate precipitate. The necessity of this operation causes large consumption of sulphuric acid and brings complications of the apparatus scheme of the process.

The authors of [4] propose to perform electrochemical oxidation of bromide ion in acid bromine-containing solutions in a cell of special design in which the anode and cathode chambers are separated with a cation-exchange membrane. In order to recover bromine, acid solutions with pH from 2 to 6 are used, which contain HBr from 5 to 35 %, or mixtures of HBr and MeBr (where Me is an alkali metal), as well as solutions containing organic bromated compounds. Bromine is released at the anode; it is removed under increased pressure or under vacuum. The process is carried out with the current density not higher than 40 A/dm² and the temperature of 40−80 °C. However, the proposed procedure is unfeasible for the electrolysis of highly mineralized brines enriched with calcium and magnesium, because of the formation of poorly soluble $Mg(OH)_2$ and $Ca(OH)_2$ precipitates on the cathode, which causes rapid obliteration of the cathode and membranes and to cessation of electrolysis.

For the brines of this type with high Br^- ion content, it is proposed to use a two-chamber electrolyzer with the chambers separated from each other with anion exchange membrane [5]. For the two-chamber electrolyzer, the flow of brine through the anode chamber passes with the rate of 65 ml/min (linear speed: 0.10 m/min). A 5—10 % solution of hydrochloric acid or a mixture of sodium chloride (16 %) with hydrochloric acid (HCl not less than 0.5 %) was circulated in the cathode chamber. The flow circulation arrangement of electrolysis in a two-chamber electrolyzer allows maintaining pH of anolyte within 1—2 thus excluding precipitation on the cathode.

The results of investigations of the electrochemical chlorine obtaining procedure involving the oxidation of bromide ion in brine flow passing through the anode chamber of two-chamber electrolyzer are shown in Table 1. One can see that high oxidation degree of bromide ion can be achieved only in case of substantial excess of chlorine. In experiments No. 3—5, the excess chlorine was absorbed by the initial brine, which allowed one to avoid its losses into the environment and to use it for the oxidation of bromide ions in additional portions of fresh brine. The technology was tested with the natural brine of the Znamenka deposit (Irkutsk Region).

On the basis of the performed investigations, the method and set-up for obtaining bromine from highly mineralized brines were proposed [5]. Such drawbacks of this method as high consumption of the acid, low stability of membranes manufactured by home industry,

and complicacy of the electrolyzer design can be mentioned.

The goal of the present work is to investigate and optimize the electrochemical oxidation of chloride and bromide ions present in highly mineralized brines of the calcium and magnesium chloride type in an electrolyzer without diaphragm.

EXPERIMENTAL

The studies of electrochemical oxidation of halides in highly mineralized brines were carried out using the model solution of the following composition, g/dm^3: $CaCl_2$ 280, $MgCl_2$ 160, KBr 10.7—11.9 (Br^- 7.2—8.0), with total salt content about 450 g/dm^3, pH ~ 3.5. Investigations were carried out with the laboratory set-up shown schematically in Fig. 1.

The main part of the set-up is electrolyzer 3 with graphite electrodes; their working area was identical and equal to 0.2 dm^2. The distance between the electrodes δ was varied from 2 to 16 mm by applying gaskets of different thickness between the electrodes. Brine circulation rate through the electrolyzer was varied from 10 to 320 ml/min with the help of peristaltic pump 4. Electrolyzer was fed from a direct current source 1 equipped with knobs and gages for voltage and current.

The principle of operation of this set-up is as follows. A definite amount of brine was loaded into vessel 6, from which the brine was circulated through the electrolyzer at a given
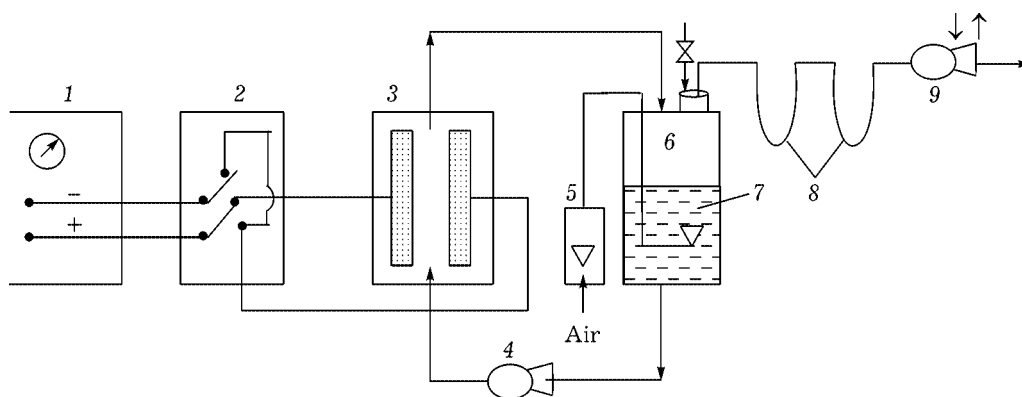

Fig. 1. Flowchart of the laboratory set-up for obtaining bromine from highly mineralized brines by the electrolysis without a diaphragm: 1 — direct current feeder, 2 — control device, 3 — electrolyzer without a diaphragm, 4 — peristaltic pump, 5 — flow meter, 6 — a vessel with the brine, 7 — bubbler, 8 — absorbing system, 9 — ventilator.

rate with the help of pump *4*. The process was monitored with the help of control devices *2* and by observing changes in the composition of brine. In order to do this, samples were taken periodically from vessel *6*; after blowing free halogens off, we determined the concentrations of bromide ions and oxyhalides in samples. In addition, gas phase composition was determined. The concentration of free halogens above the brine was measured under the equilibrium between the gas and liquid phase (brine) and under bubbling air through attachment *7*. To exclude precipitation on electrodes, current reversal was applied.

Since the initial concentration of Cl^- ions in the indicated brines is about 40 times higher than that of Br^- ions, the oxidation of the latter during electrolysis occurs both due to direct electrochemical oxidation on the anode and due to its chemical interaction with active chlorine which is evolved simultaneously. However, it is very difficult to estimate the contribution of the electrochemical oxidation of Br^- ion into the overall process. Because of this, it was conventionally assumed in calculations that the oxidation of Br^- ions occurs only as a result of its chemical interaction with active chlorine evolved at the anode.

The amount of chlorine evolved into the system was calculated using Faraday's law.

The excess of chlorine E_{exc} was determined as the ratio of the amount of chlorine evolved into the system to the amount of chlorine which is theoretically necessary to oxidize bromide ions present in the volume of circulating brine, E_{theor}. The oxidation degree of bromide ion was determined as the ratio of the difference between the concentrations of Br^- ion in the initial and final brines to its initial content: $\alpha\,(\%) = (C_{init} - C_{fin})/C_{init}$.

Analytical determination of bromide ion was carried out using Kagan's procedure described in [7]. The concentrations of oxyhalides (ClO^- and BrO^-, as well as ClO_3^- and) which are formed in the brine during electrolysis were determined by iodometric titration according to procedures described in [7, 8]. Elemental bromine in the brine after electrolysis was determined by means of extraction [7]. The determination of bromine in the gas phase was carried out according to the procedure described in [9]. The cations of divalent metals (Ca^{2+}, Mg^{2+}) were determined by chelatometry [6], the cations of alkaline metals (Na, K) by means of flame photometry [10].

RESULTS AND DISCUSSION

A flowchart of the electrochemical oxidation of chloride and bromide ions present in brine resulting in the formation of elemental chlorine and bromine is shown in Scheme 1.

The interaction between bromide ions and chlorine evolved at the anode proceeds within the volume of electrolyzer; the interaction is described by the reaction

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^- \qquad (1)$$
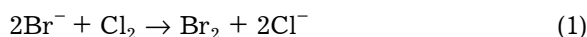
Generally, the process is much more complicated, resulting in the formation of various chlorine- and bromine-containing compounds. Chlorinated brine formed in the electrolyzer cell is a mixture of Br^-, Br_2, BrCl, Cl_2, Br_2Cl,
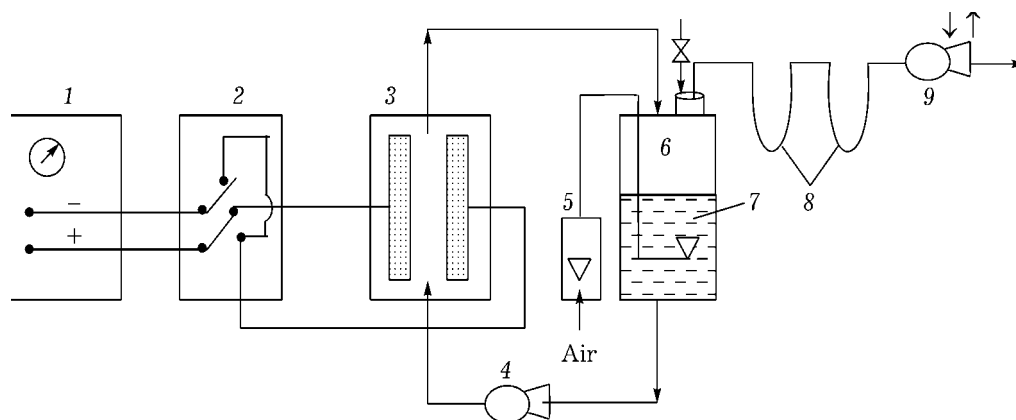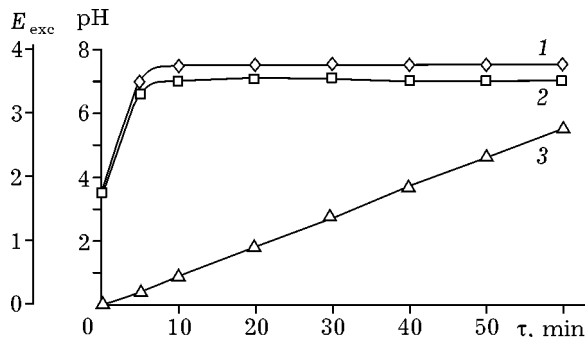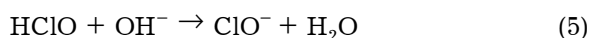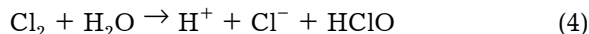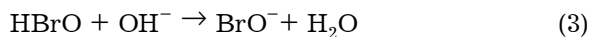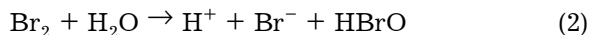

Scheme 1.

Fig. 2. Dependence of pH of the brine (*1, 2*) and chlorine excess in the system (*3*) on chlorination time. Q_{br}, ml/min: 20 (*1*), 80 (*2*).

$BrCl_2$, , [1]. All the intermediate reactions proceed almost instantly, and the equilibrium is established very rapidly. At the initial stage of the process, while the amount of the formed chlorine is small and a substantial amount of Br^- ions is present in the solution, mainly reaction (1) occurs. Further on, the brine circulating through the electrolyzer after the oxidation of Br^- and Cl^- ions contains also oxygenated compounds of bromine and chlorine, in addition to the above-indicated chlorine- and bromine-containing compounds.
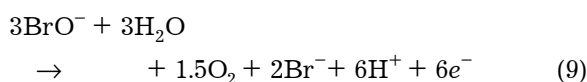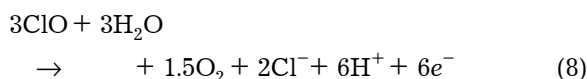
It is shown in Fig. 2 that the amount of chlorine which is necessary for stoichiometric oxidation of bromide ion (reaction (1)) is formed under the chosen conditions as early as within 20 min after the start of the electrolysis process. At the same time, decomposition of water with the formation of OH^- ions occurs as a result of the cathode process, and pH of the brine increases sharply from 3.5 to 7.0–7.5 (see Fig. 2, curves *1, 2*). This promotes the formation of oxygenated compounds of chlorine and bromine (hypochlorites, hypobromites, chlorates and bromates). One can see in Fig. 3 that their formation proceeds most intensively when an excess of elemental halogens (Cl_2 and Br_2) appears in the system while the concentration of Br^- ions decreases. It is known [1] that the hydrolysis of free halogens occurs in aqueous solutions involving the reactions:

$$Br_2 + H_2O \rightarrow H^+ + Br^- + HBrO \qquad (2)$$

$$HBrO + OH^- \rightarrow BrO^- + H_2O \qquad (3)$$

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HClO \qquad (4)$$

$$HClO + OH^- \rightarrow ClO^- + H_2O \qquad (5)$$

The accumulation of ClO^- and BrO^- ions causes the formation of the corresponding chlorate and bromate ions as a result of reactions

$$HBrO + 2BrO^- \rightarrow \qquad + 2Br^- + H^+ \qquad (6)$$

$$HClO + 2ClO^- \rightarrow \qquad + 2Cl^- + H^+ \qquad (7)$$

The formation of chlorates and bromates occurs also as a result of electrode processes accompanied by discharge of ClO^- (BrO^-) to ( ) and the evolution of oxygen:

$$3ClO + 3H_2O$$
$$\rightarrow \qquad + 1.5O_2 + 2Cl^- + 6H^+ + 6e^- \qquad (8)$$

$$3BrO^- + 3H_2O$$
$$\rightarrow \qquad + 1.5O_2 + 2Br^- + 6H^+ + 6e^- \qquad (9)$$

The degree of oxidation of bromide ion to elemental bromine depends both on the excess of chlorine in the system and on the brine circulation rate Q_{br} reaching the maximum at $E_{exc} = 2.0–2.75$ and $Q_{br} = 80–320$ ml/min (Fig. 4, curves *3* and *4*).

When bromine is evaporated with air flow during electrolysis, the equilibrium shifts towards the formation of Br_2; the degree of bromide oxidation increases (see Fig. 4, curves *2* and *3*). An increase in air flow rate for bromine evaporation from 1.5 to 7 l/h, with other conditions kept constant, helps one to decrease the consumption of chlorine for the oxidation of bromide ion and makes ~1.5 equivalents of
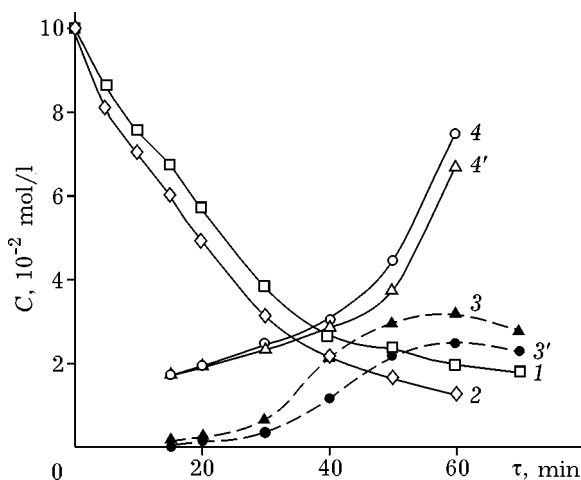

Fig. 3. Changes in the concentrations of Br^- (*1, 2*), ClO^- and BrO^- (*3, 3'*), and on the duration of chlorination ($j = 10$ A/dm², $V_{br} = 300$ dm³, $C_{Br} = 8.0$ g/dm³): *1, 2* – $Q_{br} = 40$ and 80 ml/min, respectively, $\delta = 12$ mm; *3, 3', 4, 4'* – $Q_{br} = 40$ ml/min, $\delta = 12$ (*3, 3'*) and 6 (*4, 4'*).
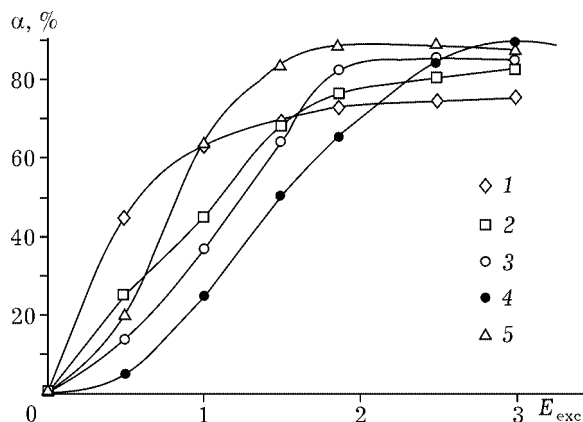
Fig. 4. Dependence of Br^- oxidation degree on the excess of chlorine, brine feed rate Q_{br} and the rate of air flow for bromine evaporation Q_{air} (j = 10 A/dm², δ = 12 mm): *1* – Q_{br} = 20 ml/min, Q_{air} = 1.5 l/h; *2* – Q_{br} = 20 ml/min, without bromine evaporation; *3* – Q_{br} = 80 ml/min, Q_{air} = 1.5 l/h; *4, 5* – Q_{br} = 320 ml/min, Q_{air} = 1.5 and 7.0 l/h, respectively.

chlorine per an equivalent of bromine for the air flow rate of 7.0 l/h (compare curves *4* and *5* in Fig. 4). Experimental values obtained for bromine evaporation from the system, that is, under the conditions close to the industrial ones, are in rather good agreement with the literature data on chlorine consumption for the oxidation of Br^- ion.

It should be noted that even without acidification of the solution containing substantial amounts of precipitate-forming cations (Ca^{2+}, Mg^{2+}), no precipitation was observed on the electrode surface under the accepted current reversal conditions. This is likely to be due to the formation of calcium and magnesium oxyhalides; their solubility is higher than that of the corresponding hydroxides [11, 12]. In agreement with the isotherm of the system $Ca(ClO)_2$ – $Ca(OH)_2$ – $CaCl_2$ – H_2O at 25 and 50 °C, the solubility of calcium hypochlorite reaches 250 g/l, while the solubility of $Ca(OH)_2$ does not exceed 0.5 g/l [12]. In our experiments, a sum of hypochlorite and hypobromite ions did not exceed 0.03 mol/dm³; the accumulation of chlorate and bromate ions during the experiment occurred till 0.08 mol/dm³ and above (calculated for elemental chlorine).

Another set of experiments on electrochemical oxidation of bromide ions was carried out with the acidification of the brine that passed through the electrolyzer. Acidification causes

decomposition of oxygenated compounds of chlorine and bromine with the evolution of elemental halogens; the concentration of the former is reduced to a minimum.

It follows from Fig. 5 that acidification of the brine allows increasing the degree of Br^- ion oxidation from 80–90 to 93–99 %. The consumption of an acid for acidification depends on the excess of Cl_2 in the system and on the composition of brine after electrolysis. Under the chosen conditions, the consumption of the acid was 0.04–0.12 mol/dm³, or 1.46–4.26 g of concentrated HCl per 1 dm³ of the brine.

It is reasonable to utilize the excess chlorine in the system by absorbing it with the fresh portions of the brine, as proposed in [5]. Special experiments involving an experimental absorption set-up were made to determine the parameters of mass transfer process during the absorption of gaseous chlorine blown out of the system with air. The set-up included an absorber as a glass column attachment of 1500 mm high and 31.5 mm in diameter, operating in irrigation mode under the counterflow of the contacting phases, and allowed providing the concentration of free halogens (Cl_2 and Br_2) at the outlet of the absorber within the limit of the sanitary standards (not higher than 20 mg/m³ for chlorine and 40 mg/m³ for bromine). It was established that with an increase in the absorber irrigation rate from 17 to
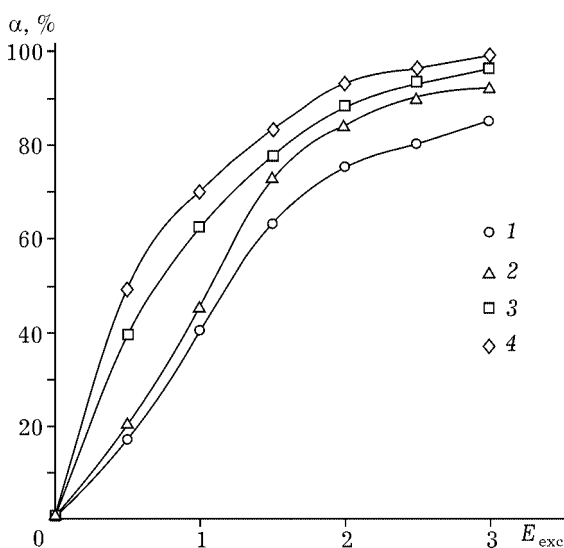

Fig. 5. Dependence of Br^- oxidation rate on chlorine excess: *1* – without acidification; *2–5* – HCl concentration, mol/dm³: 0.04, 0.08, 0.12, 0.16, respectively.

40 ml/min the height of mass transfer region for chlorine absorption decreases substantially (by a factor of ~1.7). The investigations allow us to carry out the calculations of the apparatus arrangement of chlorine absorption by brine on industrial scale.

CONCLUSION

Thus, the performed investigations allowed us to determine optimal conditions for the most complete oxidation of Br^- ion in the electrolyzer. An excess of chlorine can be directed into the absorber and get absorbed by the fresh brine. It is also established that current reversal allows excluding precipitation on the cathode during the electrolysis of highly mineralized brines containing substantial amounts of calcium and magnesium. Electrolysis can be carried out without acidification of the brine; the acid may be added directly at the stage of desorption of elemental bromine, which can reasonably be carried out by water vapour according to the traditional technology [1].

Among the two methods of the oxidation of bromide ions in the brine: in a two-chamber electrolyzer proposed in [5], and in the electrolyzer without a diaphragm as described in the present work, − the latter is preferable due to the simplicity of design of the electrolyzer, decrease in its price, as well as a decrease in the consumption of the acid.

The obtained data and the methods developed on this basis allow us to recommend electrochemical oxidation of bromide ions in the brines of the Siberian platform as a promising process for obtaining bromine from them. Keeping in mind that almost all the plants manufacturing bromine turned out to be out of Russia after the dissolution of the USSR (Ukraine, Azerbaijan, Turkmenia), the very rich hydromineral resources of Siberia can serve as the basis for the organization of the production of bromine, which is necessary for the needs of various branches of the home industry (organic synthesis, production of fire retardants, medicines, *etc*.), and will allow one to exclude any import of the valuable product from the FSU countries.

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