Combined Extraction-Electrochemical Process of Bromine Recovery from Natural Brines

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Abstract

New technology of bromine recovery from bromine-containing brines is proposed. The technology is based on the anode decomposition of metal chloride, oxidation of bromine with escaping chlorine, extraction transfer of bromine from the anode electrolyte to the recycle catholyte and reduction of bromine on a porous cathode. Commercial products of the proposed method are individual salts of bromine. It was demonstrated that the develop process is safe and involves low energy and reagent consumption.

Key words: chloride brines, bromine salts, extraction, electrolysis

INTRODUCTION

Enormous deposits of underground chloride0calcium brines with bromine content 4–5 g/L and higher had been discovered long ago in the regions of East Siberia. The major problem connected with the development of the deposits of natural brines in Siberia is their remoteness from industrial regions and therefore the absence of proper infrastructure.

Hard-to-reach deposits bring about the problems connected not so much with their development as with provisions of the safe operation of bromine-producing works. At present, all the manufacturers of bromine in the FSU countries use a cheap but very toxic reagent – chlorine; its delivery to the remote regions of Siberia is very problematical, and so is further storage of this reagent. To solve this problem, various versions of technologies providing chlorine generation through electrolysis directly at the site were proposed, for example, with the direct supply of a part of the chloride brine into the anode chamber of electrolytic tank [1]. The problems dealing with the safety of transportation of elemental bromine, which is not less toxic, may be solved using the known technologies that involve ferric bromide as the final product [2]. At the same time, there is another solution of the problem dealing with the development of Siberian deposits of bromine-containing brines: to obtain not bromine as the commercial product but its individual salts, demand for which is very high.

In modern practice, bromine salts (sodium, potassium bromides *etc.*) are obtained through intermediate isolation of elemental bromine. The general process scheme includes the following stages: oxidation of bromide ion by chlorine to form Br_2, isolation of bromine (usually by air or steam blowing) from aqueous solution, its reduction by ammonia, formaldehyde etc. to the initial bromide in the presence of an alkaline reagent. Conventionally, the technological stages of oxidation and reduction are arranged as separate works; however, the use of the electrochemical technology of obtaining chlorine makes it possible to combine them. For this purpose, along with the anode oxidation of chlorine, it is necessary to carry out the cathode reduction of bromine, replacing its reduction by reagents. The goal of the present work was to study the possibility of realizing the combined technology of obtaining bromine salts.

EXPERIMENTAL

Mineral acids, alkalis and their salts of kh. ch. and ch. d. a reagent grades, organic solvents – toluene, octane and octyl bromide of kh. ch. reagent grade, and technical-grade tributyl phosphate (TBP) purified by vacuum distillation were used in the work.

To obtain elemental chlorine and reduce bromine, we used an electrochemical cell of the filter-press type with cathode and anode spaces separated with a heterogeneous cation exchange membrane MK-40 (Fig. 1). The area of the electrodes and the membrane was 10 cm^2. A titanium plate with the oxide ruthenium-titanium coating (ORTC), which is conventional for the production of elementary chlorine, was used as the anode. The distance between the anode and the membrane was 2 mm. Porous graphitized carbon felt 8 mm thick was used as the cathode. The solutions were supplied into the cell with the liquid dispensing pumps.

Halogen extraction under static conditions was carried out in separating funnels at a temperature of 20–22 °C and 3–5 min duration of mixing the aqueous and organic phases, which was sufficient for the equilibrium to be settled.
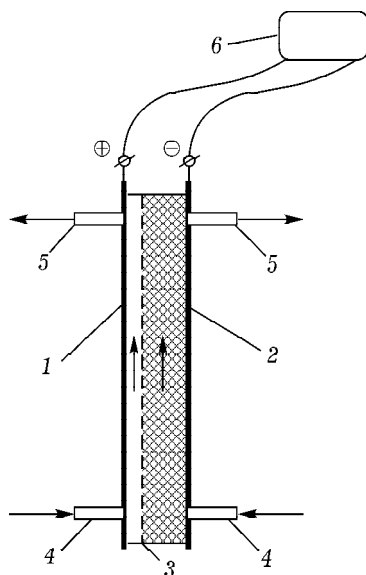

Fig. 1. Scheme of the electrochemical cell for the anode oxidation of chlorine and cathode reduction of bromine: *1* – OPRC anode, *2* – porous graphitized carbon cathode, *3* – cation exchange membrane MK-40, *4* – tubes for supplying the solutions into the anode and cathode spaces, *5* – tube for solution output from the anode and cathode spaces, *6* – DC power supply.

Isolation of bromine from solutions and its re-extraction in the continuous mode were performed in the extracting devices of the mixing-settling type; the volume of the mixing chamber was 80 mL, phase separation chamber – 300 mL. The maximal flow over the sum of phases was 20–25 mL/min, which provided the duration of mixing and settling not less than 3 and 12 min, respectively.

Anode and cathode processes in the electrochemical cell were studied using the model solution; the general technological process of obtaining bromine salts in the continuous mode was studied using the brines of calcium chloride type of the Sukhaya Tunguska deposit (Krasnoyarsk Territory) having the composition, g/L: Br$^-$ 4.5, Cl$^-$ 200, Na$^+$ 46, K$^+$ 23, Mg^{2+} 9, Ca^{2+} 60, Sr^{2+} 2.4.

The concentration of halogens was estimated through titration of the corresponding aliquots by thiosulphate in the presence of starch after addition of KI. The concentration of bromide ions in solutions was determined using the procedure described in [3] by carrying out their oxidation with manganese (III) cations and air blowing of the elemental bromine from the reaction mixture. The concentrations of cations in solutions were determined using he atomic absorption technique.

RESULTS AND DISCUSSION

A scheme of the electrochemical production of bromine salts with the extractive interphase transfer of bromine is shown in Fig. 2. The process includes the following major stages: anodic generation of chlorine during the decomposition of the chloride of a corresponding metal (lithium, sodium, potassium, calcium *etc.*); oxidation of bromide ions of the natural brine with chlorine; extractive transfer of bromine from the brine into the catholyte, with the stages of bromine extraction from natural water and re-extraction by catholyte; cathode reduction of bromine to form bromide ions; electrochemical transfer of cations from the anode space to the cathode space through the cation exchange membrane.

In this case, to obtain bromine-containing concentrate, bromine-containing natural brine
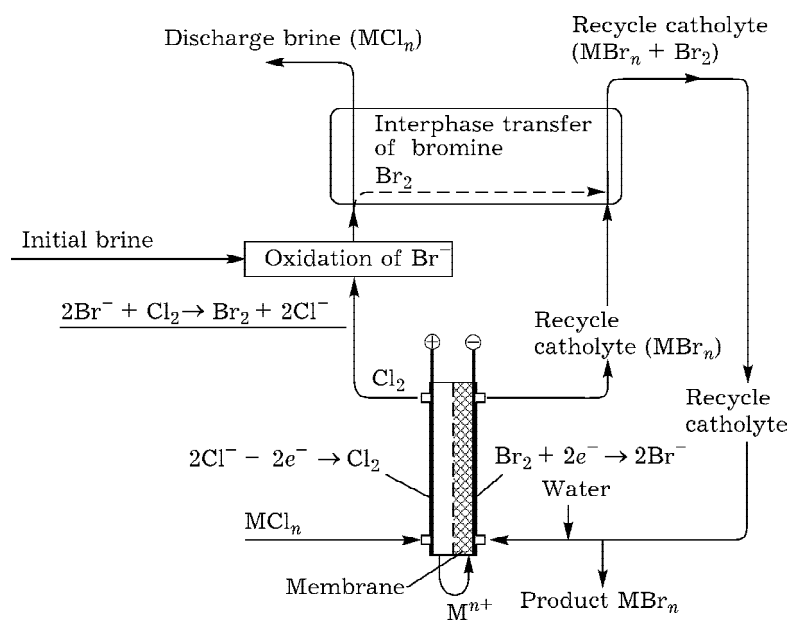
Fig. 2. Major stages of the extraction-electrochemical method of bromine recovery from natural water, leading to obtaining its salts.

instead of metal chloride is fed into the anode space of the electrolytic tank. The cation composition of the bromine product is determined by the cation composition of the initial brine and the electric mobility of the cations in the membrane.

We studied the major stages of this process.

Anode oxidation of chloride (bromide) ions, oxidation of bromide ion by chlorine

As a rule, anodes with oxide ruthenium-titanium coatings (ORTC) are used in the production of alkali through the electrolysis of sodium chloride solutions. The anodes of this type have a number of advantages in comparison with graphite electrodes that had been previously used in practice. They are characterized by higher selectivity and electrocatalytic properties, and also by substantial stability against corrosion, which allows one to increase their operational lifetime from 1 to 5−6 years. In addition, they do not change their shape during long-term usage; even in the case of the destruction of active coating, the titanium substrate may be regenerated repeatedly.

We established that the ORTC anodes work stably under decomposition of the solutions of lithium, sodium, potassium and calcium chlorides at the concentration (calculated for chloride ions) of 4−6 mol-eq/L. The yield of chlo-

rine was 91−93 % in all the cases. Unlike for the above-listed salts, decomposition of ammonium chloride solutions gave the yield of chlorine as a function of current decreased to 35 % (the concentration of NH_4Cl was 4 mol/L). The low chlorine yield in this case is likely to be due to the anode oxidation of ammonium cation, which does not allow one to use the considered technique for obtaining ammonium bromide.

It was established that the anodes of ORTC type anodes are quite suitable not only for generating chlorine during the decomposition of the solutions of alkaline metal chlorides but also for oxidation of bromide ion directly in the natural brine. For instance, during the decomposition of natural chloride calcium-sodium brines of the Sukhaya Tunguska deposit, bromide is oxidized quantitatively to form the elemental state, with the yield as a function of current 92−95 % at the solution pH 3−4. The yield as a function of current and the potential of bromine evolution remained unchanged after anode performance for more than 350 h.

Chlorine blowing through bromine-containing brine causes the formation of bromine according to the reversible reaction:

$$2Br^- + Cl_2 \rightleftarrows Br_2 + 2Cl^- \qquad (1)$$
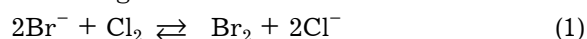
It is necessary to stress that the equilibrium of this reaction is substantially shifted to the right.

In the case of the simultaneous presence of bromine and chlorine, the formation of rather stable interhalogen compound BrCl according to reaction

$$Br_2 + Cl_2 \rightleftarrows 2BrCl \qquad (2)$$

This causes a decrease in the yield of bromine in the oxidation reaction, the degree of its isolation or to the contamination of the final product with chlorine in the attempt to increase the extent of bromine isolation. In practice, during bromine isolation by air or steam blowing, the vapour gas mixture is purified from chlorine by means of the counter-flow washing with the initial bromine-containing brine. A similar operation may be used also in the extraction isolation of bromine. Nevertheless, the choice of an extracting agent plays an important part, because the dominating isolation of any reagent under the conditions of the mobile equilibrium in the system has a substantial effect on the technological characteristics of bromine recovery process in general.

Extraction recovery of bromine from chloride solutions, re-extraction with the catholyte

For the extraction transfer of bromine from the brine phase into the catholyte phase, another important characteristic of the process in addition to extraction selectivity may be the coefficient of bromine distribution at the stages of isolation and re-extraction: these coefficients are to be rather large at the stage of bromine extraction from the brine and rather small during re-extraction.

Tributyl phosphate (TBP), saturated hydrocarbons and bromine-substituted hydrocarbons were studied as bromine extracting agents. Some results of these investigations were reported in our previous works [4−6].

It was established that the largest coefficients of bromine distribution are achieved during extraction with TBP: they exceed 300 for an 80 % solution of TBP (for comparison: the coefficient of bromine distribution for extraction with heptane is equal to 18). This is connected with the formation of stable bromine complexes with TBP of the L · Br$_2$ type. It was shown that bromine chloride forms even more stable complexes with TBP, which worsens the selectivi-

ty of extraction. In addition, TBP in the presence of elemental bromine co-extracts substantial amounts of calcium chloride in the form of complex salts of the Ca(ClBr$_2$)$_2$ type. Quite contrary, during extraction with nonpolar saturated hydrocarbons, bromine chloride is extracted much worse than elemental bromine due to binding with water and the formation of hydrate complex; co-extraction of metal chlorides is almost completely absent.

Saturated hydrocarbons extract bromine and chlorine according to the mechanism of physical distribution:

$$Br_2(aq.) \rightleftarrows Br_2(org.) \qquad (3)$$
$$Cl_2(aq.) \rightleftarrows Cl_2(org.) \qquad (4)$$

Extraction isotherms for these halogens with heptane in weakly acidic medium are linear; the constants of extraction processes are equal to 18.1±1.1 and 13.0±3.9 for equations (3) and (4), respectively.

However, it is necessary to state that these extracting agents exhibit poor stability against the action of halogens. One can see in the data presented in Fig. 3 that the concentration of free bromine in octane rapidly decreases under light due to the free-radical bromination of the extracting agent. At the same time, the reaction proceeds rather slowly in the case when irradiation of the extracting agent is absent (see Fig. 3, curve *1*).

The effect of the products of hydrocarbon bromination on the recovery of bromine and chlorine and on the stability of extracts was
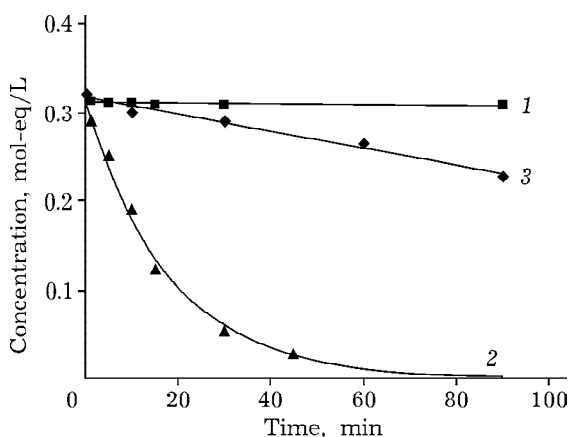
Fig. 3. Changes of the concentration of elemental bromine in octane without irradiation of the solution (*1*), in the light (*2*), in octyl bromide in the light (*3*).
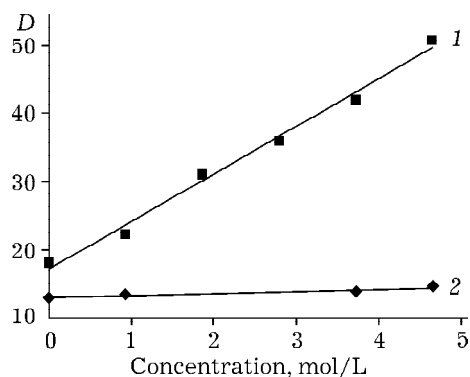
Fig. 4. Dependence of the coefficients of distribution of elemental bromine (*1*) and chlorine (*2*) on the concentration of octyl bromide in octane.

Fig. 5. Effect fot he concentrations of lithium bromide (*1*) and potassium bromide (*2*) in the re-extracting solution on the distribution coefficients of elemental bromine.

investigated. The dependencies of the distribution coefficients of these halogens (*D*) on the concentration of *n*-octyl bromide in octane are presented in Fig. 4. One can see that the degree of bromine recovery is much larger than the degree of chlorine recovery. In this situation, co-extraction of chloride salts from solution does not occur at all. An increase in the selectivity of extraction and the coefficients of bromine distribution is likely to be due to the formation of complex compounds of the $C_8H_{17}Br \cdot Br_2$ type. At the same time, it was established that the stability of bromine extracts increases substantially, which is also likely explained by bromine binding into a complex with octyl bromide and a decrease in its activity (see Fig. 3, curve *3*).

Re-extraction of bromine from the organic phase may be performed using the recycle catholyte − the solutions of bromides of alkaline metals and alkaline earth metals − due to binding bromine into a complex anion $(Br_3)^-$:

$$Br_2(org.) + Br^-(aq.) \rightleftarrows (Br_3)^-(aq.) \qquad (5)$$
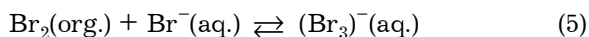
This leads to a substantial decrease in the coefficients of bromine distribution D_{Br_2} when saturated hydrocarbons are used as extracting agents. For octane, the value of D_{Br_2} changes from 18 (for the case when the extracts are treated with water) to 0.35 and 0.2 for bromine re-extraction with the aqueous solutions on lithium and potassium bromides, respectively (salt concentration: more than 4 mol-eq/L) (Fig. 5).

The isotherms of bromine extraction from chloride calcium brines using the commercial saturated hydrocarbon − extracting dearomatized solvent (RED-2) and the isotherms or
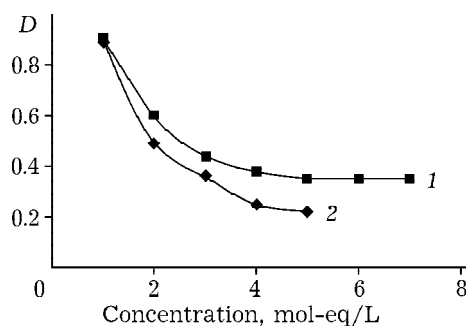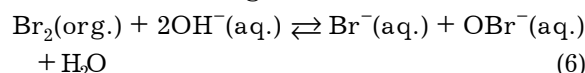
bromine re-extraction with the catholyte solutions were obtained.

Investigations demonstrated that saturated hydrocarbons (liquid paraffins) may be used for bromine extraction from brines. To achieve the bromine recovery degree equal to 95 % at the stages of counter-flow extraction and re-extraction in the case of the equal volumes of the aqueous and organic phases, the number of recovery steps should be not less than 3 and 5, respectively.

Higher re-extraction factors and a decrease in the number of steps may be achieved using alkaline re-extracting agents, subsequent cathode reduction of OBr^- and regeneration of the alkaline reagent:
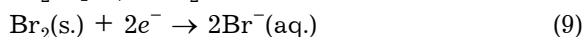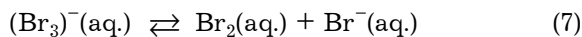
$$Br_2(org.) + 2OH^-(aq.) \rightleftarrows Br^-(aq.) + OBr^-(aq.)$$
$$+ H_2O \qquad (6)$$

However, due to the problems connected with the cathode reduction of OBr^-, it is reasonable to carry out bromine re-extraction according to reaction (5).

Cathode reduction of bromine

Different versions of bromine reduction in the recycle catholyte on porous carbon flow-through cathode were investigated.

It was demonstrated that for the overall current density in the cell less than 0.1 A/cm², the concentration of bromine decreases due to its reduction: from 0.05 to 0.001 mol-eq/L with the yield as a function of current >98 % (the yield was determined on the basis of the residual concentration of bromine and the volume of hydrogen released).

The process is likely to run in several stages with bromine adsorption on graphitized carbon fibres:

$$(Br_3)^-(aq.) \rightleftarrows Br_2(aq.) + Br^-(aq.) \quad (7)$$

$$Br_2(aq.) \rightleftarrows Br_2(s.) \quad (8)$$

$$Br_2(s.) + 2e^- \rightarrow 2Br^-(aq.) \quad (9)$$

As hydroxyl ions get accumulated in the catholyte due to water decomposition, bromine disproportionation occurs, leading to the formation of Br^- and OBr^-. Thus water decomposition with the formation of water sharply increases, while the yield of bromine as a function of current decreases to $40-60\%$.

So, to achieve the high parameters of the cathode process, it is necessary to maintain weakly acid medium of the catholyte. This is achieved by adding hydrochloric acid into the anode space of the electrochemical cell together with the chloride salt, and by subsequent electric transfer of the hydrogen cations through the cation exchange membrane.

Electrochemical transfer of cations

It is impossible to conduct the process of the electrochemical transfer of cations without separating the cathode and anode spaces with a cation exchange membrane. We studied the possibility to use a heterogeneous cation-exchange membrane MK-40 for this purpose. The optimal current density for the membrane is $0.05-0.1$ A/cm^2.

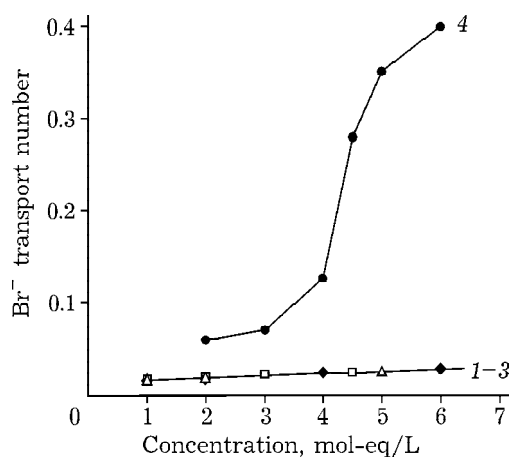It was established that the reverse transfer of bromide ions from the cathode space to the

Fig. 6. Dependence of the reverse transfer of bromide ions from the cathode to anode space on the concentration of bromides in the catholyte: *1−3* − lithium, sodium and potassium bromides, respectively; *4* − calcium bromide.

anode one increases insignificantly with an increase in the concentrations of lithium, sodium and potassium bromides in the catholyte (Fig. 6, curves *1−3*). However, even at the concentrations of sodium and potassium bromides at a level of 6 mol-eq/L, and lithium 8 mol-eq/L, the reverse transfer of bromide ions accounts for not more than only 3 % of the overall ion transport through the membrane. Unlike for the salts of alkaline metals, for calcium bromide, a sharp increase in the reverse transfer of bromide ions from the catholyte into the anolyte occurs with an increase in calcium bromide concentration above 4 mol-eq/L (see Fig. 6, curve *4*). For calcium bromide concentration $7-8$ mol-eq/L, the membrane almost completely loses its cation exchange properties, and the rate of counter-transfer of cations and anions for the MK-40 membrane equalizes. The reverse transfer of anions is likely due the sorption of calcium bromide by the cathionite and the appearance of free bromide ions in the phase of the membrane:

$$(-SO_3)Ca(s.) + Ca^{2+}(sol.) + 2Br^-(sol.)$$
$$\rightleftarrows 2(-SO_3Ca)^+ Br^-(s.) \quad (10)$$
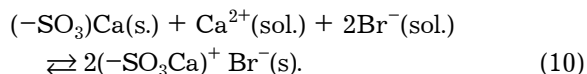
According to reaction (10), the concentration of bromide ions in the membrane phase is determined by the concentration of calcium bromide in the aqueous phase. The dependence of the equilibrium concentration of bromide ion in the membrane on the concentration of calcium bromide in the catholyte phase can be determined form the equation for the equilibrium constant for reaction (10).
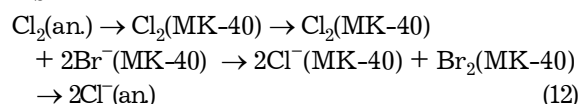
We also studied the membrane permeability with respect to chlorine according to reaction

$$Cl_2(an.) \rightleftarrows Cl_2(MK\text{-}40) \rightleftarrows Cl_2(cath.)$$
$$+ 2Br^-(cath.) \rightarrow 2Cl^-(cath.) + Br_2(cath.) \quad (11)$$

where the indices (an), (MK-40), (cath) point to the components belonging to the phases of the anolyte, MK-40 membrane or catholyte, respectively.

It was established that in the working mode of cell performance (overall current density: 0.1 A/cm^2, chloride concentration in the anolyte: $4-6$ mol-eq/L, bromide concentration in the recycle catholyte: 4 mol-eq/L) within the error of determination (0.5 %) chlorine is not transferred through the membrane into the catholyte.

Somewhat unexpected result is likely to be due to the fact that molecular chlorine diffusing

into the membrane phase gets reduced to chloride ions by the counter-flux of bromide ions accounting for as much as 3 % of the total ion flux, and returns back to the anolyte phase. In general, this process may be reproduced with a scheme:

$$Cl_2(an.) \rightarrow Cl_2(MK\text{-}40) \rightarrow Cl_2(MK\text{-}40)$$
$$+ 2Br^-(MK\text{-}40) \rightarrow 2Cl^-(MK\text{-}40) + Br_2(MK\text{-}40)$$
$$\rightarrow 2Cl^-(an.) \tag{12}$$

On the basis of investigation results, we developed a technological scheme of bromine recovery from natural calcium-sodium chloride brines leading to lithium, sodium, potassium, calcium bromides, and the bromide concentrate. Enlarged tests of the technology were carried out with the laboratory set-up having the productivity of 0.7 L/h using the natural brine from the Sukhaya Tunguska deposit (bromine content: 4.5 g/L). The corresponding bromine salts with the major product content not less than 98 % were obtained. The degree of bromine recovery was 87–90 %; the consumption of the electric power for the target electrochemical process was 0.75–1.0 kW · h/kg of bromine in the corresponding salts. The consumption of metal chlorides and hydrochloric acid (conc.) was 0.5–0.65 and 0.05 kg per 1 kg of bromide salts, respectively.

CONCLUSION

Investigation results and the results of technological tests demonstrated the possibility to realize efficient production of bromine salts according to the technological scheme combining the anode decomposition of metal chloride and oxidation of bromine with the released chlorine, with the extractive interphase transfer of elemental bromine from the catholyte phase into the anolyte phase. The use of this process will allow one to get rid of the transportation of toxic chlorine to the remote deposits of Siberia and to obtain high-quality and low-toxic bromine salts with small power and reagents consumption. In the case when the initial brine is used as the chloride-containing reagent, the bromide concentrate may be obtained with the reagents consumption at a level of not more than 0.05–0.1 kg/kg of the bromine-containing product.

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