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## Estimating the Potentialities for Extracting Salts from Calcium Chloride Pickles of the Krasnoyarsk Territory

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### Abstract

The problems of processing underground multicomponent pickles in the Krasnoyarsk Territory are mainly connected with a remote location of deposits and the absence of developed infrastructure. A variant is considered concerning direct extraction of valuable chemical elements in the form of salts. It is demonstrated that the maximal concentration level for the salts could be attained with the extraction of calcium bromide and lithium chloride (20 and 40 times, respectively). A scheme is suggested and approved for the extraction of calcium bromide using a mixture of tributylphosphate and molecular iodine. Problems concerning lithium chloride extraction are considered. By the example of lithium tetraphenylborate,  $\text{LiFeCl}_4$  и  $\text{Li}(\text{ClI}_2)$  extraction in the systems with tributylphosphate it was revealed that an increase in steric hindrance with the formation of complexes under extraction promotes the extraction of lithium from calcium chloride pickles.

**Key words:** extraction, chloride pickles, bromine, lithium

### INTRODUCTION

Multi-component highly mineralized underground waters containing bromine, iodine, lithium and some other valuable elements represent one of unique raw sources which were almost not involved in processing up till now.

Chloride underground waters with a high content of various metal salts are widespread over different areas of the western part of the Siberian platform. Of the greatest interest for processing are highly mineralized waters (pickles) of calcium chloride or sodium-calcium chloride type of the Krasnoyarsk Territory (the content of chloride ion is 200 g/L and higher, that of calcium ion being 50–65 g/L, that of sodium ion being 30–60 g/L).

### RAW MATERIAL BASE OF HIGHLY MINERALIZED UNDERGROUND WATERS OF THE KRASNOYARSK TERRITORY

Among the deposits of the Krasnoyarsk Territory, the pickles of the Turukhansk and Taseevo areas, Evenkia are most practically

feasible and promising for processing due to a high content of useful components and the large-scale resources of these waters.

#### *Pickles of the Turuhansk area (the Sukho-Tunguska area)*

In the course of surveying the Sukho-Tunguska area, large-scale inflows of industrial pickles were obtained from the sediments of the Kostino Formation for all deep boreholes. The sediments of the Kostino Formation are characterized by high water abundance, connected with the collectors of fissure, fissure-porous and the porous-cavity types, separated between each other in the section by clay sediment.

Data concerning the weighed mean content of valuable components with respect to area are presented in Table 1.

#### *Pickles of Evenkia*

The water of Wendian and Riphean of the Yurubcheno-Tokhom oil and gas field accom-

TABLE 1

Data on weighted average content of valuable components in the pickles of the Sukho-Tunguska area, g/L

Horizons	Elements							
	K	Mg	Br	I	Li	Rb	Sr	B
Lower-middle Kostino	23.05	9.5	3.17	0.028	0.22	0.028	2.45	1.93
Upper Kostino	15.00	9.3	2.32	0.001	0.12	0.01	–	–

panying oil are most promising for processing in this region. The underground waters of the Riphean complex according to the between the main components of mineral composition represent same type calcium-sodium chloride pickles with the content of bromine amounting to 2–3 g/L and water mineralization level equal to 250–300 g/L. Riphean waters compose the main part of the total amount of waste solutions resulting from oil extracting (up to 60 %).

#### *Pickles of the Taseevo district (the Karaul area)*

Of special interest for the further studying Cambrian are the pickles of the Kansk-Taseevo depression. The pickles are remarkable by a high content of bromine and low (below the industrial level) content of iodine. From the borehole No. 2 of the Karaul area, from the bottoms of the Usolye Formation, with the overflow from the depth about 1400 m, an inflow of bedded waters was obtained with the content of bromine higher than 13 g/L. The yield of the overflow amounted to 50 m<sup>3</sup>/h.

Owing to the insufficiency of geological material, any estimation concerning the water resources of the Karaul area for the present time is rather complicated.

The pickles of the Krasnoyarsk Territory represent a raw material with a high technological readiness for hydrometallurgical process-

ing. They are characterized by a low content of solid suspensions, optimum temperature (20–25 °C), they are concentrated enough and at the same time they do not crystallize with decreasing the temperature.

As far as value and the content in raw material is concerned, one could distinguish several groups of pickle components (Table 2).

The first group of salts (sodium, calcium, magnesium chlorides) is of a low market cost, but their yield resulting from pickle volume unit is maximal. It is worthwhile to use these products on the spot, which would allow obtaining significant economy due to reducing the transport expenses (an important factor for the conditions of Siberia). In particular, the mentioned chlorides isolated from pickles can find wide application as components of drilling fluids. Nowadays, for the preparation of such solutions, sodium chloride, calcium chloride of and mineralizers, such as bischofite are delivered in great amounts to borehole platforms. So, the consumption of salts for the construction of one borehole exceeds 100 t, whereas taking into account the transportation expenses their cost increases almost triply. Due to low-level requirements for the purity of components of drilling fluids, the main process of obtaining chlorides could consist in concentrating the saline *via* evaporation and the separation of crystalline sodium and potassium salts from liquid crystal

TABLE 2

Classification of pickle components in value

Saline components	Content, kg/m <sup>3</sup> (order of magnitude)	Price, USD/t
Sodium, potassium, calcium, magnesium chlorides	10–10 <sup>2</sup> (macrocomponents)	~10 <sup>2</sup>
Bromine and lithium salts, boron	0.1–5 (average content)	~10 <sup>3</sup>
Iodine, caesium, rubidium	0.001–0.03 (microcomponents)	~10 <sup>4</sup>

hydrates containing mainly calcium chloride (with the temperature of crystallization amounting to 40–45 °C). The profitability of this process depends, mainly, on the possibility of using local mineral oil as fuel.

The second group of elements, the most valuable part of pickles is composed of lithium, bromine and boron. Taking into account the average content of bromine and lithium in pickles in the cost expression, the bromine and lithium containing products are comparable in value.

Among latter group of elements (microelements) of the greatest interest is only iodine, a scarce and expensive product. However, its content in pickles, as a rule, is low amounting to several tens of grams per a cubic meter of a saline. Iodine can be taken from pickles in passing together with bromine. Cesium is the second element from this group concerning the deficiency and cost, whose content in pickles is very low (about 1 g/m<sup>3</sup>). As far as rubidium is concerned (the content up to 10 g/m<sup>3</sup>), nowadays, its consumption in the world despite of high price amounts to several hundred kilograms per year. In this connection, the extraction of both caesium and rubidium should be considered as inexpedient.

#### **EXTRACTATIONAL ISOLATION OF BROMINE AND LITHIUM FROM BEDDED WATERS**

Despite of high demand for bromine and lithium-containing production, the processing of pickles, including extracted together with oil, is not mastered in Russia.

Traditionally, bromine is extracted using the oxidative technology *via* processing the solutions with elemental chlorine and the subsequent stripping bromine by air or steam [1]. The problems of delivery highly toxic chlorine to distantly located deposits and of its storage are offered to solve *via* obtaining the reagent on the spot using electrochemical methods [2]. In order to provide safe storage and transportation of toxic bromine, an electrochemical extraction technology was proposed for obtaining of bromine concentrate or its salts [3, 4]. The disadvantages in the processes of bromine extraction include the problems of delivery and storage of toxic reagents, high cost of electrical energy at the location of deposits.

Nowadays, an almost unique comprehensible technical solution for the extraction of lithium from chloride solutions containing a great amount of alkaline earth elements consists in the sorption onto inorganic adsorbents based on aluminium hydroxides [5, 6, *etc.*]. This process is selective enough. At the same time, the operation of inorganic sorbents is connected with the problems concerning their destruction.

In this connection, at the Institute of Chemistry and Chemical Technology (ICCT) of the SB RAS (Krasnoyarsk) studies are carried out concerning the direct extraction of bromine and lithium salts into a product from highly mineralized chloride waters using liquid extraction. The research is aimed at developing an almost reagentless and low energy consumption process.

Theoretically, bromine can be isolated from pickles *via* the extraction without any use of reagents, in the form of magnesium, calcium, strontium, lithium, sodium and potassium salts, whereas lithium can be isolated in the form of chloride or bromide.

For the direct extraction of salts from pickles one could use neutral or binary extracting agents. In this case the re-extraction of the product and the regeneration of an organic phase is carried out with the use of water. In the absence of the loss of an extraction agent, the main technological parameter of the process determining the economical characteristics consists in the concentration level of the product in the re-extract.

In order to estimate the maximal concentration level for different salts in the re-extract, the extraction and re-extraction are considered as uniform and continuous process wherein an organic extraction agent circulates in the system, being fed from stage extraction to the stage of re-extraction and back, with almost no spending. Hence, the thermodynamics of the extraction process as a whole is determined by the state of components in aqueous phases supplied to the extraction and re-extraction, as well as by the state of the components leaving with the refined product and re-extract, and does not depend on the nature of an extraction agent. The extraction agent, thus, is an intermediate phase that determines only the composition of the product under extraction.

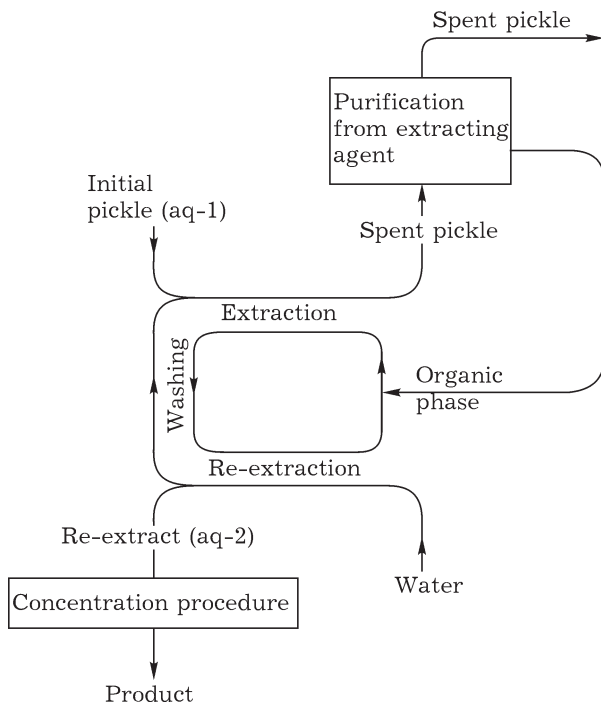


Fig. 1. Schematic diagram for the extraction of salts from pickles.

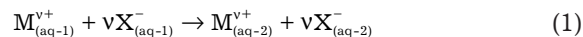
Figure 1 demonstrates the scheme of reagentless extraction process for useful components.

At the first stage (extraction) useful component  $\text{MX}_v$  (extracted salt involving cation  $\text{M}^{v+}$  and  $v$  single-charged anions  $\text{X}^-$ ) is extracted from the saline into an organic phase, the product at the final (re-extraction) stage is washed with water in order to recycle the extraction agent. A part of the product is used for washing the organic phase from impurities. All the operations are carried out in the modes of water and organic phase counterflow. The product extracted further is concentrated *via* evaporation or dialysis. The profitability of the mentioned scheme, besides the energy consumption expenses at the final stage of the re-extract concentration, would be determined by extraction agent loss with together with the waste saline. In this connection the extraction scheme provides the traces of extraction agent to withdraw from spent saline and recovering into the extraction cycle.

An estimation of maximally achieved concentration level was carried out for different products for an ideal counterflow system.

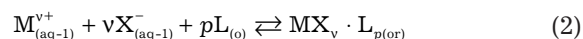
The process of salt transfer from the aqueous phase of the saline (aq-1) to the aqueous

phase of the re-extract (aq-2) could be expressed as

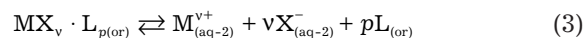


or stage-by-stage, for obtaining *via* using a neutral extraction agent (L):

extraction:



re-extraction:



Here symbols (aq-1), (aq-2) and (or) designate the belonging of a component to the aqueous phase of saline, re-extract or an organic phase, respectively.

Taking into account a decrease in the chemical potential of salts under extraction in a real counterflow system at the stages of extraction and re-extraction, the activity of extracted compounds in solutions ( $\alpha$ ) can be written as

$$\alpha_{\text{M}_{(2)}^{v+}} \alpha_{\text{X}_{(2)}^-}^v < \alpha_{\text{M}_{(1)}^{v+}} \alpha_{\text{X}_{(1)}^-}^v \quad (4)$$

For an ideal system (water insoluble extraction agent, an infinite quantity of extraction and re-extraction steps, optimum flows of solutions, the absence of water transfer), the conservation of chemical potential equality is available for the salt under extraction and, correspondingly, that is for its activity in the initial saline and re-extract:

$$\alpha_{\text{M}_{(\text{aq-2})}^{v+}} \alpha_{\text{X}_{(\text{aq-2})}^-}^v \rightarrow \alpha_{\text{M}_{(\text{aq-1})}^{v+}} \alpha_{\text{X}_{(\text{aq-1})}^-}^v \quad (5)$$

In this case, the salt activity and concentration in the product amounts up to a maximal possible value.

Taking into account stoichiometric coefficients we find this ceiling value in the form of salt molal concentration in the re-extract:

$$\begin{aligned} m_{(\text{MX}_v)_{(\text{aq-2})} \max} &= m_{(\text{X}^-)_{(\text{aq-2})}}/v = m_{(\text{M}^{v+})_{(\text{aq-2})}} \\ m_{(\text{MX}_v)_{(\text{aq-2})} \max} &= \{ [m_{(\text{M}^{v+})_{(\text{aq-1})}} m_{(\text{X}^-)_{(\text{aq-1})}}]^{1/v+1} / v^{v/v+1} \\ &\quad \times \gamma_{\pm(\text{MX}_v)_{(\text{aq-1})}} / (\gamma_{\pm(\text{MX}_v)_{(\text{aq-2})}}) \end{aligned} \quad (6)$$

Here  $m$  is the molal concentration salt  $\text{MX}_v$  in the initial saline (aq-1) or in the re-extract (aq-2);  $\gamma_{\pm(\text{MX}_v)_{(\text{aq-1})}}$  and  $\gamma_{\pm(\text{MX}_v)_{(\text{aq-2})}}$  are activity coefficients for the salt under extraction in mixed initial pickle and re-extract, respectively. This value is proportional to the concentration of cations and anions under extraction in the pickle. Thus, the extraction level of the product increases in the presence of accompanying non-extracted salts (salting-out agents), with the same ions therein.

TABLE 3

Estimation of potentialities for the extractal concentration of different products under isolation from pickles

Pickle composition		Product		Salting-out agent		Maximum concentration	
Elements	Content, g/kg of water	Composition	Content in pickle, mol/kg of water	Composition	Content in pickle, mol/kg of water	level taking $\gamma_{\pm}$ into account	no taking $\gamma_{\pm}$ into account
Ca <sup>2+</sup>	64	CaBr <sub>2</sub>	0.035	CaCl <sub>2</sub>	1.6	3.57	19.4
Mg <sup>2+</sup>	12	MgBr <sub>2</sub>	0.035	MgCl <sub>2</sub>	0.5	2.43	16.1
Sr <sup>2+</sup>	22	SrBr <sub>2</sub>	0.025	$\Sigma\text{MBr}_x^*$	0.07	1.25	5.7
Na <sup>+</sup>	51	NaBr	0.07	NaCl	2.2	5.6	15.5
K <sup>+</sup>	19.5	KBr	0.07	KCl	0.5	2.67	–
Li <sup>+</sup>	0.28	LiCl	0.04	$\Sigma\text{MCl}_x^*$	7.0	13.2	42.6
Br <sup>-</sup>	5.5	LiBr	0.04	$\Sigma\text{MBr}_x^*$	0.07	1.32	5.7
Cl <sup>-</sup>	250						

\* The content is presented in mol-eq/kg of water.

Table 3 demonstrates data concerning bromides and lithium salts those could be isolated *via* the extraction method with the use of a selective extraction agent for each salt, salting-out agents corresponding to them those are present in the pickle, data concerning their content, as well as maximally achievable concentration level values at the stage of extraction–re-extraction calculated from the concentration of components as well as more exact ones obtained taking into account the activity coefficients.

The activity coefficients of components in alkaline and alkaline earth halgenide solutions were estimated according to the Mikulin equation [7]:

$$\gamma_c = v_c m_i^* \gamma_i^* / \sum v_i m_i \quad (7)$$

where  $m_i^*$ ,  $\gamma_i^*$  are the concentration values and activity coefficients for electrolytes in a binary solution being in the isopiestic equilibrium with a multicomponent solution, respectively.

The activity of water in the solution was estimated according to an equation suggested in [8]:

$$\alpha_w = 1 / \mu \sum \mu_i \alpha_{w(i)}^0 \quad (8)$$

Here  $\mu_i$  is the ionic strength for  $i$ -th electrolyte solution of in the mixture;  $\alpha_{w(i)}^0$  is the activity of water in the solution containing only  $i$ -th electrolyte, at the ionic strength  $\mu$ .

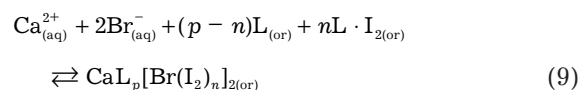
Thus, the counterflow extraction of salts could result in attaining a maximal concentration level for calcium bromide and lithium chloride (19.4-fold and 42.6-fold, respectively). As one could see from the calculated data, an insignificant concentration level of lithium bromide, one

of the most valuable products, can be attained mainly due to varying the activity coefficients.

Both products are commodity ones and being widely used in practice. Calcium bromide is used as a component of a heavy liquid for oil extraction. Moreover, it serves as a convenient initial material for obtaining elementary bromine, as well as sodium, potassium, ammonium, lithium, zinc bromides and other salts.

Lithium chloride is used for manufacturing lithium metal and its compounds as a catalyst, as a component for absorbers of moisture, carbonic gas and the vapours of organic substances in commercial conditioners, as well as for other purposes.

In the course of the studies, we have found a selective extraction agent for the extraction of calcium bromide: tributylphosphate (TBP)–molecular iodine–organic solvent. The process of calcium bromide extraction is based on the ability of molecular iodine to form hydrophobic complexes with halide anions such as  $\text{X}(\text{I}_2)^-$  or  $\text{X}(\text{I}_2)_2^-$  whose stability is much higher for bromides as compared to chlorides. In the general form, the extraction reaction can be expressed by the equation



where L is tributylphosphate.

Table 4 demonstrates data concerning the distribution and separation coefficients for ions in the course of model saline extraction by the mix containing 0.1 mol/L of iodine, 30 % of

TABLE 4

Estimation of separation coefficients for the elements under extraction by the mixes of molecular iodine with TBP

Parameters	Composition of initial pickle, g/L					
	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Br <sup>-</sup>	Cl <sup>-</sup>
	17	41	39	8	8	178
Distribution coefficient	0.079	0.0013	0.006	0.0008	1.3	0.009
Separation coefficient		Ca <sup>2+</sup> /Mg <sup>2+</sup>	Ca <sup>2+</sup> /Na <sup>+</sup>	Ca <sup>2+</sup> /K <sup>+</sup>		Br <sup>-</sup> /Cl <sup>-</sup>
		61	13	98		140

TBP, 30 % polyalkylbenzene in kerosene. One can see that process is remarkable by high selectivity, both with respect to calcium ions, and to bromine ions.

Figure 2 demonstrates extraction isotherms for calcium bromide from calcium chloride pickles and re-extraction by water, as well as operation lines for the calculation of counterflow processes. These data indicate that the extraction level for bromide higher than 90 % could be reached after six extraction steps. At the same time, due to a high extraction capacity

of the organic phase, the concentration of bromide in the re-extract almost does not exceed 20 g/L even at unlimited number of extraction steps, which corresponds to the concentration level amounting to 4 only instead of the maximal achievable value (about 80).

In order to improve the parameters of concentration procedure, we suggested to use a scheme with the mixed type of phases' flow such as cross-counterflow mode when a part of the organic phase from the medium part of the re-extraction cascade is fed to the medium

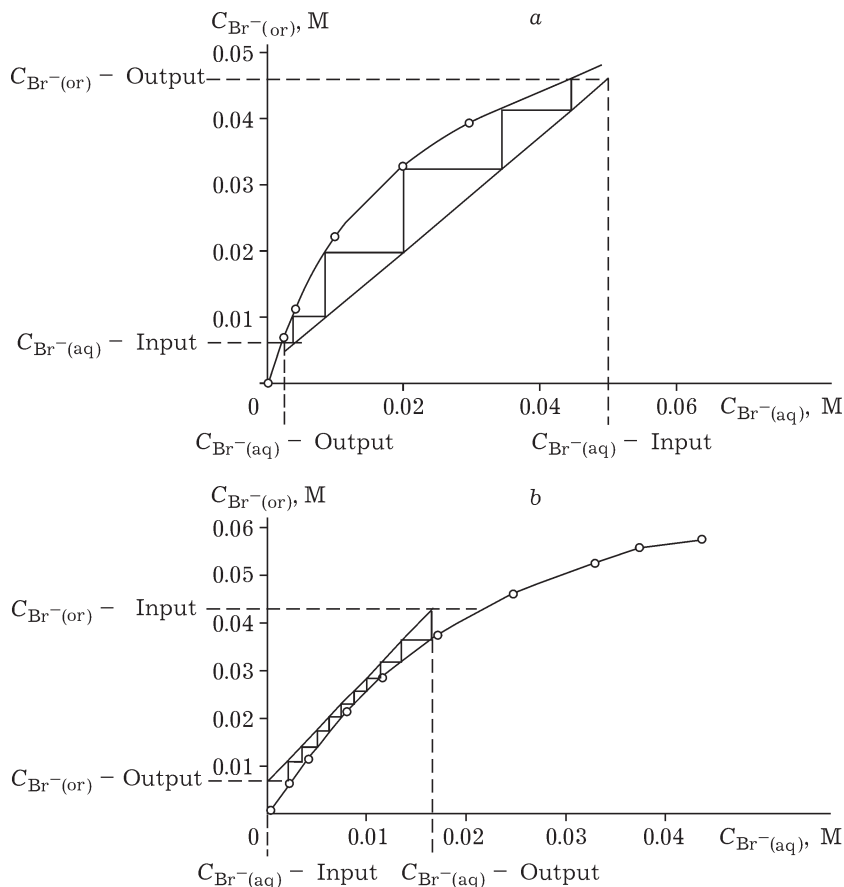


Fig. 2. Extraction isotherms for calcium bromide extraction from calcium chloride pickles (a) and for calcium bromide re-extraction from organic phase by water (b). Extracting agent: 0.1 M I<sub>2</sub>, 30 % TBP in kerosene.



part of the extraction cascade (a scheme with reflux). This allows increasing to a considerable extent the concentration of bromide in the re-extract with decreasing the number of re-extraction steps. The experimental testing of the process which was carried out within 24 extraction steps (by 8 steps for each stage of extraction, washing and re-extraction) without optimizing the process demonstrated, that the system attains more than eightfold concentration level for calcium bromide with 89–90 % product extraction level from the saline. The purity of the product in this case amounts up to 95 %; it could be increased at the total increase in the number of process steps.

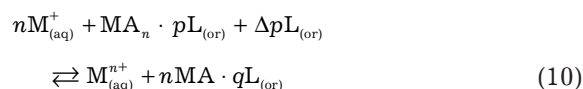
The further increase in the efficiency of the process could be attained due to a decrease of the system extraction capability aimed at decreasing the distribution coefficients for calcium bromide at the re-extraction stage with simultaneous conservation of the process selectivity.

A much more complicated problem is presented by the extraction of lithium from pickles with a high concentration of calcium and other alkaline and alkaline earth elements. To a considerable extent, the problem of separating differently charged metal cations could be readily solved.

For this purpose, one could use a cation-exchange extraction agent. In this case, the prevailing extraction of single-charged or double-charged cation from the mixture could be attained using either dilute or concentrated organic solutions of the extraction agent. Practically, to extract lithium into an organic phase is rather difficult due to low extraction  $\text{Li}^+/\text{Ca}^{2+}$  exchange constants and, respectively, due to the necessity for using very much dilute organic solutions and intense organic phase flows.

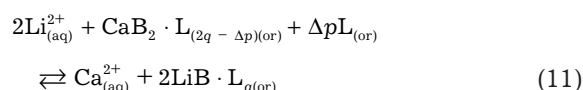
In order to solve the problem of increasing the extraction level for single-charged metal cations comparing to multicharged ions one could use the two factors. The first factor is structural one which consists in the reduction of stability of  $\text{CaA}_2$  salts as compared to  $\text{LiA}$  in the organic phase with the use of a sterically hindered hydrophobic anion  $\text{A}^-$ . The second factor is the solvation one, consisting in the fact that in the course of the cation-exchange extraction under the conditions of complete solvating the components in the organic phase,

the growth in the concentration of the solvating reagent L (at the total excess of the solvating reagent) should promote the process of single-charged cation extraction into an organic phase. This corresponds to the case when  $\Delta p > 0$  for the reaction



where  $p + \Delta p = nq$ .

In order to study the influence of the first factor, we used we used the salts of tetraphenylboric acid  $\text{H}[\text{B}(\text{C}_6\text{H}_5)_4]$  as structurally hindered cation-exchange extraction agent, and TBP was used as a solvating reagent. With no taking into account any additional interactions, the process of lithium cation-exchange extraction by calcium tetraphenylborate can be expressed by the reaction



The results of studies demonstrated that in this system the separation coefficient lithium/calcium pair can really reach very high values (up to 20–60) depending on the conditions of extraction and the composition of organic phase, at the distribution factor value for lithium ranging within 0.5–1.1 (Fig. 3). A simultaneous growth of TBP concentration results in decreasing lithium/calcium separation coefficients. Replacing tetraphenylborate anion by a less structurally hindered  $\text{FeCl}_4^-$  results in a decrease of lithium/calcium separation coefficients down to 8–12:

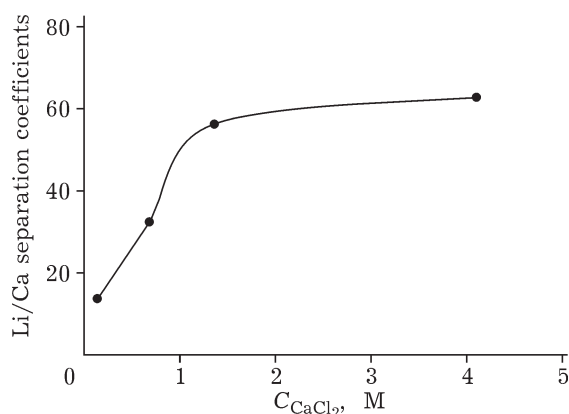
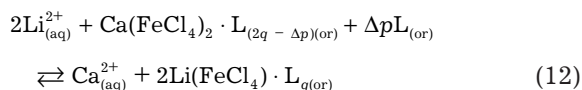
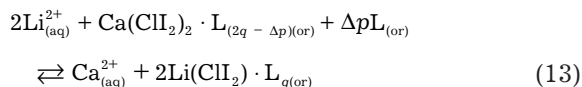


Fig. 3. Lithium/calcium separation coefficients depending on of calcium chloride concentration. Organic phase: 0.05 M tetraphenylborate lithium, 50 % TBP in toluene.



whereas in going to the systems with molecular iodine in TBP (complex anions such as  $[\text{ClI}_2]^-$ ) the coefficients decrease down to 3–5:



The increase in lithium extraction with replacing tributylphosphate by tri(2-ethylhexyl)phosphate indicates that structural factors exert a determining effect on lithium and calcium separation in these systems. In this case, the lithium/calcium separation coefficient grows up to 20–23 with the distribution factor of lithium amounting up to 0.5.

Another factor which can promote an increase of in the efficiency of lithium extraction is solvation one. It could be easily demonstrated that, when a counter ion occupies the same number of coordination sites ( $m$ ) for both cations, and the coordination number of cations irrespective of the charge does not exceed 4–6, then for reactions (11) in any case  $\Delta p > 0$  ( $\Delta p = n(4-6) - (4-6)$ ). Correspondingly, increasing the amount of a solvating reagent would promote the extraction of lithium.

In [9], we considered the influence of this factor upon the separation of cations in the course of cation-exchange extraction by the mixtures of neutral extracting agents and the salts of di(2-ethylhexyl)phosphoric acid. It was established that the increase in the concentration of solvating additives (TBP, *n*-octanol, 2-ethylhexanol) really promotes the extraction of low-charge metal cations (lithium, sodium, potassium). The same effect also takes place for the extraction of lithium by tetraphenylborates in TBP and TBP solutions with molecular iodine and with  $\text{FeCl}_3$ .

A disadvantage of the extracting agent based on the salts of tetraphenylboric acid consists in their chemical instability, especially in acidic media. For the systems with iron, it is necessary to find a solution for preventing the contamination of lithium re-extracts iron chlorides. At the same time, already today it is possible to suggest an efficient technological scheme for lithium extraction in the form of lithium chloride.

One of the most important problems of the extraction processing of pickles consists in decreasing an extracting agent loss together with spent pickles. The loss is connected with dragging-out organic components in the form of microemulsion as well as with dissolving the components of an extracting agent in the aqueous phase. So, even with the use of the cheapest extracting agent such as TBP the loss of the extraction agent only due to its dissolution could be comparable in the cost with the extracted calcium bromide. In this connection, at the finishing stage of processing of the saline, the extracting agent should be recovered. In our opinion, air flotation is most suitable for this purpose.

At the same time, in some cases one could use the extraction by an organic diluent with the subsequent separation of the extract into the phase of a diluent and the phase of concentrated extracting agent as we suggested in [10] for TBP extraction. The distribution coefficients between kerosene and chloride calcium saline are amounting for this extracting agent about 1000. One could re-extract TBP with obtaining concentrated solution and kerosene via the processing of the extract by HCl and  $\text{FeCl}_3$  mixture. In this case, the second organic phase segregation is observed in the form of  $\text{L} \cdot \text{HFeCl}_4$  complex. A prevailing amount of TBP passes into this phase, which provides kerosene recycling and TBP return into the extraction cycle.

## CONCLUSION

In the Krasnoyarsk Territory, there are large-scale resources of underground chloride multi-component waters located those contain a number of valuable chemical elements. Of the greatest interest for the processing are the side waters of the Yurubcheno-Tokhom oil field (Evenkia). According to the content and value of chemical elements in pickles, it is seems to be expedient to extract bromine and lithium, and, to all appearance, iodine.

Modern methods for liquid extraction allow selectively extracting the concentrate of salts required almost without any reagent consumption. The analysis of continuous counterflow processes for the selective extraction of metal



salts from calcium chloride pickles and the re-extraction them by water demonstrates that the extraction of bromine and lithium in the form of calcium bromide and lithium chloride could be most economic. For these salts, it is quite achievable non-reagent 20- and 40-fold extraction and concentration levels, respectively, are quite available for the mentioned salts.

The most promising extraction agent for calcium bromide is presented by a mixture based on molecular iodine and tributylphosphate which allows obtaining a high-purity product. A similar system could be used for the subsequent extraction of lithium chloride. A promising direction of developing the process of lithium extraction consists in the use of structurally hindered solvating reagents in the mixture with electron accepting substances.

#### REFERENCES

- 1 Ksenzenko V. I., Stanisevich D. S., *Khimiya i Tekhnologiya Broma, Yoda i Ikh Soyedineniy*, Khimiya, Moscow, 1995.
- 2 RU Pat. No. 2171862, 2001.
- 3 Kuzmin D. V., Kuzmin V. I., Pashkov G. L., *Chem. Sust. Dev.*, 16, 3 (2008) 275.  
URL: <http://www.sibran.ru/English/csde.htm>
- 4 RU Pat. No. 2360039, 2009.
- 5 Isupov V. P., Kotsupalo N. P., Nemudry A. P., *Zh. Prikl. Khim.*, 69, 8 (1996) 1385.
- 6 RU Pat. No. 2050330, 1995.
- 7 G. I. Mikulin (Ed.), *Voprosy Fizicheskoy Khimii Rastvorov Elektrolitov* (A Collection of Papers), Khimiya, Leningrad, 1968.
- 8 Teruya K., Hosako S., Nakano T., Nakamori I., *J. Chem. Eng. Japan*, 1 (1976) 1.
- 9 Kuzmin V. I., Gudkova N. V., *Khim. Tekhnol.*, 8, 10 (2007) 255.
- 10 RU Pat. No. 2123976, 1998.