As a manuscript

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SORPTION OF GALLIUM FROM ALKALINE ALUMINATE SOLUTIONS

Specialty 05.16.02 - Metallurgy of ferrous, non-ferrous and rare metals

Abstract
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GENERAL DESCRIPTION OF THE WORK

Relevance of the work: Currently semiconductor technology, nuclear energy and other industries take great interest in rare and trace metals, such as gallium. As a consequence of this trend, new, advanced and highly efficient technologies are required for their extraction. The unique value of rare and scattered metals is due to the fact that they have exceptional properties necessary for application in high-tech areas of industry, science and technology.

A significant part of the rare and scattered elements in the earth's crust is in amounts of the order of thousandths of a percent, which is a relatively small quantity. Thereby, these elements rarely form industrial clusters. Ores of rare and scattered metals usually have a complex composition, often containing several extremely valuable for industry metals. Consequently it is a matter of great importance to extract them in a comprehensive manner. Generally rare and scattered metals are extracted along the way during the development of deposits of metals concentrated in large quantities.

Methods for the extraction of gallium, which is a by-product, are selected so as not to violate the technological schemes for the production of aluminum. There are two methods for processing aluminum ores - the Bayer method and the method of sintering bauxite or nepheline ore with soda. In both processing methods, gallium behaves like aluminum and, when leached, passes into solution in the form of a soluble tetrahydroxocomplex.

Further processing of the working alkaline solutions is difficult due to a low concentration of gallium, as opposed to a significantly higher concentration of aluminum and the presence of impurity elements. Depending on the production methods of gallium, its extraction is possible directly from technological solutions or from gallium-containing concentrates.

There are several methods for the extraction of gallium from complex salt technological solutions, among which the most promising is the sorption method of concentrating the metal with ion-exchange resins. The use of this method provides the primary concentration of gallium compounds from technological solutions and industrial products of various composition and origin, and subsequent purification from related components.

Effective sorption of gallium from alkaline technological solutions is achieved by selective absorption of anion-exchange resins and elution from the solid phase of the resin using selective agents.

The quantitative relationship of the anionic composition of the resin phase with the anionic composition of the test solution is determined primarily by the laws of ion exchange equilibrium. The value of the ion exchange constant is an important characteristic of anion exchange resin, which determines the equilibrium distribution of ions between the solid and liquid phases and the selectivity of sorption by this ion exchanger.

Objective: To increase the efficiency of the hydrometallurgical method for the extraction of gallium from circulating solutions obtained during the processing of bauxite by the Bayer method, based on sorption using anion-exchange resins.

The following tasks were set to be achieve in the work:

1) Identification of selective ion-exchange resins for sorption extraction of gallate ions from alkaline aluminate solutions.

2) Obtaining isotherms of sorption of gallate ions on ion exchange resins from alkaline aluminate solutions both in the presence and without aluminate ions.

3) Thermodynamic analysis of the isotherms of ion exchange of gallate and aluminate ions with the calculation of thermodynamic constants and Gibbs energies of the equilibrium of ion exchange at the liquid-solid phase interface, as well as determining the sorption characteristics of anion exchangers.

4) Establishment of the forms of adsorbed gallate and aluminate ions from alkaline solutions in the Stern-Helmholtz layer in the solid phase of anion exchange resin.

5) Obtaining sorption isotherms of impurity components (chromates and vanadates) contained in the Bayer production solutions.

6) Calculation of the thermodynamic characteristics of the sorption of chromate and vanadate ions from alkaline solutions.

7) Determination of the kinetic features of the ion-exchange extraction of gallium from alkaline solutions.

8) Extraction of gallium from alkaline aluminate solutions using ion exchange chromatography.

9) Calculation of the main parameters of ion-exchange plants designed to isolate gallium.

10) Modernization of the technology for the extraction of gallium from aluminate solutions of Bayer production.

Scientific novelty of the research:

Thermodynamic data were obtained on the sorption of gallium and aluminium hydroxocomplexes on weakly basic anion exchangers from strongly alkaline solutions. The values of the limiting sorption, the total capacity of anion exchangers, apparent constants, the activation energy of the ion exchange process, and the Gibbs differential energies of sorption of gallate, aluminate, chromate, and vanadate ions were determined using the law of effective masses in a weakly basic anion exchange resin D-403. The forms of sorbed gallium ions and aluminum on synthetic ion-exchange resins AN-31 and D-403. The value of sorption capacity of anionic metal complexes (gallium, aluminum, chromium, vanadium) on a weakly basic ionite D-403 was determined. A basic process flow and instrumentation diagram was developed that allows to adapt the proposed technical solutions to the existing industrial complex for producing alumina.

Theoretical and practical significance:

- the choice of selective anion exchangers in the process of sorption of complex rare-metal ions has been substantiated;
- the method for the extraction of anionic gallium hydroxocomplexes from alkaline aluminate solutions in anionite D-403 was proposed;
- the possibility of separating gallate ions from chromate, vanadate, and aluminate ions in anionite D-403 was established by applying the method of the frontal version of ion-exchange chromatography.

Methodology and research methods

The thermodynamic description of the sorption isotherm of gallate ions was carried out by linearizing the modified Langmuir equation. The following modern methods of chemical and physico-chemical analysis were used: X-ray fluorescence, spectrophotometric, pH metric, and acid-base titration to determine the concentration of anions in the initial and equilibrium model solutions.

Defence provisions:

1. The concentration of gallium in anion exchange resin and its separation from the main macrocomponent - aluminium and associated impurities of chromium and vanadium, is due to an increase in a number of hydroxyl groups of the complex gallate ion and the Gibbs energy of ion exchange, which determines the number of ion sorption in the Stern-Helmholtz layer:

Anion	$[Ga(OH)_6]^{3-}$	CrO_4^{2-}	VO_4^{3-}	$[Al(OH)_4]^-$
$-\Delta_r G_{298}^0$, kJ/mol	15,2±0,3	9,4±0,5	5,8±0,2	2,91±0,15

2. The method of extracting gallium from aluminate solutions involves the use of weakly basic anion exchange resin D-403 followed by its regeneration with an alkali solution of 2 N concentration and using a three-section ion-exchange process unit with a fluidized bed of ion exchanger.

Approbation of work:

The main results of the work were presented at the following conferences:

1. 6th scientific and technical conference of young scientists, dedicated to the 100th anniversary of the professor of the Department of Organic Chemistry SPSIT O.F. Ginzburg, "Week of Science 2016. Technology and Innovations" (with international participation). St. Petersburg, 2016;
2. International forum-competition of young scientists "Topical Issues of Subsoil Use ". St. Petersburg, 2016;
3. 57th students' scientific session. Krakow, 2016;
4. 12th Freiberg-St. Petersburg Colloquium of Young Scientists. Freiberg, 2017;
5. 12th All-Russian Forum of Students, Graduate Students and Young Scientists "Science and Innovation in Technical Universities". St. Petersburg, 2018;
6. 26th international "Lomonosov" conference of students, graduate students and young scientists Moscow, 2019.

Publications: Based on the dissertation, 5 articles were published, 2 of them in journals recommended by the Higher Attestation Commission of the Ministry of Education and Science of Russia, 1 article in the journal registered in international citation database Scopus, abstracts of 4 reports and one patent.

Scope and structure of the work: The dissertation consists of an introduction, five chapters, findings, conclusions and references, including 133 items. The work is a typed text of 130 pages, it contains 25 tables and 33 figures.

MAIN CONTENT OF WORK

In introduction the author justifies the relevance of the work, defines objective and tasks to be solved, formulates the provisions to be defended and substantiates scientific novelty and practical significance.

Chapter 1 contains an analysis of scholarly works on the raw materials of gallium and use of gallium and its compounds. The world market and gallium production has been evaluated. Various technologies for the production of gallium have been considered, including sorption methods of concentration and extraction. The analysis of thermodynamic theories describing sorption equilibria has been carried out.

In chapter 2 the objects and methods of research, experimental techniques, as well as the characteristics of the anion exchangers D-403 and AN-31 are described. The developed thermodynamic model for describing ion-exchange equilibria is presented.

Chapter 3 presents the results of an experimental determination of the degree of gallium extraction by weakly basic ion-exchange resins. The thermodynamic description of the sorption isotherms of anionic gallium and aluminium hydroxocomplexes in the ion-exchange resins AN-31 and D-403, of chromate and vanadate ions in the D-403 anion exchange resin, including, in the joint presence, the values of the limiting sorption of anion exchangers, ion exchange equilibrium constants and Gibbs energies of ion exchange.

Experimental results are presented that determine the mode of desorption of gallate ions from the ion exchange resin D-403.

Chapter 4 presents the results of the study of the kinetics of sorption of gallate ions in anion exchange resin D-403 at temperatures of 298, 308, 318, and 328 K. The limiting stage of the ion-exchange process has been determined - external diffusion through the film of the solution adjacent to the solid surface of the ion-exchange resin, which is proved by a linear dependence $\ln(1-F(t))=-k\cdot t$, where k is a constant for the given conditions, varying with the change in the flow rate of the solution in accordance with the change in the mass transfer coefficient, t is the current time, min; F(t) is the relative fraction of the sorbed ion.

Chapter 5 describes the results of the sorption separation of gallium from aluminium by ion exchange chromatography.

Based on the obtained experimental data and the specified technological characteristics, the parameters of a single-section and multi-sectional ion-exchange units of continuous operation with a fluidized bed have been calculated.

Findings contain information about the possibility in principal to use D-403 anion exchange resin in the processes of concentration and extraction of gallium from alkaline aluminate solutions based on the obtained experimental data, confirmed by the calculated thermodynamic characteristics of sorption of anionic complexes of gallium, aluminum, vanadium, and chromium. The values of the Gibbs energy of ion-exchange equilibria determines a series of sorbability of various anionic forms of metals, which allows to predict the process of extraction of gallium from alkaline aluminate solutions in anion exchangers D-403 and AN-31. It is recommended to use a solution of sodium hydroxide with a concentration of 2 mol / L as a desorbing agent, providing a degree of gallium recovery of 98%.

The main research results are given in the following protected provisions:

1. The concentration of gallium in anion exchange resin and its separation from the main macrocomponent - aluminium and associated impurities of chromium and vanadium, is due to the increase in the number of hydroxyl groups of the complex gallate ion and the Gibbs energy of ion exchange, which determines the number of ion sorption in the Stern-Helmholtz layer:

Anion	$[Ga(OH)_6]^{3-}$	CrO_4^{2-}	VO_4^{3-}	$[Al(OH)_4]^-$
$-\Delta_r G^0_{298}$, kJ/mol	15,2±0,3	9,4±0,5	5,8±0,2	2,91±0,15

To determine the sorption characteristics of the ion-exchange resins D-403 and AN-31, the values of the total dynamic exchange capacity (TDEC) and dynamic exchange capacity before breakthrough (DEC) was determined. The output curves are shown in Figure 1.

For D-403 anion exchange resin, the DEC was 7.6 g of gallium per 1 kg of dry resin, TDEC - 0.265 mol per 1 l or 0.379 mol (26.3 g) per 1 kg of resin. And for anion exchange resin AN-31 - TDEC 27.4 g of gallium per 1 kg of resin. Thus, the sorption capacity of D-403 anion exchanger from alkaline solutions relative to gallate ions is not inferior to the sorption ability of the AN-31 selective sorbent while the capacitance to breakthrough of D-403 is much higher.

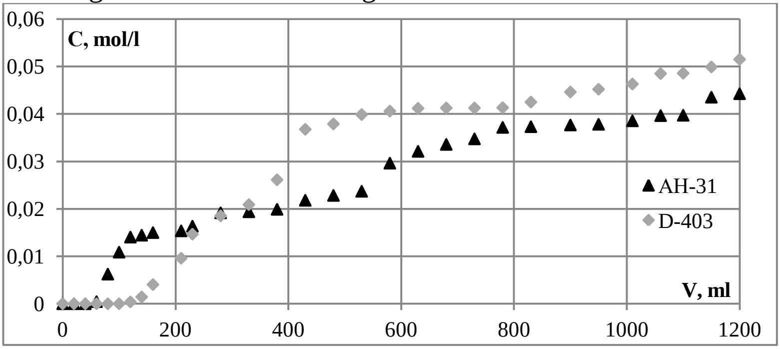

Figure 1 - Output sorption curves of the gallate ion in the ion exchangers AN-31 and D-403

Sorption isotherms of hydroxogallate and hydroxoaluminate ions in anionite AN-31 are shown in Figure 2.

The presence of interionic interactions in the internal electrolyte of an ion-exchange resin can lead not only to partial or complete dehydration of sorbed ions, but also to an alteration in their shape. In order to establish the features of the ion exchange of gallate and aluminate ions on weakly basic anion exchangers, the sorption of all possible anionic forms of these elements was examined: $[Me(OH)_4]^-$, $[Me(OH)_5]^{2-}$, $[Me(OH)_6]^{3-}$.

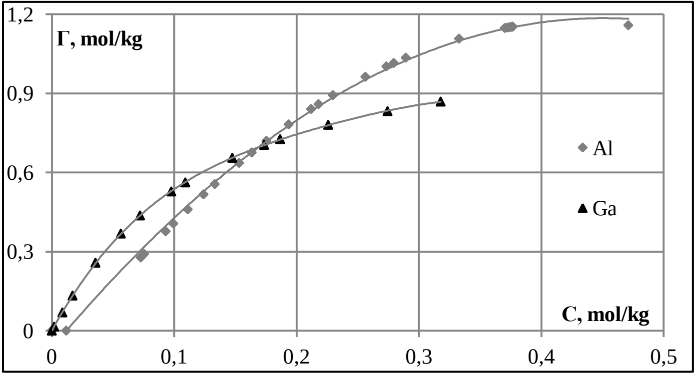

Figure 2 - Isotherms of sorption of gallate and aluminate ions in the ionite AN-31

The ion exchange process of tetrahydroxogallate and tetrahydroxoaluminate ions with the change in the shape of the adsorbed ions was expressed by the following equations (1-3), simulating an increase in the coordination number due to an increase of interionic interaction in the internal electrolyte of the solid phase of the ion-exchange resin:

$$R-OH+[Me(OH)_4]^- \rightarrow R[Me(OH)_4]+OH^- \qquad (1)$$

$$2R-OH+[Me(OH)_4]^- \rightarrow R_2[Me(OH)_5]+OH^- \qquad (2)$$

$$3R-OH+[Me(OH)_4]^- \rightarrow R_3[Me(OH)_6]+OH^- \qquad (3)$$

For ion exchange reactions, using the law of acting masses, the values of the constants of ion-exchange equilibria were expressed (4-6):

$$\mathrm{K}=\frac{\Gamma_{[Me(OH)_4]^-}\cdot a_{OH^-}}{\Gamma_{OH^-}\cdot a_{[Me(OH)_4]^-}}=\frac{\Gamma_{[Me(OH)_4]^-}\cdot[OH^-]\cdot\gamma_{OH^-}}{\Gamma_{OH^-}\cdot[Me(OH)_4^-]\cdot\gamma_{[Me(OH)_4]^-}}, \qquad (4)$$

$$\mathrm{K}=\frac{\Gamma_{[Me(OH)_5]^{2-}}\cdot a_{OH^-}}{\Gamma^2_{OH^-}\cdot a_{[Me(OH)_4]^-}}=\frac{\Gamma_{[Me(OH)_5]^{2-}}\cdot[OH^-]\cdot\gamma_{OH^-}}{\Gamma_{OH^-}\cdot[Me(OH)_4^-]\cdot\gamma_{[Me(OH)_4]^-}}, \qquad (5)$$

$$\mathrm{K}=\frac{\Gamma_{[Me(OH)_6]^{3-}}\cdot a_{OH^-}}{\Gamma^3_{OH^-}\cdot a_{[Me(OH)_4]^-}}=\frac{\Gamma_{[Me(OH)_6]^{3-}}\cdot[OH^-]\cdot\gamma_{OH^-}}{\Gamma_{OH^-}\cdot[Me(OH)_4^-]\cdot\gamma_{[Me(OH)_4]^-}}, \qquad (6)$$

where K is the ion exchange equilibrium constant;

a_{OH^-}, $a_{[Me(OH)_4]^-}$ - the activity of the corresponding anions in solution, mol/kg;

$\Gamma_{[Me(OH)_4]^-}$ - the values of the concentration of anions in the ionite phase, mol/kg;

Γ_{OH^-}- the equilibrium amount of free bases, mol / kg;γ_{OH^-}, $\gamma_{[Me(OH)_4]^-}$ - the activity coefficients of the corresponding anions.

Linearizing the equations of the law of the mass action under the assumptions of the ideality of the solid phase and the dependence of the average ionic activity coefficients of electrolytes on the ion charge and ionic strength of the solution, we obtained a system of equations (7-9), the graphic solution of which determined the values of the limiting sorption of ions and the ion-exchange equilibrium constant:

$$\frac{1}{\Gamma_{[Me(OH)_4]^-}}=\frac{1}{\Gamma_\infty}+\frac{1}{\Gamma_\infty \mathrm{K}}\cdot\frac{[OH^-]\cdot\gamma^2_{\pm NaOH}}{[Me(OH)_4^-]\cdot\gamma^2_{\pm Na[Me(OH)_4]^-}}, \qquad (7)$$

$$\frac{1}{\Gamma_{[Me(OH)_5]^{2-}}}=\frac{1}{\Gamma_\infty}+\frac{1}{2\Gamma_\infty \mathrm{K}^{1/2}}\cdot\frac{[OH^-]^{1/2}\cdot\gamma_{\pm NaOH}}{[Me(OH)_4^-]^{1/2}\cdot\gamma_{\pm Na[Me(OH)_4]}\cdot\Gamma^{1/2}_{[Me(OH)_4]^-}}, \qquad (8)$$

$$\frac{1}{\Gamma_{[Me(OH)_6]^{3-}}}=\frac{1}{\Gamma_\infty}+\frac{1}{3\Gamma_\infty \mathrm{K}^{1/3}}\cdot\frac{[OH^-]^{1/3}\cdot\gamma^{2/3}_{\pm NaOH}}{[Me(OH)_4^-]^{1/3}\cdot\gamma^{2/3}_{\pm Na[Me(OH)_4]}\cdot\Gamma^{2/3}_{[Me(OH)_4]^-}}. \qquad (9)$$

The linear forms of sorption isotherms constructed on the basis of calculated data are shown in Figures 3 and 4 (1 for tetra-, 2 for penta-, and 3 for hexahydroxyl ions of gallium and aluminium, respectively).

The obtained values of the maximum sorption of pentahydroxogallate ions and pentahydroxoaluminate ions are in satisfactory agreement with the value of the total static exchange capacity of anion exchange resin AN-31 for hydroxyl ions and the value given in the certificate.

For the sorption isotherm of the gallate ion in the ionite D-403, shown in Fig. 5, constructed from experimental data, the dependence of the concentration argument of the one-, two-, and three-charged hydroxocomplex (1-$[Ga(OH)_4]^-$, 2-$[Ga(OH)_5]^{2-}$, 3-$[Ga(OH)_6]^{3-}$) of the inverse sorption value is shown in Figure 6.

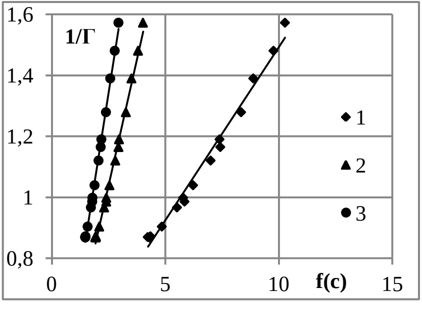

Figure 3 - Linear forms of isotherms of sorption of gallate ions in the ionite AN-31

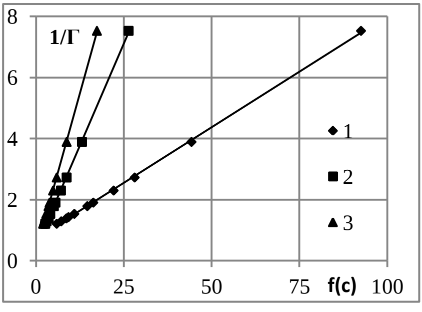

Figure 4 - Linear forms of isotherms of sorption of aluminate ions in the ionite AN-31

The value of the limiting sorption of the triple-charged ion $[Ga(OH)_6]^{3-}$ agrees well with the value of the TDEC of the anion exchanger D-403 of gallate ions, which is equal to the value of the anion exchanger according to the certificate and the value of the hydroxyl ion capacity, which confirms sorption in the surface layer namely the triple-charged ion $[Ga(OH)_6]^{3-}$.

Based on the experimental data on the sorption isotherm of gallate ions in the presence of aluminate ions, shown in Figure 7, the dependence of the concentration argument on the inverse sorption value was expressed, a graphic expression of which is shown in Figure 8.

The obtained value of the ion exchange constant of the gallate ion in the presence of aluminium hydroxocomplexes coincided with the value of the ion exchange constant during the sorption experiment in the absence of $[Al(OH)_4]^-$ ions.

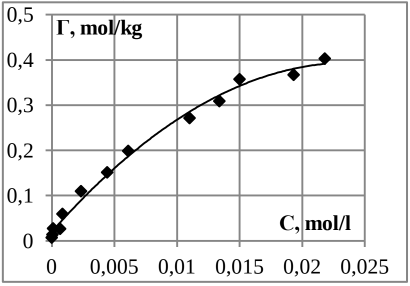

Figure 5 - Isotherm of sorption of gallate ions in the ion exchanger D-403

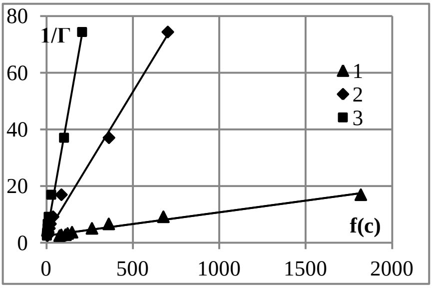

Figure 6 - Linear forms of isotherms of sorption of gallate ions in the anionite D-403

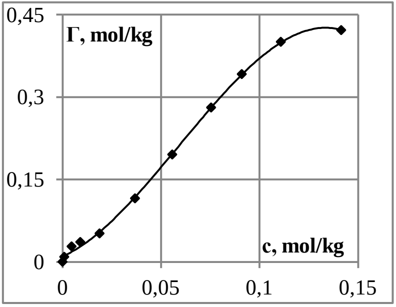

Figure 7 - Isotherm of sorption of gallate ions in the presence of aluminate ions in the ionite D-403

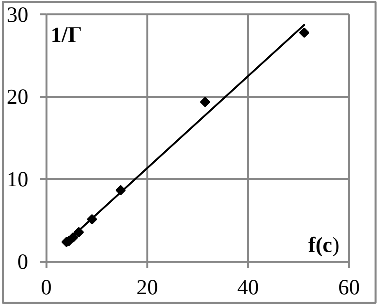

Figure 8 - The linear form of the sorption isotherm of gallate ions in the presence of aluminate ions in the anionite D-403

During the experiment on the sorption of gallium in the ion-exchange resin D-403, with an increase in the aluminum content in the solution up to a ratio of gallium 120:1, which is typical for technological aluminate alkaline solutions, no extraction of aluminate ions into the anionite solid phase has been observed.

To determine the thermodynamic characteristics of sorption of chromate and vanadate ions, which are impurity components of reverse alkaline technological solutions, we studied the process of ion exchange of these ions (Figure 9) in the ionite D-403. The linear forms of sorption isotherms of chromate and vanadate ions are shown in Figure 10.

Using the approximating equation, the value of the resin capacity, the ion-exchange equilibrium constant, and the Gibbs energy of ion exchange were calculated.

Based on the obtained Gibbs energy of ion exchange, a number of sorption capacities of anions from model alkaline solutions were established:

Anion	$[Ga(OH)_6]^{3-}$	CrO_4^{2-}	VO_4^{3-}	$[Al(OH)_4]^-$
$-\Delta_r G^0_{298}$, kJ/mol	15,2±0,3 15,0±0,4*	9,4±0,5	5,8±0,2	2,91±0,15,

* in the presence of 0.12 mol/l aluminate ions

where with the decrease in the Gibbs energy of the ion-exchange process, the displacement ability of anions increases.

The selectivity of the ion-exchange resin D-403 is higher for gallate ions, which determines the strong ion pair between gallium ions and fixed ions in the ion-exchange resin matrix. This property allows the use of this anion exchange resin for the selection of gallium from alkaline solutions and the separation of gallate ions not only from impurity anions, but also from aluminate ions, the content of which is more than 100 times of the amount of rare metal in negotiable technological solutions.

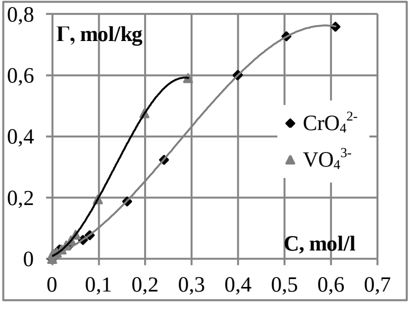

Figure 9 - Isotherm of sorption of chromate and vanadate ions in ion exchanger D-403

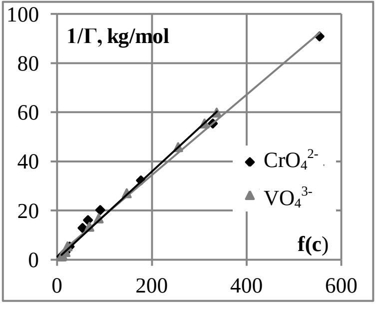

Figure 10 - The linear form of sorption isotherms of chromate and vanadate ions in D-403 ion exchanger

A lower value of the ion-exchange equilibrium constant of aluminate, chromate, and vanadate ions in comparison with gallate ions characterizes a less strong bond of these ions with the ionogenic groups of resin D-403.

2. The method of extracting gallium from aluminate solutions involves the use of weakly basic anion exchange resin D-403 followed by its regeneration with an alkali solution of 2 N concentration and using a three-section ion-exchange process unit with a fluidized bed of ion exchanger.

The results of the sorption separation of gallium from aluminum by ion exchange chromatography are presented in Figure 11, which allows complete separation of gallium and aluminium in anion exchange resin D-403 in 4 sorption-desorption cycles and in AN-31 in 9 cycles.

In Figure 11, three sections are clearly visible, the first of which corresponds to the simultaneous sorption of anions and the achievement of the DEC value for aluminate ions, the second one to the achievement of the DEC value of gallate ions, and the third section corresponds to the achievement of the TDEC value. The number of cycles providing a complete separation of aluminium and gallium is calculated by the formula (10):

$$N = \frac{S_{III}}{S_{II} \cdot \omega_{Me} + DEC_{[Me(OH)_4]^-} \cdot m_{sorb}} + 1, \qquad (10)$$

where S_{II} is the area of the second section, numerically equal to the total amount of aluminate ions in the solution that passed through the sorbent layer in the ion-exchange column;

S_{III} - the area of the third section, equal to the total amount of aluminate and gallate ions in the solution that passed through the sorbent layer in the ion-exchange column;

$DEC_{[Me(OH)_4]^-}$ - dynamic exchange capacity of aluminate ions, mol/kg;

ω_{Me} - mass fraction of aluminum;

m_{sorb} - mass of sorbent in the column, kg.

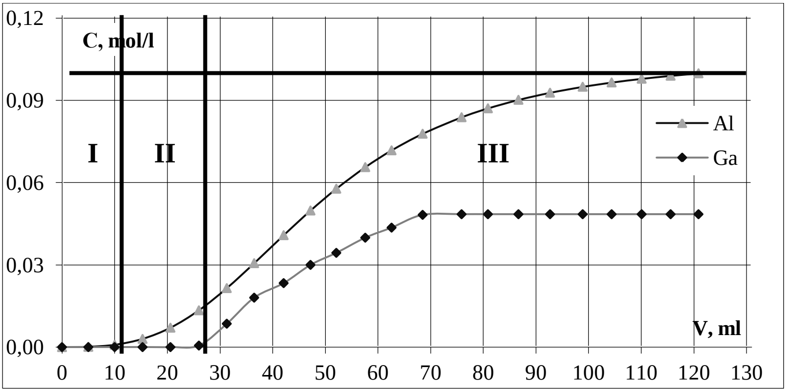

Figure 11 - Output curves of joint sorption of gallate and aluminate ions in the ion exchanger D-403

Based on the obtained experimental data and the specified technological characteristics, the parameters of a single-section and multi-sectional ion-exchange units of continuous operation with a fluidized bed have been calculated. The calculated number of sections is 3 pcs. The scheme of the ion-exchange installation with a fluidized bed of ion exchanger is shown in Figure 12.

The redistribution scheme of sorption extraction of gallium from working solutions of alumina production is shown in Figure 13.

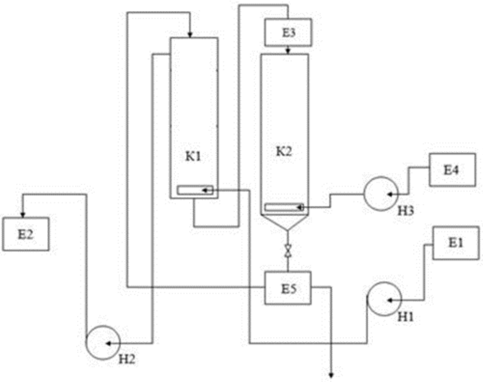

Figure 12 - Diagram of an ion exchange units with a fluidized bed of ion exchanger
K1 and K2 - anion exchange and regeneration columns; E1 and E2 - tanks for the initial solution and purified water; E3 and E5 - receivers of spent and regenerated anion exchangers; E4 - tank of the regenerating solution; H1-H3 - pumps.

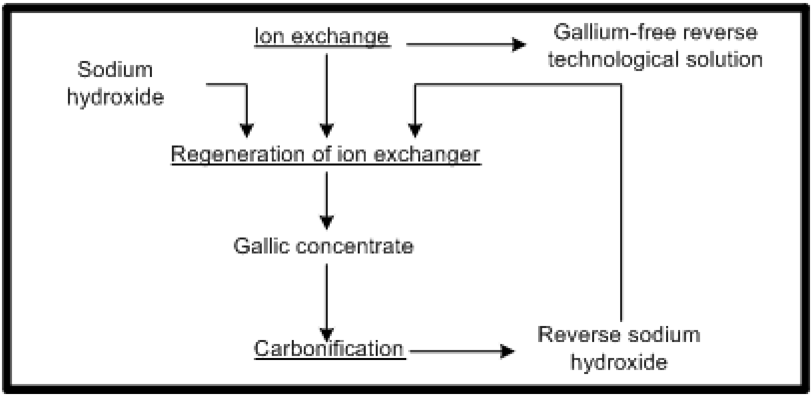

Figure 13 - Diagram of the redistribution of sorption extraction of gallium from technological reverse solutions of alumina production

According to the results of the experiment, desorption by sulphuric acid is more effective than by hydrochloric and nitric acids. The degree of extraction of gallium from anion exchange resin D-403 is 98, 96 and 95 %, respectively. A solution of sodium hydroxide with a concentration of 0.5 mol/l is a weak desorbing agent; desorption with sodium chloride is not effective. A significant increase in salt concentration leads to an increase in the degree of extraction from only 78 to 85 %.

Gallium ions are most effectively desorbed from the solid phase of the resin D-403 by 2 M sodium hydroxide solution. The resulting recovery of 98 % is equivalent to one obtained by using solution of 2 N sulphuric acid, however, to achieve this indicator, a smaller volume of eluent was required.

Conclusions:

The fundamental possibility of selective sorption extraction of gallium by weakly basic anion exchange resin D-403 has been proved. The experiment confirmed the equivalence of the exchange of hydroxyl ions from the resin phase to gallate ions from the solution.

Based on the congruence of the sorption values of the corresponding ions calculated experimentally from the specific features of the ion exchange of the linear equation of the effective masses, the values of the limiting sorption according to the certificate and the total dynamic exchange capacity of the anion exchangers D-403 and AN-31 determined under dynamic conditions, ion exchange stoichiometry that characterizes the change forms of adsorbed tetrahydroxogallate ions from alkaline aluminate solutions was established.

The value of the limiting sorption of gallium in the form of a triple-charged ion is in agreement with the TDEC value of the anionite D-403 for gallate ions, the value of the anion exchange capacity according to the certificate and the value of the capacity for hydroxyl ions, which confirms the prevalence of the ionic form in the surface layer $[Ga(OH)_6]^{3-}$ and does not contradict a literature data on the form of the presence of gallium in alkaline solutions in the form of $[Ga(OH)_4]^-$.

In the anion exchange resin AN-31, in the solid phase of the ion-exchange resin, gallium is sorbed in the form of pentahydroxogallate ions: the obtained values of the limit sorption of $[GaOH)_5]^{2-}$ are in satisfactory agreement with the value of the total static exchange capacity of the anion exchange resin AN-31 according to hydroxyl ions and certificate data.

The calculated constants and Gibbs energy of ion exchange on weakly basic anion exchangers, characterizing the nature of the bonding of sorbed gallate ions to the solid phase of ion-exchange resins, correlate with the coordination number of gallium hydroxocomplexes.

Using thermodynamic calculations, it was established that the sorbed aluminium ion in the Stern-Helmholtz layer of ion exchanger D-403 does not change its coordination number and charge, while in the internal electrolyte of the AN-31 anion exchange resin it undergoes changes and corresponds to the shape of pentahydroxoaluminate ions.

The difference in the chemical properties of aluminium and gallium is related to the difference in their electronic structure and ionic radii. For gallium, the atomic radius is slightly smaller than the atomic radius of aluminium, which leads to a higher polarizing ability, and as a result, to an increase in the charge and coordination number of the complex ion in the internal electrolyte solution, compared to aluminium ions.

The use of Chinese-made ion-exchange resin D-403 in the process of gallium extraction and its separation from related components is preferable due to the higher chemical affinity of tetrahydroxogallate ions to the solid phase of the resin compared to anionite AN-31.

Such characteristic of technological aluminate alkaline solutions as an increase of the aluminium content to a ratio of gallium 120:1 in the solution, does not lead to a competing effect of sorption of aluminate ions.

The chemical affinity of complex gallate ions to the solid phase of resin D-403 is higher than the affinity of chromate and vanadate ions, which are characteristic impurity components of reverse alkaline technological solutions.

Based on the thermodynamic values of ion exchange, a number of sorption abilities of metal anions in anionite D-403 from alkaline solutions were determined:

Anion	$[Ga(OH)_6]^{3-}$	CrO_4^{2-}	VO_4^{3-}	$[Al(OH)_4]^-$
$-\Delta_r G^0_{298}$, kJ/mol	15,2±0,3	9,4±0,5	5,8±0,2	2,91±0,15

The limiting stage of the ion-exchange process, which is the external diffusion through the solution film adjacent to the solid phase of the ion-exchange resin, has been determined. The calculated value of the activation energy of the process 19.00±0.95 kJ/mol characterizes the diffusion resistance of inorganic ions of large geometric dimensions, which include tetrahydroxogallate ion.

As desorbing agents, NaOH solutions of 0.5 and 2 mol/l, NaCl 5 % and 25 %; HCl 2 N.; HNO_3 2 N; H_2SO_4 2 N were tested in dynamic conditions. According to the results of the experiment, desorption by sulfuric acid is better than hydrochloric and nitric. The degree of extraction of gallium from anion exchange resin D-403 is more than 95 %. The most effective eluent, providing a degree of gallium recovery of 98 %, is a solution of sodium hydroxide concentration of 2 mol/l.

Sorption separation of gallium from aluminium was carried out by ion exchange chromatography, which allows complete separation of gallium and aluminium in the anionite D-403 through 4 sorption-desorption cycles and from AN-31 in 9 cycles.

Based on the obtained experimental data and the specified technological characteristics, the parameters of a single-sectional and multi-sectional ion-exchange units of continuous operation with a fluidized bed have been calculated.

The basic technological scheme of sorption extraction of gallium from reverse solutions of alumina production from bauxite according to the Bayer method is presented.

THE LIST OF MAIN PAPERS ON THE THEME OF THE DISSERTATION

In journals recommended by the Higher Attestation Commission:

1. Sagdiev V.N. Sorption recovery of gallium and aluminum from alkaline solutions on an AN-31 anion exchanger / O.V. Cheremisina, M.A. Ponomareva, V.N. Sagdiev // Universities′ Proceedings. Nonferrous Metallurgy. 2017. № 3. P. 56-64;

2. Sagdiev V.N. Process of extraction of gallium from technological solutions with the use of ion exchange resins / O.V. Cheremisina, M.A. Ponomareva, V.N. Sagdiev, E.S. Zatula // Metallurgist. 2019. № 2. P. 74-79;

Works in journals of the international citation database Scopus:

3. Sagdiev V.N. Prospects of rare elements sorptive recovery and ion-exchange separation from complex salt solutions / V.N. Sagdiev, O.V. Cheremisina, M.A. Ponomareva // 6th International Multidisciplinary Scientific GeoConference SGEM 2016, SGEM2016 Conference Proceedings. 2016. Book 1. Vol. 2. P. 1175-1182. (Scopus);

In other publications:

4. Kinetics of ion exchange of tertahydroxogallate ions on weakly basic anion exchange resin from alkaline solutions / O.V. Cheremisina, M.A. Ponomareva, V.N. Sagdiev, E.S. Zatula // Natural and Technical Sciences. 2019. № 3. P. 33-41;

5. Sagdiev V.N. Current state of the World’s production of gallium / V.N. Sagdiev, O.V. Cheremisina, M.A. Ponomareva // Innovations in Geology, Mining, Processing, Economics, Safety and Environmental Management. Scientific Reports on Resource Issues. 2017. Vol. 1. P. 294-300;

6. Sagdiev V.N. Sorption of gallium and aluminum on a weakly basic anion exchange resin / V.N. Sagdiev, O.V. Cheremisina // Technologies and innovations. WEEK OF SCIENCE VI scientific and technical conference of students, graduate students, young scientists, dedicated to the 100th anniversary of prof. Department of Organic Chemistry SPSIT O.F. Ginzburg. St. Petersburg. 2016. P. 23;

7. Sagdiev V.N. Sorption of gallium and aluminium on a weakly basic anion exchange resin / V.N. Sagdiev, O.V. Cheremisina // Problems of Subsoil Use: Proceedings of the International Forum-Competition for

Young Scientists. Part II. St. Petersburg: St. Petersburg State University. 2016. P. 236;

8. Sagdiev V.N. Sorption extraction of gallium on weakly basic ion exchanger / V.N. Sagdiev, O.V. Cheremisina, M.A. Ponomareva // Science and Innovation in Technical Universities. Abstracts of the twelfth forum of graduate students and young scientists, St. Petersburg. 2018. P. 58-60;

9. Sorption of vanadates and chromates from alkaline solutions on weakly basic ion exchanger / V.N. Sagdiev, E.S. Kostromitina, O.V. Cheremisina, M.A. Ponomareva // Science and Innovation in Technical Universities. Abstracts of the twelfth forum of graduate students and young scientists, St. Petersburg, 2018. P. 117-118.

Patents:

10. Pat. 2667592 RF, IPC C22B 58/00 (2006.01), C22B 3/24 (2006.01). The method of separation of gallium and aluminium on weakly basic anion exchange resin D-403 from alkaline solutions [text] / Cheremisina O.V., Litvinova T.E., Sagdiev V.N.; applicant and patent holder St. Petersburg Mining University. - № 2018106769; declared 02/22/2018, publ. 09/21/2018, Bull. № 27. 9 p.: ill.