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Improvement of Extraction Technology and Electrotechnological Equipment for Obtaining Gallium from Alumina Production Solutions

High-purity gallium, not worse than 6N, with the concentration of controlled impurities (except H, C, N, O) of maximum 0.00007, including, wt.%·10^{-8}: Fe — 2, Cu — 5, Pb — 4, Mn — 1, In — 2, and Sn — 2.5 was produced by electrolysis of preliminarily purified aluminate solutions of alumina production. An improved design of electrolyzer with increased efficiency has been developed for gallium electroextraction. It was proposed to divide the casing of the advanced-efficiency electrolyzer by longitudinal partitions into two parts, each of which was divided by transverse partitions into 8 sections. The width of these sections was one-third smaller than that of available electrolyzers. The dimensions of the sections and the arrangement of electrodes in them were reduced by half, from 140 to 70 mm — a distance covered by gallate and zincate ions from electrolyte depth to cathodes, which decreased the duration of electrolysis. The optimal current density of 7.5 kA/m^3 at the calculated density of 5.8 kA/m^3 was proposed, which allowed electrical energy consumption to be reduced. The polarization component of voltage on the electrolyzer was decreased by lowering the average current density achieved by a three-fold enhancement of the anode surface. The technological order of seven sequential operations of metallic gallium extraction from cycling aluminate solutions is shown: 1) purification of electrolyte by an air or vapor-air mixture; 2) purification of solution by lime; 3) galvanization of cathodes and dissolution of cathode precipitate; 4) purifying electrolysis; 5) basic electrolysis with precipitation of zinc-gallium alloy; 6) cementation of gallium by aluminum gallam; 7) removal of impurities. Preliminary purification of gallate-zincate alkaline solution allows decreasing the granular aluminum consumption to the weight ratio Al : Ga = 1 : 1 during gallium cementation.

Keywords: gallium, electrolysis, aluminate solution, solution purification, alumina production, interelectrode distance.

Introduction

Gallium is a dispersed metal, contained in small concentrations in non-ferrous metal ores. In the world, gallium is obtained mainly as a by-product during the processing of bauxite, the basic technological scheme of the Bayer process is shown in Figure 1, where the source of gallium is recycled solutions of alumina production.

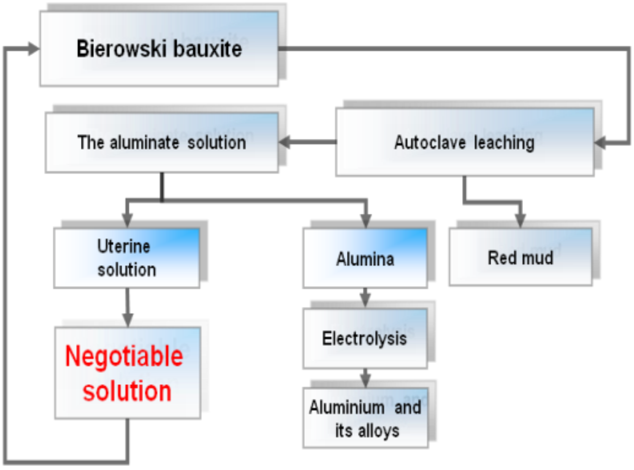


Figure 1. Schematic diagram of bauxite processing by the Bayer method

The main field of application of gallium is the electronic industry. LEDs, solar panels, smartphones "eat up" much more than half of the gallium produced, about 6 % goes to alloys, the most important use of gallium is the synthesis of compounds of the $A^{III}B^{V}$ type (GaN, GaP, GaAs, GaSb) — basic materials for modern opto- and microelectronics. The main producer of gallium is China and it continues to increase production, despite the fall in metal prices [1, 2], and subsequently came close to becoming a global monopolist, because the output of primary gallium in China this year amounted to 90 % of the world [3, 4]. The CIS countries, on the contrary, reduce the production of gallium. The main reason is the lack of demand in the Russian Federation due to absence of factories for the production of LEDs, semiconductors, etc. However, according to Rusnano, there are potential producers and consumers of semiconductors [5]. Gallium arsenide can rightfully be considered the engine of progress in the field of electronics [6], and the rise to the modern level of industrial production of semiconductor materials will contribute to solving the problems facing the country [7].

This may require developing a theoretical and practical implementation of various methods for obtaining gallium based on various sources and by various physicochemical methods [8–11]. There are several methods for obtaining gallium from alkaline aluminate solutions of alumina production [12, 13], but the most effective is electrolytic extraction [14–20]. However, electroextraction of gallium from solutions that have not undergone preliminary preparation will not provide serious extraction, productivity, cost reduction and reliable release of high purity metal (6N). This is largely due to the change in the composition of bauxite extracted from the new mine to SUBR-e (for the plant of JSC "BAZ-SUAL") and the transfer of JSC "UAZ-SUAL" to 100 % use of bauxite from the STBR deposits. The conducted studies found that the indicators of JSC "BAZ-SUAL" deteriorated: the concentration of gallium in the electrolyte decreased from 0.36 to 0.33 kg/m^3 — by 10 %, and the extraction of gallium by electrolysis lessened by 5 %, the purity of gallium deteriorated to 5N, the indicators of JSC "UAZ-SUAL" deteriorated significantly more, for example, the purity of gallium reduced to 4N. A significant change in the impurity composition of the initial bauxite (for the plant of JSC "BAZ-SUAL" and to a lesser extent for JSC "UAZ-SUAL"), caused by the launch of a new mine at the SUBR, required a more thorough cleaning of the initial electrolyte. These changes require technological improvements, first of all, to improve the purification of the initial electrolyte, which will increase the extraction of gallium, reduce the time of operations and increase the number of gallium concentration cycles to increase its release.

The purpose of this work was to improve the technological scheme for the extraction of gallium from alumina solutions, which will allow the production of high-purity metal gallium (6N), suitable for semiconductor production (Fig. 2).

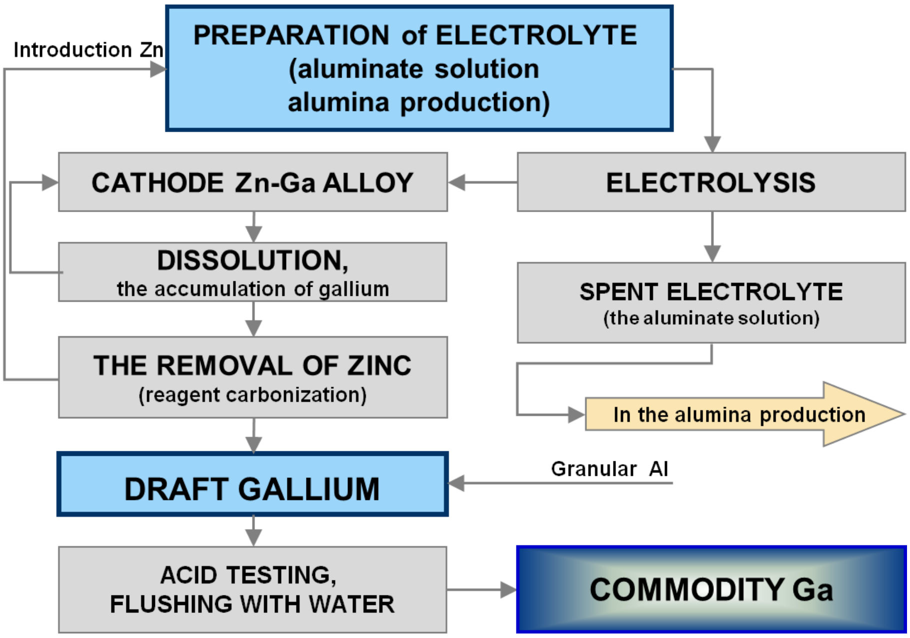


Figure 2. Technological scheme for obtaining gallium from aluminate solutions

Experimental

The separation of gallium from aluminate solutions was performed via the electrochemical method using an electrolytic bath made of stainless steel 1X18H9T with external water cooling (Fig. 3), a cathode made of the same stainless steel and two nickel anodes. Nickel prolongs anode lifespan by 2–2.5 times due to a decrease in the anode potential by ~0.2 V, and the thiosulfate ion is reduced to sulfur on the nickel anode, forming a protective layer of NiS. Direct current was supplied from the T1021 charger through a laboratory rheostat and an ammeter.

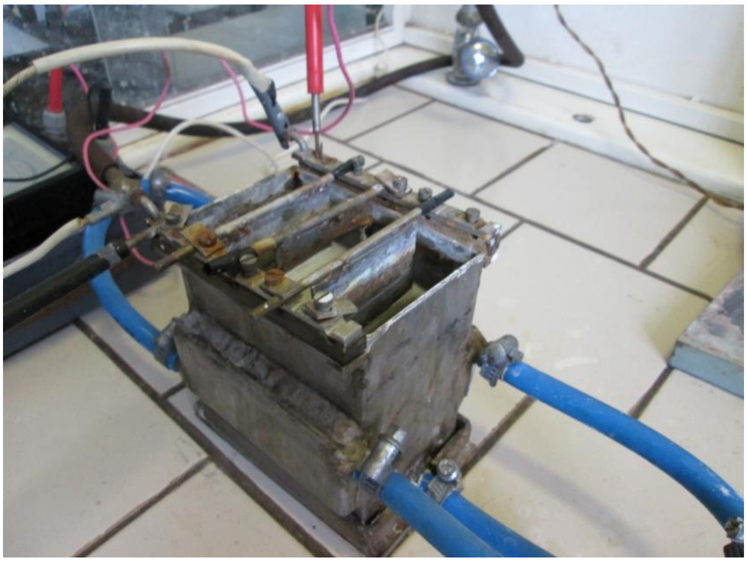


Figure 3. Water-cooled electrolyzer for laboratory extraction of gallium from alkaline-aluminate solutions

The studies were carried out on solutions of alumina production of JSC “UAZ-SUAL” and JSC “AZ-SUAL”. The results are presented by average values considering previous production experience.

The probable discharge mechanism during gallium electrodeposition can be represented as follows [21]:

$$[H_2GaO_3]^- + \bar{e} \rightarrow [HGaO_2]^- + OH^-$$

$$2[HGaO_2]^- + H_2O + \bar{e} \rightarrow Ga^\circ + [H_2GaO_3]^- + 2OH^-$$

standard electrode potential in acidic solution of gallium salts (Ga/Ga^{3+}): –0.56 V, in alkaline solution: –1.226 V.

The chemical composition of the starting materials and products was monitored on an inductively coupled plasma mass spectrometer ELAN 9000, Perkin Elmer.

Results and Discussion

1. Comparison of electrolyte purification by air and steam-air mixture by bubbling hot solution

The initial mixture is prepared: 150 m^3 of circulating solution (Table 1, p. 1), cooled to 30±5 °C and aged for at least a day in the reactor for the separation of soda-sulfate sludge, and 133 m3 of the mother (Table 1, p. 2) solution (volume ratio 1:0.887), this mixture of solutions is heated to a temperature of 85–90 °C and treated with a vapor-air mixture in the amount of 0.3–0.4 nm^3/hour per 1 m^3 for 2.0–2.5 hours with a ratio of air and steam volumes = 1.0 : 2.5 with a steady temperature at the outlet of the nozzle 250 °C. As a result, according to the analysis data, the content of organic substances decreases by 25–31 %, sulfide sulfur by 95 %, which is mainly oxidized into sulfate form (Table 1, p. 4). In comparison to the Chinese electrolyte processing method that uses only air and no steam, the operation time was reduced. Since aluminate solutions no longer require the introduction of sodium sulfide (up to 0.20 kg/m^3, counting for sulfur), the corrosion of the equipment has decreased, a better removal of zinc (less than 0.010 kg/m^3) and organic substances from solution was achieved.

2. Cleaning the solution with lime (consumption of 0.5 mol of CaO per mol of alumina in solution)

Lime milk (composition of 56 kg of $CaO_{act.}$ and 18 kg of water) is fed into the solution at a temperature of 80–90 °C with stirring for 1.5 hours. The precipitate is filtered out at a temperature of 70 °C to remove tricalcium hydroaluminate, on which iron, manganese, vanadium compounds and up to 25–30 % of organic substances are sorbed (Table 1, p. 5). The precipitate is returned to alumina production. Reducing the content of impurities during lime cleaning: vanadium by 30 times (up to 0.01 kg/m^3), iron by 3 times (up to 0.002 kg/m^3), manganese is completely removed (Table 1, p. 5).

Table 1

Compositions of solutions: alumina production (circulating (1), masterbatch (2), mixed (3), their double purification with a vapor-air mixture (4) and lime (5), synthetic alkali-zinc (6), purification electrolysis (7), initial and final (spent) electrolytes (8, 9), during carburization of the initial (10) and final (11), processing of slags of the initial (12) and final (13)

Components	Name (numbering) and compositions of solutions, kg/m^3												
	1	2	3	4	5	6	7	8	9	10	11	12	13
$Na_2O_{com.}$	314	157	240	230	235	220	210	233	235	105	103	170	168
$Na_2O_{caustic}$	290	145	222	220	231	200	200	230	232	100	100	165	165
$Na_2O_{soda.}$	24	12	18	18	4	20	10	3	3	3	4	5	4
Al_2O_3	138	69	106	105	87,5	–	87,0	87,0	88,0	50	63	4,2	4,3
Ga	0,46	0,23	0,35	0,34	0,33	–	0,34	0,34	0,18	10,2	0,25	100	100
Zn	0,06	0,03	0,04	0,004	0,004	20	0,003	0,45	0,04	3,0	0,06	2,9	1,25
S^{2-}	0,42	0,21	0,32	0,013	0,010	–	0,010	0,008	0,02	–	–	–	–
$S_2O_3^{2-}$	1,4	0,7	1,07	0,84	0,65	–	0,60	0,65	0,60	2,0	2,0	–	–
SO_4^{2-}	1,8	0,9	1,4	2,2	0,8	–	0,80	0,8	0,65	1,0	1,0	–	–
$C_{organic\ subst.}$	3,0	0,5	2,3	1,66	1,30	–	1,30	1,30	1,25	1,8	1,8	–	–
V_2O_5	0,42	0,21	0,32	0,31	0,01	–	0,08	0,01	0,005	–	–	–	–
$Fe_2O_3 \cdot 10^{-4}$	80	40	60	50	20	–	10	20	–	–	–	–	–
Cu 10^{-5}	13	10	12	12	10	–	1,1	1,0	6,0	10,0	1,0	12	1,0
$Mn \cdot 10^{-4}$	60	30	50	45	н/об.	–	12	–	–	–	–	–	–
$Pb \cdot 10^{-4}$	80	80	78	80	80	–	5	80	5,0	80	3,0	85	4,0

3. Galvanizing of cathodes and dissolution of cathode sediment

Before applying the zinc coating, the cathodes are cleaned by reverse current from the existing impurity sediment. To apply a zinc layer to the cathodes, a zinc solution prepared from a sodium hydroxide solution with an alkali concentration of 150–200 kg/m^3 and zinc oxide 15–20 kg/m^3 is used, followed by dilution before electrolysis with condensate to the composition, kg/m^3: sodium oxide ~125 and zinc ~12.5 (Table 1, p. 6). Electrolysis is carried out at a temperature of 45–55 °C and a volumetric current density of 4–5 kA/m^3. A layer of zinc 10–15 microns thick is increased in 12–15 minutes. This thickness of the cathode layer is sufficient for carrying out four to five operations of the main deposition of the zinc-gallium alloy and subsequent removal of the sediment after the last operation.

4. Purification electrolysis from impurities

Cleaning is carried out in a separate electrolyzer at low densities: cathode current (40–50 A/m^2), anode current densities 100–140 A/m^2 (volumetric current density 4–5 kA/m^3), temperature 60–70 °C and the voltage on the bath ~1.9 V (the bath body is also a cathode). The duration of the electrolyte cleaning operation is ~ 4-6 hours. The content of impurities during this period decreased by more than an order of magnitude, kg/m^3: copper from 0.000125 to 0.000011; lead from 0.0078 to 0.0005; iron and manganese by two to three times. The concentration of gallium in the electrolyte under the recommended electrolysis conditions practically does not decrease (Table 1 p.7). The precipitates isolated on the cathodes are dissolved in an alkaline synthetic solution at a temperature of 70–85 °C with the imposition of a reverse current. The resulting solution after settling is filtered out with the removal of impurities. The resulting purified alkaline solution is used for galvanizing the electrodes.

5. Conducting basic electrolysis with deposition of zinc-gallium alloy

Into the purified electrolyte with a content, kg/m^3: Na_2O_3 220–230, Al_2O_3 75–90, Ga_2O_3 0.33–0.35 a dilute solution of zincate is introduced in an amount of ~1/30 of the volume of the initial electrolyte. As a result, the zinc content in the electrolyte reaches 0.2–0.3 kg/m^3. The electrolyte prepared and cooled to ~30 °C is poured into a water-cooled electrolyzer and electrolysis is carried out on galvanized cathodes at a volumetric current density of 6.0–6.2 kA/m^3, a process temperature of 25–30 °C and an electrolysis duration of 2.0–2.15 hours. During this time, about 43 % of gallium and at least 80 % of zinc are released (Table 1, p. 8, 9).

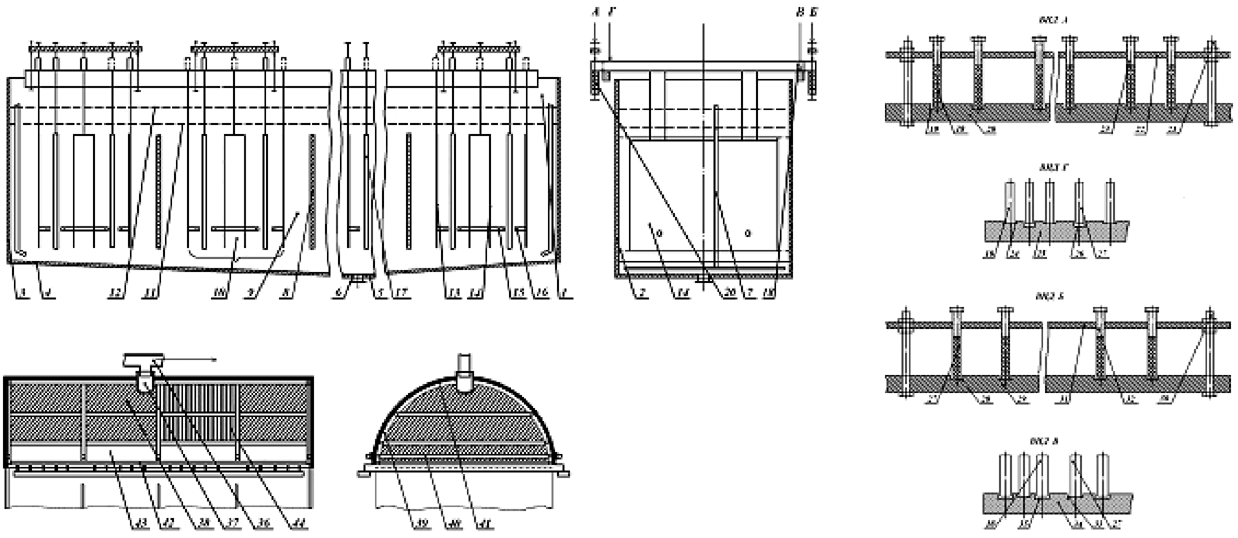
6. Cementation of gallium with aluminum gallam

Cementation is carried out in apparatuses with a capacity of up to 2.5 m^3 equipped with a stirrer, a device for filling granulated aluminum, level and potential sensors, a jacket for heating and the necessary hatches and pipes. For cementation, a settled filtered receiving solution, sufficiently rich in gallium (10.0 kg/m^3), and granular aluminum are used. ~2.0 m^3 of mortar and 40 kg of cement base are poured into the 2.5 m^3 cementator, aluminum is supplied according to the program with the EMF measurement of the cementation base – earth system. 97.5 % of gallium passes from the solution to the rough gallium (approximately 0.25 kg/m^3 remains in the solution) and almost all zinc (~4% remains). The consumption of aluminum is ~1.1 kg per 1 kg of isolated gallium (Table 1, p. 14, 15).

7. Removal of impurities from sludge

After dissolving the pressed sludge in a solution of sodium hydroxide (Na_2O — 150–200 kg/m^3), the impurities are removed by electrolysis under the following conditions: The cathode current density is 40–50 A/m^2, the anode current is 100–120 A/m^2, the volumetric current is 2–3 kA/m^3 and the process duration is up to 5 hours. The concentration of gallium ~100 kg/m^3 remains unchanged. The impurity content decreases by at least an order of magnitude (Table 1, p. 12, 13).

To organize the gallium production at alumina plants, based on existing experience, it is advisable to use the improved design of electrolyzers (Fig. 4) combined with the gallium electrolysis technology described above. The body of the electrolyzer is divided by a longitudinal partition into two parts, each of which in turn is divided by transverse partitions into 8 sections.



1 — steel case; *2* — the longitudinal wall; *3* — transverse, end wall; *4* — bottom; *5* — horizontal platform; *6* — drain hole; *7* — flushing device (flushing device); *8* — partition; *9* — section; *10* — a block of electrodes; *11* — electrolyte level during electrolysis; *12* — the initial level of the electrolyte; *13* — single anode; *14* — "П"-shaped anode; *15* — position lock; *16* — electrical insulation cap; *17* — box-shaped water-cooled cathode; *18* — anode rod; *19* — groove in the anode rod; *20* — anode tire; *21* — mounting bolts on the anode bus; *22* — steel plate for clamping anode rods; *23* — fixing screws for clamping anode rods; *24* — slots in the anode electrical insulation plate; *25* — anode electrical insulation plate; *26* — deep grooves in the anode electrical insulation plate; *27* — cathode rods; *28* — a groove in the cathode bus; *29* — cathode bus; *30* — mounting bolts on the cathode bus; *31* — steel plate for clamping cathode rods; *32* — fixing screws for clamping cathode rods; *33* — slots in the cathode insulating plate; *34* — cathode electrical insulation plate; *35* — deep grooves in the cathode insulating plate; *36* — exhaust ventilation; *37* — corrugated rubber pipe; *38* — the frame of the shelter; *39* — the arches of the frame; *40* — tie rods; *41* — covering the frame; *42* — horizontal support tube; *43* — an opening in the frame; *44* — sliding curtains

Figure 4. Gallium electrolyzer

The two sections are symmetrically arranged along the width of the housing, forming a compartment, where a package of electrodes is placed, divided in two along the length, and each half is connected to one copper rod resting on a conducting busbar of the corresponding polarity. The accepted dimensions of the sections and the location of the electrodes in them were reduced by 2 times, from 140 to 70 mm — the distance that gallate and zinc ions pass from the depth of the electrolyte to the cathodes. Accordingly, the duration of electrolysis is reduced. In the space occupied by the sections, there is more than 80 % of the electrolyte with minimal gas filling, so it maintains an optimal current density of 7.5 kA/m^3 at an estimated density of 5.8 kA/m^3, which reduces electricity consumption. The polarization component of the voltage on the electrolyzer is reduced due to a reduction of the average current density achieved by a 1.5-fold increase in the surface of the anodes; a decrease in the interelectrode distance; a reduction of foaming, which increases the active component of the electrolyte resistance. As a result, the voltage on the bath is decreased by 16 %.

Conclusions

The refinement of gallate-zinc alkaline solution helps reduce the consumption of granular aluminum during carburization to a mass ratio of Al : Ga = 1 : 1. Sludge formation is also reduced. In practical terms [22], at least 2 kg of sludge is formed per 1 kg of obtained gallium, but this solution reduces the amount of sludge to 0.1 kg — twenty times less.

The gallium ingots obtained after purification using this technology have a total composition of controlled impurities (excluding impurities H, C, N, O) of no more than 0.00007, including $\%\cdot 10^{-8}$: Fe — 2, Cu — 5, Pb — 4, Mn — 1, In — 2, Sn — 2.5. The gallium content in the ingot is not less than 99.9999 %.

The effectiveness of the proposed solution has been tested on an industrial scale. The purity of gallium obtained at the industrial plant of JSC UAZ-SUAL was 5N (99.999 %), on solutions of JSC BAZ-SUAL using the proposed technology, the purity of metallic gallium was 6N (99.99995 %), produced at the plant in Ping-Guo (PRC) according to our technology (transferred under contract) also corresponds to the brand 6N.

For the production of 10 tons of gallium per year, it is technically and economically feasible to use electrolyzers developed at the IHTT of the Ural Branch of the Russian Academy of Sciences with increased productivity. It is recommended to use 10 electrolyzers of the described type for the convenience of their operation, rational organization, technological and production processes, and to create an optimal DC power supply system ensuring high energy security of the enterprise. The electrolyzers are connected in series by five in chain, forming 2 chains of gallium electrolysis; each circuit of gallium electrolyzers receives power from an individual DC converter unit; the power supply system of electrolytic gallium production should contain a third, backup converter unit; nominal output parameters of the converter unit: rectified voltage of 20 V, rectified current of 30 kA.

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Жербалшық өндірісінің ерітінділерінен галлий алу үшін экстракция технологиясын және электротехнологиялық жабдықты жетілдіру

Жербалшық өндірісіне алдын ала тазартылған алюминатты ерітінділерді электролиздеу әдісімен тазалығы жоғары галлий алынды, 6н төмен емес, бақыланатын қоспалардың құрамы (H, C, N, O қоспаларын қоспағанда) 0,00007-ден аспайды, оның ішінде массалар %·10^{-8}: Fe — 2, Cu — 5, Pb — 4, Mn — 1, In — 2, Sn — 2,5. Галлийді электроэкстракциялау үшін өнімділігі жоғары электролизердің жетілдірілген конструкциясы жасалды, өнімділігі жоғары электролизер корпусын бойлық бөлімдермен екі бөлікке бөлу ұсынылды, олардың әрқайсысы өз кезегінде көлденең қалқалы 8 секцияға бөлінеді, ені бойынша бұл секциялар электролизерлердің қолданыстағы әзірлемелерінің секцияларынан үштен бір есеге аз. Секциялардың қабылданған өлшемдері мен олардағы электродтардың орналасуы 2 есе азайды, 140-тан 70 мм-ге дейін қысқарды, яғни электролит тереңдігінен катодтарға галлат пен цинкат иондары өтетін қашықтық, бұл электролиз ұзақтығын қысқартты. Токтың 5,8 кА/$м^3$ есептелген тығыздығы кезіндегі 7,5 кА/$м^3$ оңтайлы тығыздығы ұсынылған, бұл электр энергиясын тұтынуды азайтуға мүмкіндік береді. Электролизерде анодтар бетінің 1,5 есе ұлғаюымен қол жеткізілген орташа ток тығыздығының азаюы есебінен кернеудің поляризациясы төмендеді. Алюминатты айналым ерітінділерінен металл галлийді алу операцияларының технологиялық реттілігі көрсетілген, ол жеті жүйелі операциядан тұрады: 1) электролитті ауа және бу-ауа қоспасымен тазалау; 2) ерітіндіні әкпен тазалау; 3) катодтарды мырыштау және катод тұнбасын еріту; 4) тазарту электролизі; 5) мырыш-галлий қорытпасын тұндыратын негізгі электролиз; 6) алюминий галлийін цементтеу; 7) қоспаларды алып тастау. Галлат-мырыш сілтілі ерітіндісін алдын-ала тазарту галлий цементтеу кезінде түйіршікті алюминий шығынын Al : Ga = 1 : 1 массалық қатынасына дейін азайтуға мүмкіндік береді.

Кілт сөздер: галлий, электролиз, алюминатты ерітінді, ерітіндіні тазарту, глинозем өндірісі, электрод аралық қашықтық.

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Совершенствование технологии извлечения и электротехнологического оборудования для получения галлия из растворов глиноземного производства

Методами электролиза предварительно очищенных алюминатных растворов глиноземного производства получен галлий высокой чистоты, не ниже 6N, состав контролируемых примесей (исключая примеси H, C, N, O) не более 0,00007, в том числе, масс.%·10^{-8}: Fe — 2, Cu — 5, Pb — 4, Mn — 1, In — 2, Sn — 2,5. Разработана усовершенствованная конструкция электролизера повышенной производительности для электроэкстракции галлия, предложено разделить корпус электролизера повышенной производительности продольными перегородками на две части, каждая из которых, в свою очередь, разделяется поперечными перегородками на 8 секций, по ширине эти секции меньше на треть по сравнению с секциями имеющихся разработок электролизеров. Принятые размеры секций и расположение в них электродов уменьшили в 2 раза, со 140 до 70 мм, — расстояние, которое проходят ионы галлата и цинката из глубины электролита к катодам, что сократило продолжительность электролиза. Предложена оптимальная плотность тока — 7,5 кА/м^3 при расчетной плотности 5,8 кА/м^3, что позволяет снизить потребление электроэнергии. На электролизере снижена поляризационная составляющая напряжения за счет уменьшения средней плотности тока, достигнутого увеличением в 1,5 раза поверхности анодов. Показана технологическая последовательность операций извлечения металлического галлия из алюминатных оборотных растворов, состоящая из семи последовательных операций: 1) очистка электролита воздушной и паровоздушной смесью; 2) очистка раствора известью; 3) цинкование катодов и растворение катодного осадка; 4) очистительный электролиз; 5) основной электролиз с осаждением цинк-галлиевого сплава; 6) цементация галлия галламой алюминия; 7) удаление примесей. Предварительная очистка галлатно-цинкатного щелочного раствора позволяет снизить при цементации галлия расход гранулированного алюминия до массового отношения Al : Ga = 1 : 1.

Ключевые слова: галлий, электролиз, алюминатный раствор, очистка раствора, глиноземное производство, межэлектродное расстояние.

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