



ELECTROCHEMICAL REACTOR FOR GALLIUM RECOVERY FROM THE BAUXITE TREATING BAYER PROCESS

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SUMMARY

As currently in industry for gallium recovery from Bayer process of bauxite processing is used electrolysis with mercury cathode, due the tightening of rules on environmental protection, it was necessary to replace this method with new methods, environment-friendly. Thus, one has studied electrolysis methods with liquid gallium cathode or solid cathode (fixed, rotated or vibrated) made of various materials. The paper presents, among the electrolysis methods with solid cathodes, an electrochemical reactor for metallic gallium recovery from Bayer process of bauxite processing which uses solid, vibrated cathode.

Keywords: bauxite, Bayer process

INTRODUCTION

The chemical element, gallium, symbolized as "Ga", atomic number 31, is a post-transitional metal; its properties are similar with transition metals. It is silvery-white with blue reflections, (figure 1), is relatively soft, 1.5 units on the Mohs scale, brittle, diamagnetic, non-malleable and easily fusible, melts at 29.7 °C and boils at 2237 °C (2403 °C according to Ullmann).



Figure 1. Pieces of gallium metal

The liquid gallium is bright and has the tendency to undercool below its melting temperature and to solidify above it, when heated. When frozen, it extends by 3.1%; at normal temperature gallium is kept in glass jars and plastics (PP) and at high temperature in quartz, clay or graphite vessels. Solid gallium having a density of 5.907 g/cm^3 , liquid gallium at $35 \text{ }^\circ\text{C}$ has 6.094 g/cm^3 , so the solid form floats on the molten metal.

Semiconductive properties of inter-metallic compounds of gallium, the lack of toxicity and the low melting point makes them very important for modern technology. The need for gallium increased since 1996 with the introduction of gallium arsenide in photovoltaic technology. Gallium production reached about $70,000 \text{ kg / year}$, the greatest manufacturers are Australia, Russia, Japan and Kazakhstan. Among the producers are Hungary and Slovakia, they recover gallium from the recycled solutions from the alumina production [1].

In nature, gallium is found in aluminum-, zinc-, iron-, copper-, titanium-ores, as well as bauxite, blendes, pyrites, chalcopyrite, germanite and others [2].

Since the values of ionic radius of Ga^{3+} and Al^{3+} ions are very similar, the gallium replaces aluminum in much bauxite. CuGaS_2 is one of the few known gallium minerals, containing 34% gallium, found in ores from South Africa. Bauxite extracted from Russia contains 0.003 to 0.01% Ga, ores from India about 0.005 to 0.007% Ga, Indonesia, 0.005 to 0.0065% Ga, Vietnam, 0.007 to 0.009% Ga, and the Hungarian ores contain 0.0024 - 0.004% Ga. The gallium content of bauxite which is extracted in Romania is also between these limits.

The nuclear technology is one of the areas in which gallium metal is used, the gallium metal and the alloy with composition of 35-55% Bi, 17-18% Sn, 15 - 40% Pb and 3-10% Ga is used as heat transfer agents. Gallium metal has replaced sodium as the heat carrier in nuclear reactors due to its effective section of neutron absorption over five times higher than for sodium. Due to good adhesion to glass and high reflectivity, gallium is used

to manufacture high quality mirrors. Gallium arsenide and phosphide of are used to make rectifiers and power amplifiers [3].

Currently, worldwide [4], there are certain technologies developed for gallium recovery from natural minerals that contain gallium, such as the alkaline solution resulting from the Bayer process, the volatile dust removed from the collection system in the electrolysis process, in the residues from zinc refining, in the recyclable materials containing gallium and other materials which contain gallium enough to be able to recover.

The of gallium recovery technologies are followed by advanced purification processes; the obtained highly pure gallium (99.9999%) which is used in the semiconductor manufacturing industries, requiring several stages of processing technologies, such as the concentration, purification and refining.[5-8]

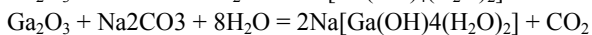
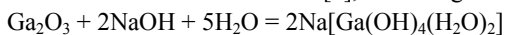
Gallium recovery technologies use multiple methods and techniques such as: gallium recovery from ores by hydrometallurgical process in the concentrate form, the gallium separation from concentrate by solvent extraction to obtain a solution extraction which contains 10 g/l gallium followed by precipitation and refining phase, etc.[9]

Gallium recovery via electrolysis, using the solutions resulted from the alumina manufacturing process from bauxite; consisting mainly of the following stages

- separation of vanadium salts;
- primary electrolysis;
- separation of gallium-sodium amalgam;
- decomposition of gallium-sodium amalgam;
- secondary electrolysis.

The raw gallium metal, obtained after separation, contains about 99% Ga. It is purified using complex procedures, such as: dissolving in acids or bases, electrolysis, vacuum distillation to obtain ultra-pure gallium (99.99% Ga).[8,9]

The gallium from bauxite is dissolved during the leaching phase with sodium hydroxide solution or sodium carbonate [4], according to the following reactions:

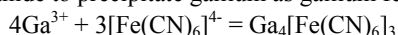


By passing a carbon dioxide current, the alkalinity of the solution is reduced to pH = 10.6, causing the precipitation of $\text{Al}(\text{OH})_3$, while the gallium is concentrated in the solution as a complex combination. Only a small fraction of gallium is solubilized in aluminum hydroxide and is then extracted from the electrolytic refining of aluminum residues [10]. Distribution of gallium in the final and intermediate products in the Bayer process is presented in table I:

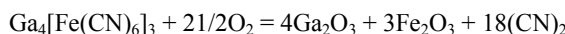
Table I: Distribution of gallium in the Bayer process

Intermediate or final product	Gallium content, mg/L
Aluminate solution before dilution	70 mg/L
Aluminate solution after dilution	58 mg/L
Kelly filter washing water	4 mg/L
Washing of aluminum hydrate	12 mg/L
Aluminum hydroxide	8 mg/L
Alumina	10 mg/L
Red mud	20 mg/L

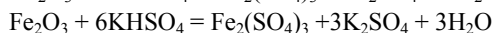
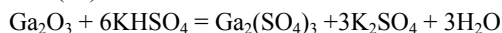
Filtrate resulted after separating the $\text{Al}(\text{OH})_3$ precipitate is treated with alkaline ferrocyanide to precipitate gallium as gallium ferrocyanide:



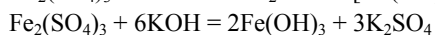
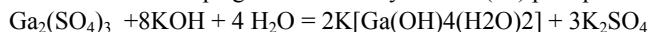
Through strong calcination in the presence of air, gallium ferrocyanide decomposes into gallium and iron oxide:



By melting the mixture of oxides with hydrogen-sulfate potassium, the gallium (III) and iron (III) sulfates are formed:



In the presence of alkaline hydroxides, the gallium (III) and iron (III) sulfate passes into soluble tetrahydroxodiaquagalat and iron hydroxide (III) precipitate:



The recovery of gallium from the Bayer process, (with a relatively high content of gallium between 200-600 mg/L), can be made by:

- direct electrolysis of these solutions,
- solvent extraction,
- ion exchange.

For the recovery of gallium by direct electrolysis, from the Bayer process solutions, industrially, mercury cathodes are used. The disadvantage of this process occurs when high organic content solutions are used and the process becomes economically unprofitable because of low current efficiency. Also using the mercury cathodes has extremely toxic effects on the environment. In these circumstances preliminary separation of gallium and partial enrichment are achieved by fractional precipitation (by neutralizing the alkaline solution with CO_2) or by removing a portion of alumina by adding calcium hydroxide and subsequent recovery of gallium by precipitation with CO_2 .

The recovery of gallium metal from the Bayer process or any alternative solution

from the production of alumina from ores by electrolysis using solid electrodes such as stainless steel or nickel, is a difficult process because of the low concentrations of gallium, the presence of impurities such as Fe, V, Cr and organic materials that are often present in higher concentration than gallium and interferes with the process of electrolytic deposition of gallium.[4,5]

Current processes for the recovery of gallium from aluminate solution involving complete or partial destruction of the sodium aluminate content or by the addition of CO₂, in two phases, to precipitate a part of the alumina and then to co-precipitate the rest of alumina and gallium hydroxide or by the addition of calcium oxide to precipitate alumina as part of a mixture of calcium aluminate followed by the addition of CO₂. [12]

From both methods gallium rich alumina results, gallium can be recovered by mercury cathode electrolysis; gallium is dispersed after deposited on the mercury cathode's surface. Using CO₂ and CaO to form gallium rich alumina, destroys the aluminate solution and cannot be reintroduced in the Bayer process without proper treatment.

The usage of mercury cathodes involves handling large amounts of mercury that is currently considered dangerous. Also, by stirring the solutions, there is a risk that very fine mercury droplets will be thoroughly dispersed in the aluminate solution.

Gallium removal from the cathode surface can be made by physical and / or chemical methods. When Sn, Pb, Sn-Pb alloy cathodes are used, it is possible to obtain a content of over 4% gallium on the surface. The diffusion and absorption processes and the time needed for the gallium to accumulate, influence the economic aspect of gallium. Basically, there are two aspects taken into consideration, the ease of extracting gallium from aluminate solution or the costs of aluminate solutions electrolysis.[10]

The cathodes can be in the form of thin sheets or foil with thickness between 0.01 to 0.3 mm or a thicker block from which gallium is physically or chemically removed, or a 1-50 μm deposit on an inert substrate such as stainless steel. Such listed methods allow easy separation of gallium and also can minimize the time required for electrolysis. Other metallic impurities such as Fe, V, and Cr in aluminate solutions that block the deposition of gallium on conventional metallic cathodes, may deposit on the cathodes forming hard deposits which are eventually displaced by gallium.

There can be used one or more insoluble metallic anodes or a slightly soluble metal but one that does not produce unwanted impurities.

The platinum anodes or platinum covered titan, bright nickel and stainless steel are equally efficient for gallium recovery; pure aluminum also can be used as anode because through dissolution does not contaminate the aluminum solution and it does not prevent the deposition of gallium on the cathode. The Ni and Sn/Pb cathodes are also suitable.

The electrolyte temperatures above 80 °C are not usable because the recovery of

gallium at this temperature is negligible. Cathodic current densities higher than 1.5V produce negligible deposition efficiency because the current efficiency is reduced due to foaming and warming of the electrolyte occurs. The process can be applied in every step of the Bayer process, but it is preferred to be applied when the gallium concentration is at least 0.2 g/l. It is also applied discontinuously when a Bayer process solution volume is subjected to electrolysis for a sufficient time so that the gallium deposit from the cathodes will reach an economical level; or continuously when dealing with a stream of aluminates solution, in which case the cathodes are changed after reaching a well defined content of gallium.[13-15]

MATERIALS AND METHODS

INCENM Timișoara achieved a laboratory technology for gallium recovery, schematically presented in figure 2.

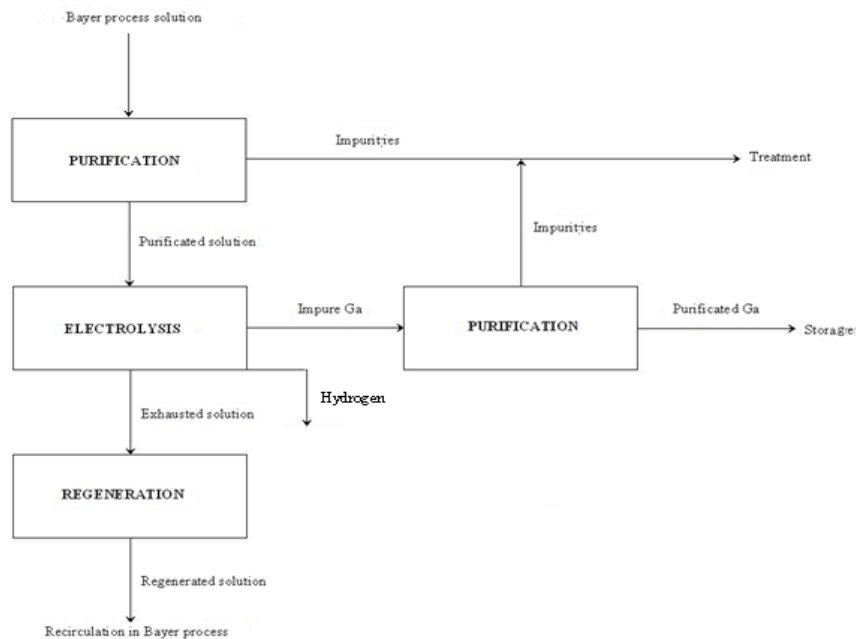


Figure 2. Electrochemical technology for gallium obtainment

The technology includes the following stages:

- Purification of the electrolyte solution (If is necessary, this stage include 2 phases);
- Electrolysis.

Nowadays, the industrially used mercury cathode electrolysis was replaced with other electrolysis methods due to environment protection concerns; so liquid gallium cathode electrolysis or solid cathode electrolysis using different materials are experimented.

The purification of the obtained gallium (this stage can be absent in function of gallium purity and the requested final product purity.

Regeneration of the electrolyte solution (this stage has in view the possible correction of the characteristic parameters of the electrolyte solution in order to recycle them in the Bayer process).

The electrolyte solution: all experiments regarding gallium electrodepositions (from solution) utilized as base-electrolyte 1M NaOH solution. Two types of synthetic solutions were used, prepared as presented in the followings

Solution 1- metallic gallium transfer in solution. Two different gallium quantities (0.05g respective 0.24g) were dissolved in nitro-hydrochloric acid, or Aqua Regis, at 80°C, then NaOH solution was added, to 25 ml volume (pH 12.5). Solution 2- exact quantities of gallium sulphate dissolved in NaOH solution. The volume of electrolyte used for all determinations was 25 ml.

In the following studies we are looking for gallium deposition from Bayer solutions containing: NaOH; Na₂CO₃; NaCl; Al(OH)₃; Ga₂SO₄; with Fe, Mo, V and W impurities and other organic substances formed by cellulose and lignin decomposition, present in the bauxite ores (sodium formate, sodium acetate, sodium oxalate and sodium succinate).

The studies were focused on investigation of Pt, Cu, graphite, Pb and stainless steel as cathode material. Using platinum cathode there were two different potential scanning rates studied stationary stirred/agitated conditions.

Platinum cathode is very good for kinetic studies because of his great stability. Unfortunately its price prohibits industrial applications, although when absolutely necessary can be used for cathode material.

For a thoroughly cleaning and good reproducibility, before the experiments platinum electrode was pre-polarized using 20% sulphuric acid solution, between 0-2000 mV potential.

All potentials are measured using the calomel saturate electrode (ESC). Working temperature was 22°C.

The influence of gallium ions concentration in processes on platinum cathode deposition is presented in figures 3 and 4.

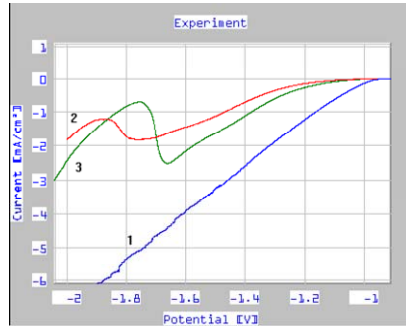


Figure 3. Cathodic curves on platinum, (first) base solution, without (1) and in presence gallium (2) at two different concentrations: 0.2% (2) and 0.9% (3).

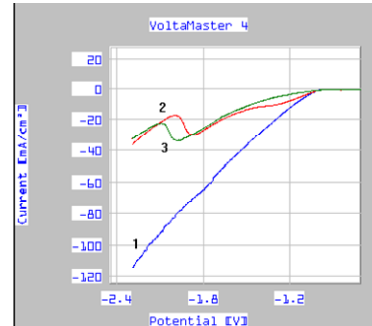


Figure 4. Cathodic curves on platinum, (second) base solution, 1M NaOH (1) with 0.6% Ga (2), 0.9% Ga (3); Scanning rate 50 mV/s.

Figure 5 are presented cathodic curves on Pt electrode; stationary and stirred conditions.

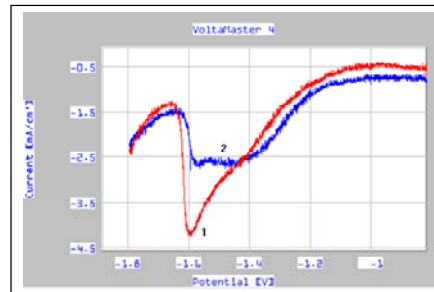


Figure 5. Cathodic curves on platinum, (second) base solution, 1M NaOH with 0.9% Ga (0.7 g gallium sulphate), Scanning rate 1 mV/s; (1) without and (2) with stirring.

Polarization rate change from 50 to 1 mV/s generates a reduction potential displacing to positive values.

Based on our studies, results of our experiments and the available laboratory technology, there were four electrolysis cells for electrochemical deposition of gallium by other methods that mercury cathode; were designed.

- Electrolysis cell using gallium liquid cathode
- Electrolysis cell using solid cathode (2 types)
- Electrolysis cell using stirred solid cathode
- Electrolysis cell using vibrated solid cathode

In case of gallium deposition on solid cathode, metallic gallium depositions will be

liquid, after accumulation on the cathode's surface it will form droplet that won't adhere will be collected on the bottom of the reactor.

Three sorts of electrolytic cells with solid cathode were made: with fixed cathode, with turning cathode and with vibrating cathode

In present work we present only the solid, vibrating electrode, schematically represented in figures 6, 7, 8.

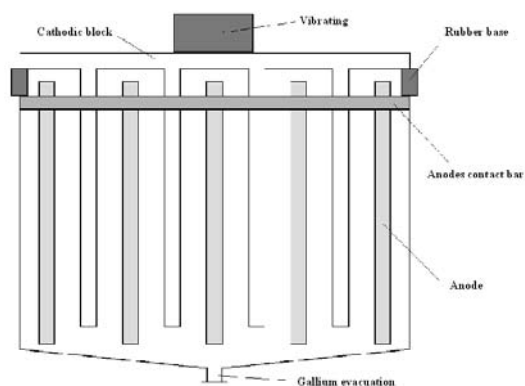


Figure 6. Electrolytic cell with solid vibrating cathode, front view.

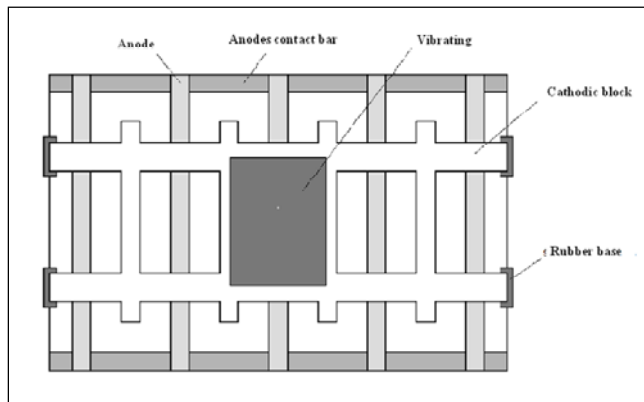


Figure 7. Electrolytic cell with solid vibrating cathode, top view.

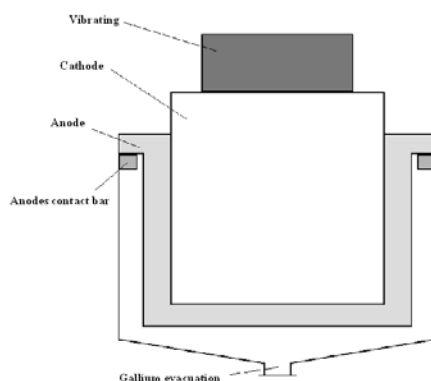


Figure. 8. Electrolytic cell with solid vibrating cathode, side view.

The anodes are connected by the anode contact bar. Anodes contact bars are assembled on the electrolytic cell borders. The vibrating unit is fixed on the cathodic block that rests on rubber supports fixed on the electrolytic cell border, which fade out the vibrations.

If is necessary de hydrogen may be captured. The solution resulted by hydrogen separation was recycled

RESULTS AND DISCUSSION

The cathode curves presented in figure 3, for platinum work-electrode, solution no. 1, composition mentioned earlier, as base-solution, in the presence (1) and in the absence (2 and 3) of gallium; at two different concentrations, 0.2 % (2) and 0.9 % (3). Also, figure 4 presents the cathode curves, for platinum work-electrode, solution no. 2, 1M NaOH (1), 0.6 % gallium (2) respectively 0.9 % (3); showing that the presence of gallium ions will modify the allure of base-lines, by the existence of cathodic peaks which tend to intensify as the concentrations of gallium increases. The hydrogen is formed at around -950 mV, also seen from the electrochemical curves and the reduction of gallium ions takes place at a more negative potential as the one where hydrogen is formed.

According to figure 5, the stationary conditions, [platinum work electrode, 1M NaOH base solution and 0.9 % gallium (0.7 g of gallium sulphate)] are compared to the stirred conditions; the effect of the stirred/agitated actions will increase the cathodic peak. The work parameters must assure the presence of electrochemical processes in the reactor, within the stability range of the metallic gallium; the cathode material, temperature, conductivity, inter-electrode distance, sufficiently negative electrode potential, must be

chosen, so that gallium will be deposited as metallic gallium, no oxidized or passivated gallium forms will occur and the hydrogen won't be able to evolve. By decreasing the inter electrode distances, the anodic drop is reduced and the current efficiency will be higher; although a too small inter electrode distance will cause problems due to the electrochemical reactor's dimensions and the risk of short circuits is much higher.

The pH value must be over 11.7, highly alkaline; in case the pH value drops below this value, a supplementary pH correction, must be added, by adding NaOH. The presence of concentrated NaOH won't disturb the Bayer process, the processing of bauxite is done at very alkaline conditions.

A very important parameter is the temperature, two values were proposed: 22 and 50 °C. The laboratory experiments were carried out at 22°C, because only synthetic solutions, at room temperature were used (not the solutions from the Bayer process). The solutions weren't heated; only the electrolysis experiments were carried out at precisely 22°C, thermostated conditions, for reproducibility and repeatability issues.

At 22°C, the electrochemically obtained metallic gallium is solid and adheres to the cathode; so if run sufficiently the cathode is gradually covered by metallic gallium, the electrolysis taking place on the surface of the gallium deposition, slightly decreasing the current efficiency, increasing the current consumption and, directly, the costs. For the laboratory pilot experiments, these inconveniences were not taken into consideration, the time of electrolysis is short and the related costs were negligible; although a higher temperature is needed to intensify the mass transfer on the cathode's surface. At the laboratory scale experiments the effect of relatively low temperature is compensated by extensive stirring of the base-solution. The deposited metallic gallium obtained at 50 °C is liquid, which will gather on the bottom of the reactor vessel or can be moved on the top of the solution as foam by the evolving hydrogen gas. On the industrial scale reactor, the electrode must be cleaned mechanically, in order to continuously remove the deposited metallic gallium so the electrochemically active surfaces will remain gallium free. Other advantages, of working at 50°C, are: the mass transfer to the electrode is intensified and the reaction speed increases (productivity increases), the solutions from the Bayer process won't have to be cooled to enter the reactor and reheated afterwards, before reentering the Bayer process. By moving the electrode, stirring, vibration or ultrasonication, or by increasing the temperature, an important parameter, the mass transfer to the electrode is intensified, necessary because of the Bayer process's low gallium content

CONCLUSION

From the above presented, we can conclude the followings:

The work parameters must assure the reactions from the reactor in the gallium's stability range.

The current parameters must be chosen so the potential of the electrode to be sufficiently negative, in order to achieve the deposition of metallic gallium before hydrogen gas evolves and also no gallium oxides or passivated gallium must be formed.

The pH value must be kept over 11.7.

In case of the laboratory experiments 22°C are sufficient; the electrodeposited gallium is solid and adheres to the cathode.

The mass transfer to the electrode is intensified by increasing the temperature (50 °C is the proposed value) or by stirring the electrolyte, by vibrating the work electrode, ultrasonication, etc.

The productivity of the various reactor types is different; the highest productivity is achieved by working with the vibrating electrode.

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