Electrochemical Characterization of Synthetic Basic Solutions with Ga and Al Content

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Using cyclic voltammetry method (CV), the electrochemical behaviour of Ga and Al like compounds, present in synthetic alkaline solutions with concentrations similar to sodium aluminates solutions resulted from Bayer process of bauxite processing, it was reported. This paper describes the electrochemical behaviour of Ga in NaOH, under the form of sodium galate, $NaGaO_2$, the electrochemical behaviour of Al like aluminium hydroxide, and also the electrochemical behaviour of Ga and Al in known concentrations of NaOH solutions. These investigations achieved by cyclic voltammetry were aimed to monitor the cementation process of gallium on gallium-aluminium alloy, by identifying the electrode potentials at which should be monitored the cementation process for a maximum yield in gallium recovery by proposed method.

Keywords: gallium, aluminium, alloy, cementation mechanism

Indigene and import bauxites processed by well known different procedures for the extraction of alumina, besides the main valuable components (Al_2O_3) also contained a series of accompanying elements, including gallium. In bauxite, the isomorphic Ga_2O_3 replace the Al_2O_3. Low content of this metal (Ga) in bauxite (an average of 0.005% Ga) is offset by the large amount of bauxite processed in industry to obtain Al_2O_3.

Currently, in the world [1-2] were developed some technologies for recovery of gallium starting from natural ores containing small amounts of gallium. By processing the bauxite at high temperatures (cca.220-240°C) and high pressure (around 30 atmospheres), according to Bayer process, main alumina and recently gallium can be recovered by new extraction methods such as the cementation method of Ga from sodium aluminate solutions by liquid Ga-Al alloy.

Under solubilisation conditions of bauxite, Ga_2O_3 content is dissolved in NaOH caustic solution forming meta-galic acid sodium salt, which goes largely in solution, forming sodium galate $NaGaO_2$ and in the same time Al_2O_3 is dissolved forming sodium aluminate.

$$Ga_2O_3 + 2NaOH + 3H_2O \Leftrightarrow 2Na[Ga(OH)_4] \qquad (1)$$

As the concentration of Ga_2O_3 in solution is much smaller than the Al_2O_3 in decomposition of alumina solutions, aluminium hydroxide $Al(OH)_3$ is precipitated before gallium hydroxide $Ga(OH)_3$ and mother solutions are richer in gallium. A small part of Ga_2O_3 remains open to attack in the solubilization process and another part is incorporated in red mud. Our team was concerned for the extraction of gallium from sodium aluminate solutions from Bayer process through cementation method of Ga-Al alloy containing 0.2 ÷ 6% Al.

Cementation method of Ga from sodium aluminate solutions with Ga-Al alloys (aluminium galame) is based on the normal potential difference between the systems [3]:

$$Al/Al(OH)_4^- = -2{,}35V \quad \text{and} \quad Ga/Ga(OH)_4^- = -1{,}22V \qquad (2)$$

General galium cementation reaction from sodium aluminate solutions with Al is the following:

$$Al + [Ga(OH)_4]^- \rightarrow Ga + [Al(OH)_4]^- \qquad (3)$$

The alloy necessary for cementation operation is obtained during cementation process so if the potential field is measured in the range -1.6 ÷ -1.8 V, aluminium is added in alloy cementation plant to main potential value of -2V, [4-6].

Experiments carried out by cyclic voltammetry technique are aimed to monitorize the gallium hardening process on gallium-aluminium alloy, to identify the driving electrode potential of gallium cementation process from aluminate solutions focused on achieving maximum efficiency in the recovery of gallium by proposed method.

Experimental part

In this paper, a typical installation of Cyclic Voltammetry (CV) with three electrodes was used:

- the working electrode was a Pt rod;
- the reference electrode was a Ag/AgCl electrode;
- as counter electrode was used an aluminium rod with 6mm Φ. The experiments were performed at room temperature, around 22^{0}C.

The experiments for performed investigations by cyclic voltammetry method were realized with a Volta lab galvanostat potentiostat, PST006-Education Model.

To determine the electrode potential, anode or cathode peak intensities, three scanning speeds of 50, 100, 200mV/s were used.

Cyclic voltammetry measurements were performed on synthetic solutions as follows:

- sodium hydroxide solution with 200g/L $Na_2O(S_0)$ content which was used as base;
- synthetic solutions with different Ga content;
- synthetic solutions of gallium and aluminium with similar chemical content to sodium aluminates solutions coming from industrial plant of bauxite processing using Bayer process.

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Table 1
CHEMICAL COMPOSITION OF THE BASIC SOLUTIONS

	U.M.	Chemical composition – Solutions of Ga with different concentrations										
	g/l	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
Ga	g/l	0,27	0,26	0,24	0,22	0,20	0,18	0,16	0,14	0,12	0,1	0,08
Na_2O	g/l	200	200	200	200	200	200	200	200	200	200	200

All the used chemicals are analysis pure reagents. For solutions obtaining, distillate water was used.

Results and discussions

Study of the cementation process monitoring from synthetic solutions with different Ga concentrations using cyclic voltammetry method

The chemical compositions of sodium galate synthetic solutions with different Ga [10] concentrations starting from 0.27g/L to 0.08g/L on which were performed the CV experiments are presented in table 1.

For synthetic solutions of sodium galate with different concentrations of Ga (0.27; 0.26; 0.24; 0.22; 0.20; 0.18; 0.16; 0.14; 0.12; 0.10; 0.08 g/L), typical cyclic voltammogram is represented in figure 1 for a concentration of 0.22 g/ L and in figure 2 for a concentration of 0.10 g / L. It is observed the cathode and anode peaks intensity increase with scanning rate increasing , the dependence between peak currents and square root of scanning speed is linear with the very good correlation coefficients demonstrating fast, reversible electrode reaction character, as theory predicts (fig. 3 for the concentration of 0.22g/L and fig. 4 for the concentration of 0.10 g/L).

Comparing the two cyclic voltammograms of Ga concentrations of 0.22 g/ L and 0.10 g/L, we can notice the two cathodic peaks at about -0.725 to 0.750 V and at about -0.9 V a cathodic peak increased on account of decreases of the less cathodic peak. The change of the appearance of the peak cathodic shoulder at -0.9 V to a little very pronounced and sharp decrease occurs simultaneously with Ga concentration in synthetic solutions.

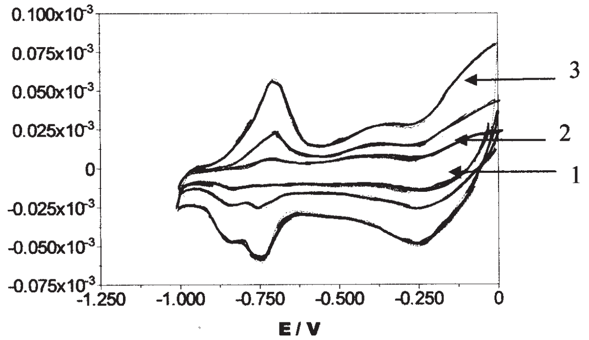

Fig. 1. Representation of Pt/Ga (0.22 g/L) superposition by CV, at speed of 50 mV/s (1-red cycle), 100 mV/s (2-blue cycle), 200 mV/s (3-green cycle), in the 0.0 – 1.0– 0.0V domain, first scanning is cathodic, second scanning is anodic for working electrode potential

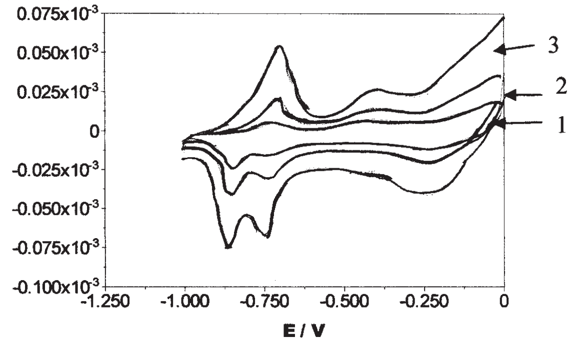

Fig. 2. Representation of Pt/Ga (0.22g/l) superposition by CV, at speed of 50 mV/s (1-red cycle), 100 mV/s (2-blue cycle), 200 mV/s (3-green cycle), in the 0.0 – 1.0– 0.0V domain, first scanning is cathodic, second scanning is anodic for working electrode potential

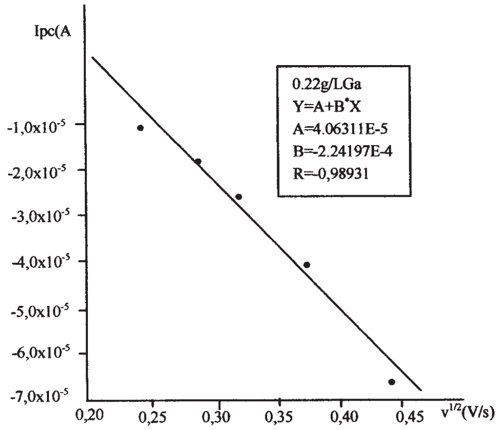

Fig. 3. Peak intensity representation from -0.7 V in function of square root of scanning speed for 0.22 g/L Ga

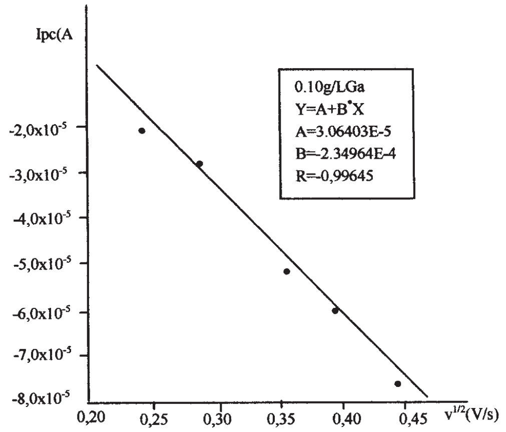

Fig. 4. Peak intensity representation from 0.7 V in function of square root of scanning speed for 0.10 g/L Ga

The data regarding the electrode potential values and cathodic peak intensities from 0.725-0.50V for all Ga concentrations from solutions used at scanning speed of 50mV/s, are presented in table 2.

Table 2
THE VALUES OF CATHODIC ELECTRODE POTENTIAL AND THE VALUES OF CATHODIC PEAK INTENSITY FOR DIFFERENT CONCENTRATIONS AT 50mV/s RATE

Concentration (g/L)	E_{pc} (V)	I_{pc} (A)
0.24 Ga	-0.736	-0.140e-4
0.22 Ga	-0.738	-0.012e-4
0.20 Ga	-0.741	-0.108e-4
0.18 Ga	-0.752	-0.219e-4
0.16 Ga	-0.752	-0.190e-4
0.14 Ga	-0.751	-0.190e-4
0.12 Ga	-0.747	-0.208e-4
0.10 Ga	-0.748	-0.234e-4
0.08 Ga	-0.731	-0.106e-4

Table 3
THE VALUES OF ANODIC AND CATHODIC ELECTRODE POTENTIAL AND THE VALUES OF ANODIC AND CATHODIC PEAK INTENSITIES AT VARIOUS Al_2O_3 CONCENTRATIONS FOR DIFFERENT RATES 50; 100; 200mV/s

Concentration (g/L) Al_2O_3	Speed (V/s)	E_{pa} (V)	I_{pa} (A)	E_{pc} (V)	I_{pc} (A)
62	0.05	-0.375	0.040e-3	-0.209	-0.150e-4
	0.1	-0.372	0.510e-4	-0.224	-0.287e-4
	0.2	-0.371	0.814e-4	-0.235	-0.561e-4
67	0.05	-0.358	0.008e-3	-0.236	-0.228e-4
	0.1	-0.361	0.016e-3	-0.239	-0.376e-4
	0.2	-0.357	0.286e-4	-0.247	-0.643e-4
72	0.05	-0.384	0.011e-3	-0.238	-0.015e-3
	0.1	-0.375	0.017e-3	-0.244	-0.028e-3
	0.2	-0.370	0.028e-3	-0.242	-0.052e-3
77	0.05	-0.380	0.091e-4	-0.247	-0.122e-4
	0.1	-0.370	0.146e-4	-0.244	-0.232e-4
	0.2	-0.384	0.246e-4	-0.236	-0.432e-4
82	0.05	-0.389	0.115e-4	-0.239	-0.098e-4
	0.1	-0.376	0.170e-4	-0.235	-0.203e-4
	0.2	-0.369	0.269e-4	-0.230	-0.398e-4
87	0.05	-0.378	0.117e-4	-0.230	-0.088e-4
	0.1	-0.373	0.175e-4	-0.222	-0.182e-4
	0.2	-0.355	0.275e-4	-0.219	-0.350e-4
92	0.05	-0.373	0.107e-4	-0.222	-0.075e-4
	0.1	-0.364	0.146e-4	-0.216	-0.166e-4
	0.2	-0.355	0.233e-4	-0.216	-0.327e-4
97	0.05	-0.373	0.088e-4	-0.219	-0.083e-4
	0.1	-0.363	0.131e-4	-0.205	-0.169e-4
	0.2	-0.356	0.210e-4	-0.202	-0.326e-4
102	0.05	-0.372	0.090e-4	-0.210	-0.081e-4
	0.1	-0.363	0.136e-4	-0.204	-0.157e-4
	0.2	-0.349	0.212e-4	-0.182	-0.307e-4

The electrode process monitoring study from synthetic solutions with different Al concentrations by cyclic voltammetry method

The experimental data regarding the anodic and cathodic electrode potential values, cathodic peak intensities and anodic peak intensities Ga concentrations from solutions used at scanning rate of 50,100,200 mV/s, are presented in table 3. Typical cyclic voltammetry for sodium aluminate synthetic solutions with Al_2O_3 content at different concentrations (62 – 67 – 72 – 77 – 82 – 87 – 92 – 97 – 102 g/L) is represented in figure 5 for the concentration of 67g/L Al_2O_3 and in figure 6 the representation for 97g/L.

It is observed the cathode and anode peaks intensity increase with increasing scanning rate, the dependence between peak currents and scanning speed radical is linear with the very good correlation coefficients demonstrating fast and reversible electrode reaction character, as cementation theory predicts (fig. 7 for the anodic peak for the concentration of 67g/L and figure 8 for the concentration of 97g /L).

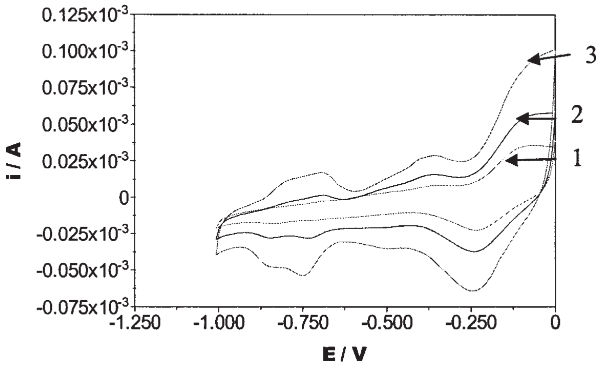

Fig. 5. Representation of Pt/Al (67g/l) superposition by CV, at speed of 50 mV/s (1-red cycle), 100 mV/s (2-blue cycle), 200 mV/s (3-green cycle), in the 0.0 – 1.0– 0.0V domain, first scanning is cathodic, second scanning is anodic for working electrode potential

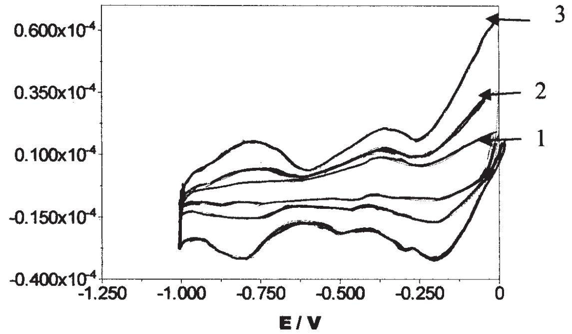

Fig. 6 Representation of Pt/Al (97g/l) superposition by CV, at speed of 50 mV/s (1-red cycle), 100 mV/s (2-blue cycle), 200 mV/s (3-green cycle), in the 0.0 – 1.0– 0.0V domain, first scanning is cathodic, second scanning is anodic of working electrode potential

The electrode process monitoring study from synthetic solutions of Al_2O_3 and Ga by cyclic voltammetry method

By cyclic voltammetry method (CV), the behaviour of a sodium aluminate solution was studied in sodium galate mixtures, synthetic mixtures with different Al_2O_3 and Ga [10]contents, with the following compositions: (1-red cycle) -62 g/L Al_2O_3 and 0.26g/L Ga; (2-blue cycle) – 87g/L Al_2O_3 and 0.18 g/L Ga, (3-green cycle) – 102g/L Al_2O_3 and 0.10g/L Ga, as in figure 9. The widest voltammogram was obtained for the mixture 62 g/L Al_2O_3 and 0.26 g/L Ga and less wide voltammogram for the mixture of 102 g/L Al_2O_3 and 0.10 g/L Ga.

The cyclic voltammogram superpositions of the following synthetic solutions are presented in figure 10: red cycle - Al_2O_3 (87 g/L) + Ga (0.18 g/L), green cycle - Al_2O_3 (87 g/L), blue cycle - Ga (0,18 g/L).

In comparison with the separated solutions containing only Al_2O_3 (87 g/L) and only Ga (0,18 g/L) respectively, at around -0.2V for the solution containing Al_2O_3 (87 g/L) + Ga (0,18 g/L) it can be observed the disappearance of cathodic peak. By comparing the solution containing only Ga(0.18g/L), with the solution containing Al_2O_3 (87 g/L) +

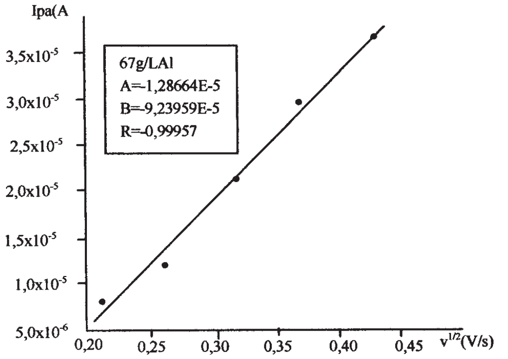

Fig.7. Anodic peak intensity representation in function of square root of scanning speed for Al_2O_3 concentration of 67 g/L

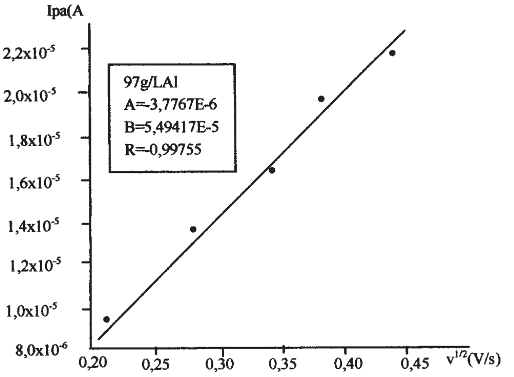

Fig.8. Anodic peak intensity representation in function of square root of scanning speed for Al_2O_3 concentration of 97 g/L

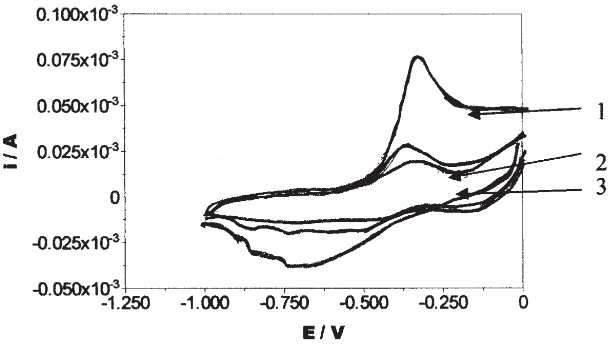

Fig. 9. Representation of cyclic voltammogram superposition for different mixtures of Al_2O_3 and Ga (1-red cycle), (Al2O3-2-blue and magenta cycle), (Ga -3-green cycle)

Ga (0.18g/L) both of them have the cathodic peaks from -0.725 to -0.75V and are practically disparent (only the cathodic peak seems to remain remnant and analogous, anodic peak from -0.7V existent in Ga solution 0.18g/L like a small peak and in Al_2O_3 solution (87g/L) like a small and large peak, this practically disappears in the case of Al_2O_3 solution (87g/L) + Ga(0.18g/L). In the cathodic region, the behaviour with more then -0.5V of the mix Al_2O_3 (87 g/L) + Ga (0.18 g/L) solution is significantly different of the one of separated solutions containing only Al_2O_3 (87 g/L) and Ga (0.18 g/L). One can see from figure 10 that in the cathodic region the peak is missing while the peak in the anodic region exists and presents a corresponding amplification.

In this less cathodic region, both for mixture solution and also for solutions separated by components, the both anodic and cathodic behaviour is different by the behaviour of a synthetic electrolytic solution insensitive to sodium hydroxide concentration (NaOH, 2 M), according to figure 11.

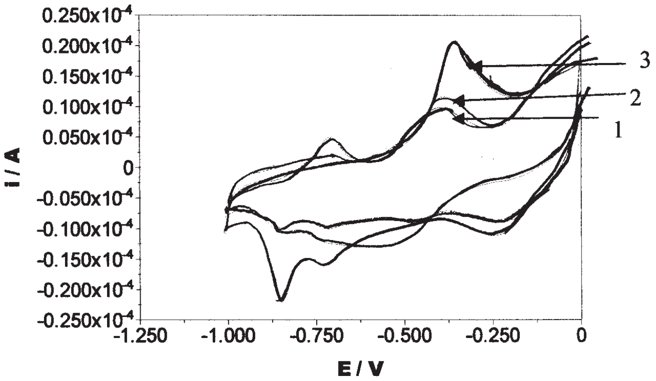

Fig. 10. Representation of cyclic voltammogram superposition for: 1- Pt/ Al_2O_3 (87 g/L) + Ga (0.18 g/L) red cycle (3), 2 - (Pt/ Al_2O_3 (87 g/L) green cycle (2) and 3 - Pt/Ga (0.18 g/L blue cycle (1), at speed of 50mV/s, in the 0.0 – 1.0– 0.0V domain

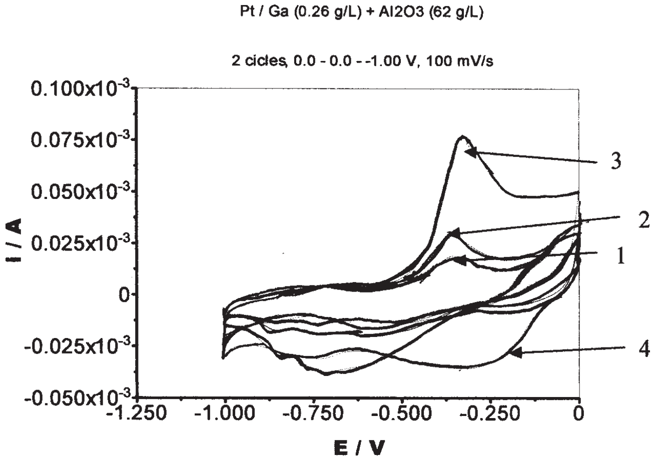

Fig. 11. Representation of CV superposition for: 1- Pt/ Al_2O_3 (87 g/L)+ Ga (0.18 g/L) red cycle (3), 2 - Pt/ Al_2O_3 (87 g/L) green cycle (2), 3 - Pt/Ga (0.18 g/L) blue cycle (1) and Pt/NaOH (2 M) magenta cycle (4), at rate of 50mV/s, in the 0.0 – 1.0– 0.0V domain

Conclusions

The results obtained in this work recommends the cyclic voltammetry method for cementation process monitoring and electrode potentials identification to which is necessary to monitor the process [7-8].

The electrochemical behaviour of Ga and Al (as compounds) was studied using cyclic voltammetry method using synthetic basic solutions and the anodic and cathodic electrode potenţial values (E_{pa}, E_{pc}) and anodic and cathodic peak intensity values (I_{pa}, I_{pc}) for different concentrations were determined.

By realizing this CV studies, it was performed the cementation process monitoring on synthetic solutions. The determinations were performed on different solutions according to initial, partial and final concentrations of Al and Ga liquid phase, simulating the component compositions from real solutions during cementation process.

Thus, it was proved and verified that the cementation system electrode potential has to be maintained in the range of -1.92V/-2V. If the potential reaches the value of -1.6V, the aluminium is added in alloy, [3;9].

During the cementation process, aluminium activation introduced in liquid Ga-Al alloy through intermediary pure Al working-road electrode take place. As consumption continues, this electrode advances through a directed and controled system. The aluminium activation unde anodic polarization can be controlled by a difusion type process which is given by aluminium difussion in liquid galium film, [6-7].

The E_{pa}, E_{pc},I_{pa} and Ipc values were determined through the experiments run for decreasing variable concentrations of Ga from 0.24g/L to 0.08g/L and increasing variable concentration of Al_2O_3 from 62g/L to 102g/L simulating the gallium extraction process through cementation method which involves Ga deposition in the reactor and Al from Ga-x%Al dissolving in the permanent basic solution for the duration of Ga extraction using the cementation method. The aluminium quantity dissolved from the alloy during the Ga extraction process can be permanently controlled and is advantageous for the return of enriched aluminat solution in the Bayer process. The I_{pa} values decrease from 0.510e^{-4}A (at 62g/L Al_2O_3) to 0,136e^{-4}A(at 102g/L Al_2O_3) for increasing aluminium concentration at 0,1V/s scanning rate, [3].

Furthermore, it should be intensified the study using CV method for more mixture solutions. Also, quantitative correlations from possible chemical reactions should be established; species quantities which are present in solution, in different mixtures should be mainly evaluated and afferent standards from electrochemical point of view should be established, [11].

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