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**APPLIED ELECTROCHEMISTRY  
AND CORROSION PROTECTION OF METALS**

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## Electrodialytic Purification of Calcium Gluconate

A. A. Konarev

*NIOPIK State Research Center, Federal State Unitary Enterprise, Moscow, Russia  
e-mail: konarev.niopik@gmail.com*

Received February 8, 2011

**Abstract**—Possibility of using the electrodialytic method for purification of calcium gluconate to remove sodium bromide was examined. The electro dialysis conditions were optimized.

**DOI:** 10.1134/S1070427212020103

Calcium gluconate is industrially produced by oxidation of glucose with sodium hypobromide formed as a result of electrochemical oxidation of sodium bromide (15–20 g l<sup>-1</sup>) on a graphite anode at current densities of 1.2–5.0 A dm<sup>-2</sup> and temperature of 20–40°C in the presence of CaCO<sub>3</sub> in a concentration of 5–7%, followed by crystallization of the target product and its washing with distilled water to remove sodium bromide [1].

One of bottlenecks of the industrial method for production of calcium gluconate is the stage in which residual sodium bromide is removed from calcium gluconate by its washing with distilled water. The washing of the target product to remove the inorganic salt is labor-consuming and poorly efficient, which is indicated by the large consumption of distilled water for this procedure (7–8 kg of distilled water per 1.0 kg of the product). The large amount of water used for washing of calcium gluconate results in an increase in its solubility, which diminishes the yield of the preparation to 30.0–40.0%. In addition, isolation of calcium gluconate from mother liquor and washing water is an energy-consuming process because large volumes of water are to be evaporated and the sodium bromide concentration is comparatively high.

To raise the yield of calcium gluconate in purification to remove sodium bromide, it seemed appropriate to examine the possibility of employing the electrodialytic purification technique. This method has been successfully used under industrial conditions at Kursk

bioplant in purification of tuberculin solutions to remove ammonium sulfate [2]; at Farmstandart-Leksredstva Open Joint-Stock Company (Kursk), this technique has been used during about 20 years for purification of taurine solutions to remove sodium sulfate and sulfite [3].

### EXPERIMENTAL

Reaction masses of calcium gluconate were obtained in a capacitive electrolyzer with graphite electrodes (cathode and anode), equipped with a stirrer and thermostating jacket. Glucose was oxidized at a temperature of 40°C and current density of 3.0 A dm<sup>-2</sup> in the presence of sodium bromide in a concentration of 15.5 g l<sup>-1</sup> and CaCO<sub>3</sub>. The electro-oxidation of glucose was considered complete when the concentration of calcium gluconate in solution reached a value of 215–220 g l<sup>-1</sup>. After being filtered to remove CaCO<sub>3</sub>, the calcium gluconate solution was subjected in portions to electrodialytic desalination to remove sodium bromide on a laboratory installation comprising an electrodialyzer, jacketed intermediate vessels for calcium gluconate and “concentrate” solutions, two phase separators, two gear pumps, current rectifier, control transformer, ammeter, voltmeter, and reinforced pipelines.

The laboratory electrodialyzer was a multiple-chamber apparatus of the filter-press design having MA-40 and MK-40 ion-exchange membranes with paronite intermediate frames and turbulizer separators.

**Table 1.** Effect of the amount of washing water on the yield of calcium gluconate.

Starting solution			Mother liquor			Washing filtrate			Yield of calcium gluconate, %
content, g l <sup>-1</sup>	solution volume, ml	volume of washing water, ml	content, g l <sup>-1</sup>	volume, ml	loss, %	content, g l <sup>-1</sup>	volume, ml	loss, %	
$\frac{165.0^a}{10.3}$	360	420 <sup>b</sup>	$\frac{71.5}{10.6}$	280	35.8	$\frac{40.6}{1.4}$	435	31.6	31.5–41.0
$\frac{165.0}{10.3}$	360	202	$\frac{70.0}{10.9}$	265	32.5	$\frac{31.1}{3.2}$	230	20.7	48.9 <sup>c</sup>

<sup>a</sup> Numerator, calcium gluconate; denominator, sodium bromide; the same for Tables 2–4.

<sup>b</sup> Volume of washing water conforming to regulations.

<sup>c</sup> Calcium gluconate not conforming to the requirements of FS.

**Table 2.** Purification of the calcium gluconate suspension by the electrodialytic method. Calcium gluconate concentration 165 g l<sup>-1</sup>; sodium bromide concentration 10.3 g l<sup>-1</sup>; reaction mass volume 350 ml; temperature 25–30°C; linear flow velocity of calcium gluconate, 4 cm s<sup>-1</sup>

Current density, A dm <sup>-2</sup>	Concentrate		Mother liquor with washing water <sup>a</sup>		Yield of calcium gluconate, %	Degree of purification, %
	content, g l <sup>-1</sup>	loss, %	content, g l <sup>-1</sup>	loss, %		
1.5	$\frac{44.0}{11.0}$	13.6	$\frac{41.0}{2.48}$	26.3	40.0	74.5
0.5	$\frac{40.6}{14.0}$	13.6	$\frac{59.2}{1.4}$	37.0	41.5	85.1
1.0	$\frac{48.4}{14.0}$	15.9	$\frac{63.3}{1.1}$	38.6	37.8	89.2
0.5	$\frac{33.1}{11.0}$	13.5	$\frac{74.0}{2.16}$	45.1	32.6	79.0

<sup>a</sup> Washing water constitutes 14 vol %.

A Kh18N10T stainless steel plate with a working surface area of 1.0 dm<sup>2</sup> served as the cathode, and a platinum-plated titanium with the same surface area, as the anode.

The laboratory electrodialyzer comprised 6 anion-exchange and 7 cation-exchange membranes forming 6 “purification” chambers, 7 “concentration” chambers, and two electrode chambers. The working surface area of each membrane was 1.0 dm<sup>2</sup>, with the distance between the membranes being 1.5 mm. The total working surface area of the membranes was 12 dm<sup>2</sup>.

Solutions of calcium gluconate and isolated preparation were analyzed in conformity with FS (Pharmacopeia article) no. 121 [4].

The results obtained on washing calcium gluconate with distilled water to remove sodium bromide are presented in Table 1, whence it can be seen that the yield of calcium gluconate strongly depends on the amount of washing water. In washing of calcium gluconate with distilled water by the presently used technique is 31.5–41.0%, with the loss of the product in the mother liquor and washing water being 32.5–35.8 and 31.6%, respectively.

The yield of calcium gluconate increases if the amount of washing water is diminished, but its quality fails to meet the requirements of FS no. 121 [4].

The reaction mass of calcium gluconate, subjected

**Table 3.** Effect of the current density on the electrodialysis of a calcium gluconate solution. Linear flow velocity of the calcium gluconate solution,  $3.0 \text{ cm s}^{-1}$ ; calcium gluconate concentration  $218 \text{ g l}^{-1}$ ; sodium bromide concentration  $15.2 \text{ g l}^{-1}$ ; temperature  $20\text{--}30^\circ\text{C}$

Current density, $\text{A dm}^{-2}$	Yield of calcium gluconate, %	Current efficiency by calcium gluconate, %	Degree of desalination, %	Energy consumption, $\text{W h kg}^{-1}$	Specific throughput, $\text{kg m}^{-2} \text{ h}^{-1}$
0.15	55.0	60.0	91.5	75.0	0.45
0.25	51.5	53.6	91.9	126.0	0.50
0.50	50.3	42.4	91.7	340.0	0.76
1.00	46.2	39.8	86.2	716.0	1.40
1.50	35.0	30.0	85.2	800.0	1.95

to electrodialytic desalination to remove sodium bromide, was a suspension or a solution. The results of desalination of the calcium gluconate suspension are presented in Table 2.

It can be seen in Table 2 that sodium bromide can be removed from the calcium gluconate suspension by electrodialysis, with a 32.6–41.5% yield of the target product, depending on the process conditions. An increase in the yield of calcium gluconate is favored by lowering the current density and the degree of desalination. It was found that at degrees of desalination of 85.0–90.0%, the sodium bromide concentration in the mother liquor is  $1.1\text{--}1.4 \text{ g l}^{-1}$  and calcium gluconate isolated from solution meets the requirements of FS no. 121 in the content of bromides [4].

In electrodialytic desalination, not only sodium bromide, but also calcium gluconate pass into the concentrate, with the loss of calcium gluconate being 13.5–17.0%. However, the whole amount of the concentrate can be used to prepare the electrolyte in the stage of electrochemical oxidation of glucose, because the concentration of sodium bromide is  $11.0\text{--}14.0 \text{ g l}^{-1}$  and, when necessary, the electrolyte can be adjusted.

It was found in electrodialytic desalination of the calcium gluconate suspension that the process is unstable, which is manifested in the unsatisfactory reproducibility of the results. The reason is that using the suspension leads to mechanical loss of the product (10.0–20.0%) in the purification chambers of the electrodialyzer. In addition, the solid phase of calcium gluconate hinders transfer of ions across the membranes and circulation of the suspension through the electrodialyzer.

These shortcomings were eliminated by using

electrodialysis of calcium gluconate solutions, instead of suspensions. The results obtained in purification of calcium gluconate solutions to remove sodium bromide are presented in Tables 3 and 4.

It can be seen in Tables 3 and 4 that the yield of calcium gluconate and the current efficiency by this compound noticeably decrease with increasing current density. In addition, this also makes markedly higher the power consumption by the process. The yield of the target product also falls with increasing degree of desalination of the calcium gluconate solution.

The study demonstrated that, as in the case of a suspension, desalination of the calcium gluconate solution should be performed to a residual concentration of sodium bromide not exceeding  $1.4 \text{ g l}^{-1}$ . At higher salt concentrations in solution, calcium gluconate fails to satisfy the requirements of FS no. 121 [4] in the content of bromides.

As a result of the study, the conditions of electrodialytic desalination of calcium gluconate solutions containing  $218\text{--}220 \text{ g l}^{-1}$  of calcium gluconate and  $15.2 \text{ g l}^{-1}$  of sodium bromide were found: current density  $0.25\text{--}0.50 \text{ A dm}^{-2}$ ; temperature  $20\text{--}35^\circ\text{C}$ ; linear flow velocity of the calcium gluconate solution,  $3.0 \text{ cm s}^{-1}$ ; and degree of desalination, 91.9–92.0%. Under these conditions, the yield of calcium gluconate is 55.0–57.5% against 42.0% for the existing technique, the energy consumption by the process was  $126\text{--}340 \text{ W h kg}^{-1}$ , and the specific throughput of the electrodialyzer is  $0.5\text{--}0.7 \text{ kg m}^{-2} \text{ h}^{-1}$ .

As follows from the data presented in Tables 1 and 4, the sodium bromide concentration in the mother liquor with washing water, obtained upon electrodialytic desalination of calcium gluconate solutions, is

**Table 4.** Purification of a calcium gluconate solution to remove sodium bromide by the electrodiolytic method. Linear flow velocity of the calcium gluconate solution,  $3.0 \text{ cm s}^{-1}$ ; calcium gluconate concentration  $218 \text{ g l}^{-1}$ ; sodium bromide concentration  $15.2 \text{ g l}^{-1}$ ; temperature  $20\text{--}35^\circ\text{C}$

Current density, $\text{A dm}^{-2}$	Concentrate		Mother liquor with washing water <sup>a</sup>		Yield of calcium gluconate, %	Degree of purification, %
	content, $\text{g l}^{-1}$	loss, %	content, $\text{g l}^{-1}$	loss, %		
0.5	$\frac{25.6}{10.2}$	6.2	$\frac{55.8}{10.3}$	24.1	69.5	36.5
0.5	$\frac{33.6}{18.8}$	7.8	$\frac{63.7}{7.6}$	23.4	66.8	60.2
0.5	$\frac{53.4}{22.2}$	12.7	$\frac{72.8}{4.5}$	27.7	59.4	75.4
0.5	$\frac{59.2}{27.2}$	13.8	$\frac{58.9}{2.7}$	21.8	58.3	85.8
1.0	$\frac{79.4}{28.3}$	19.9	$\frac{60.5}{2.45}$	24.3	52.0	86.0
0.5	$\frac{65.9}{24.6}$	16.5	$\frac{57.2}{1.4}$	22.9	55.0	91.2
0.25	$\frac{61.9}{26.2}$	15.6	$\frac{52.7}{1.37}$	21.2	57.5	91.8

9–10 times lower than that required by technological regulations, which simplifies recovery from the target product from this solution. In addition, the amount of distilled washing water becomes 6–7 times smaller in this case and the deficient sodium bromide is recycled into the process.

### CONCLUSIONS

(1) A preparative electrodiolytic method was developed for purification of calcium gluconate solutions to remove sodium bromide with concentrations of up to  $15.2 \text{ g l}^{-1}$ .

(2) The developed electrodiolytic method for

purification of calcium gluconate solutions can raise the yield of the preparation to 55.0–57.5%. With the possible use of the concentrate and processing of the mother liquor, the yield of calcium gluconate may become as high as 70.0%.

### REFERENCES

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