# **Electrochemical Removal of Beryllium from Acid Process Solutions**

Sergey S. Kruglikov, Dmitri Yu. Turaev, Nadezhda Kolotovkina & Natalia A. Andrianova, S.S. Kruglikov Consultants, Moscow, Russia

Acid process solutions used in the surface treatment of beryllium containing copper-based alloys (beryllium bronze) gradually accumulate beryllium ions. Therefore, they are contained both in rinse waters and spent process solutions. A process has been developed which eliminates the periodic dumping of spent process solutions and considerably reduces beryllium ion input into the rinse tanks. A three-compartment cell with cationic membranes is used for the removal of beryllium cations from hydrochloric-hexamethylene tetramine solutions and a two-compartment cell with one cationic membrane is used with a mixture of chromic and sulfuric acids for the same purpose as well as for the anodic oxidation of trivalent chromium back to chromic acid.

### For more information, contact:

Prof. Sergei S. Kruglikov Bolshaya Spasskaya, 33-107, Moscow, 129090, Russia Phone/Fax: +7-095-680-0281 Mob. phone: +7-916-616-9699 e-mail: mhasina@mail.ru

#### Introduction

Parts made of beryllium bronze (copper-based alloys containing 2 to 2.5 % of beryllium) are treated in various solutions. Partial dissolution of surface layer in the course of such treatment leads to the accumulation of copper and beryllium ions in these solutions and in corresponding rinse water. Therefore there are two sources of the input of beryllium ions into waste water: (a) spent process solutions and (b) waste water from rinsing tanks. Regeneration of beryllium ion the course of the operation of such solutions may reduce considerably its input into rinse water. Additional reduction can be achieved by introducing a reclaim tank as a first rinsing step after the treatment of parts in the process solution. Beryllium ions are removed from the reclaim tank in the same way as from the process solution. A combination of the regeneration of process solutions and the removal of beryllium ions from both process solutions and reclaim tanks may prevent beryllium contamination of waste water in the surface treatment operations.

Membrane electrolysis has been used in the present study for the regeneration of chromatebased solutions (A) and for the removal of beryllium ions from such solutions and from rinse water in the reclaim tank.

Second type of beryllium containing solution (B) studied was a hydrochloric-hexamethylene tetramine solution also used in industry for the surface treatment of beryllium bronze.

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Components, g/l	А	В
CrO <sub>3</sub>	70	-
H <sub>2</sub> SO <sub>4</sub>	10-20	-
- ĤCI	-	220
Hexamethylene tetramine	-	40-50

### **Experimental Procedure**

Basic composition of two process solutions is given in Table 1:

Initial concentration of beryllium in solutions varied from 0.0014 to 10 g/l. Such wide range of concentrations allows to represent both actual process solutions and solutions in the reclaim tanks. Sulfuric acid (1N) was used as an auxiliary solution. Two types of cells were used for the experiments.

A two-chamber cell with the cationic membrane was used for the removal of beryllium and simultaneous regeneration of the chromate-based solution (A) (Fig. 1). Cathode and anode chambers contained 50 ml of solutions. Copper and lead plates  $(12 \text{ cm}^2)$  were used as the cathode and the anode.

Regeneration of solution (A) includes the removal of cupric ions from the solution and anodic oxidation of  $Cr^{3+}$  into chromate and is accompanied by the formation of free acid (H<sup>+</sup>-ions).



Fig. 1. Removal of beryllium from the chromate-based solution.

The process in the reclaim tank does not differ principally from that in the chromatetreatment tank, since in the long-term operation the composition of these solutions will differ only with respect to the concentrations of cupric and beryllium ions.

A three-chamber cell with two cationic membranes (Fig. 2) was used for the chloride-based solution (B) and corresponding reclaim tank. Cathode and anode compartments contained 30 ml of the auxiliary solution. Copper plate (8 cm<sup>2</sup>) and graphite rod ( $\sim$ 10 cm<sup>2</sup>) were used as the cathode and the anode.

Beryllium and cupric ions migrate into the cathode compartment. Chloride and sulfate ions practically do not take part in the migration between the process solution and the two auxiliary solutions since the cathode and the anode compartments are separated from the process solution by the cationic membranes.

It should be noted that the same composition of the auxiliary solution in all experiments is more convenient for the comparative evaluation of the rates of beryllium removal from different solutions. For practical use the composition of each auxiliary solution should be optimized with respect to both the nature of the chemicals and their concentrations. For example, lower concentrations of sulfuric acid in the catholyte will facilitate the transfer of all cations (including beryllium ones) from the chromate-based process solutions and corresponding reclaim tank.



Fig. 2. Removal of beryllium from solution B.

For the three-chamber cell hydrochloric acid instead of sulfuric acid should be used in the catholyte in order to exclude completely sulfate contamination of the process solution. Optimum concentration of sulfuric acid in the anolyte should be determined afterwards on the principle of equalizing the rates of transfer of hydrogen ions to and from the intermediate compartment. However all these modifications in the composition of auxiliary solutions will not change principal conclusions from the date given below.

### **Results and discussion**

Experimental data on the removal of beryllium ions from the chromate solution (A) are given in Table 2.

Concentration of beryllium, g/l		Electric charge	Removal rate of
initial	final	passed, Ah/l	beryllium, mg/Ahr
0.0023	0.0017	68	0.0088
1.50	1.08	41	10
1.58	1.43	34	6.1
2.96	1.95	71	14.1
8.26	6.44	55	32.8

Concentration of beryllium ions in a given solution is a major parameter, which determines the rate of removal. The mechanism of the removal process is an electrolytic migration through the membrane. Each type of ions contained in a solution is characterized by its particular transport number:

$$t_{j} = \frac{\left|z_{j}\right|c_{j}u_{j}}{\sum\left|z_{j}\right|c_{i}u_{i}}$$

(1).

Here t<sub>j</sub> is the transport number,  $z_j$  is the formal charge of the ion,  $u_i$  is its mobility and  $c_j$  is its molar concentration. The rate of the transfer through the membrane is always equal to the rate of ions migration,  $U_{M}$ :

$$U_{\rm M} = \frac{M \cdot I}{|z_j|F} t_{\rm j}, g/hr$$
(2).
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(2).

Here M is the molecular mass of the ion, I is electric current, A, and F is the Faraday's number, Ahr.

By combining equations (1) u (2) we obtain:

$$\mathbf{U}_{\mathrm{M}} = \frac{\mathbf{M} \cdot \mathbf{I}}{\left|\mathbf{z}_{\mathrm{j}}\right| \mathbf{F}} \cdot \frac{\left|\mathbf{z}_{\mathrm{j}}\right| \mathbf{c}_{\mathrm{j}} \mathbf{u}_{\mathrm{j}}}{\sum \left|\mathbf{z}\right| \mathbf{cu}}$$
(3).

It should be taken into account that the actual concentrations of different ionic species in the equation (3) may differ from corresponding values calculated on the assumption of a complete dissociation. For example, the composition of the solutions of chromic acid is usually expressed in terms of  $CrO_3$  content, i.e. nonionic chromic anhydride. In fact, such solutions contain a combination of several different ions, e.g.  $CrO_4^{2-}$ ,  $Cr_2O_7^{2-}$ . Apart from that ionic mobilities are not constants and vary depending on the overall composition of the solution. Therefore the accuracy of equation (1) should be proved experimentally for every particular system. Experimental transport numbers were calculated for beryllium ions in the following way from the data in Table 2:

$$t_{Be} = \frac{U_{Be} \cdot 1000 \cdot 26,8}{M_{Be}/2}$$

(4).

Here  $U_{Be}$  is the rate of beryllium removal, given in Table 2,  $M_{Be}$  is beryllium atom mass expressed in relative atomic units ( $M_{Be}$ =9).

Calculated transport numbers turned to be in good agreement with theoretical predictions (Fig. 3) over very wide range of beryllium concentrations.

Concentration of beryllium, g/l		Electric charge	Removal rate of
initial	final	passed, Ah/l	beryllium, mg/Ahr
1.53	1.32	36	5.9
2.57	2.18	29	13
3.17	2.6	46	12
9.73	7.84	45	41

Similar data on the removal of beryllium from chloride solution are given in Table 3.



Fig. 3. Transport number of beryllium ions in the process of migration from the chromate solution.



*Fig. 4. Transport number of beryllium ions in the process of migration from hydrochloric-hexamethylene tetramine solution.* 

Calculated transport numbers for beryllium are shown in Fig. 4. They change proportionally to the concentration of beryllium in the solution (Fig. 4). Thus, for both solutions studied (and for every new beryllium-containing process solution or solution in a reclaim tank) it is possible to calculate in advance the rate of removal and to create conditions for maintaining the concentration of beryllium ions below prescribed level. This means that it is possible to keep under control the input of beryllium into waste water in the plating shop. The only initial information needed is the input of beryllium into the corresponding process solution. As soon as its is known following sequence of calculations can be applied:

1. Let the input is equal to 0.1 g/hr and the acceptable maximum steady-state concentration of beryllium in the process solution is equal to 1 g/l.

2. The removal rate is assumed to be equal to 5 mg/Ahr at the concentration of 1 g/l.

3. For a desirable concentration and the input of beryllium equal to 0.1 g/hr required current is equal to 20 A. In case of 10 times lower steady-state concentration other conditions being constant required current will be 10 times higher.

## Conclusions

- 1. Beryllium ions can be removed from process solutions and reclaim tanks by electrolytic transfer through cationic membranes.
- 2. Removal rate is directly proportional to the concentration of beryllium ions and current which passes through the cell.
- 3. Specific consumption of electric energy depends on the desirable steady-state concentration of beryllium in the process solution.