The Use of Anionic Membranes for the Removal of Cationic Impurities from Chromium Plating Solutions

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Iron and other cationic impurities are usually removed from conventional chromium plating solutions by the electrolytic transfer through cationic membranes. This process is characterized by relatively high specific energy consumption due to very low transport numbers of cationic impurities. A reversed process is based on the recovery of pure chromic acid from contaminated solutions by the electrolytic transfer of chromate ions through an anionic membrane. This process is characterized by lower energy consumption and is especially efficient, when it is combined with the use of reclaim tanks in the chromium plating line. Anodic half-cells with anionic membranes are installed directly in these reclaim tanks and are used for the recovery and concentrating of chromic acid free of any cationic impurities.

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1. Introduction

Conventional chromium plating baths should be purified from cationic impurities such as ferric or cupric ions. These impurities can be removed by an electrolytic transfer through cationic membranes. Since the concentration of chromic acid in conventional baths is very high - 250 g/l as CrO_3, about 99 % of electric charge which passed through the cell is transferred through the cationic membrane by hydrogen ions and only small part - by metal cations. This explains very low efficiency of the membrane electrolysis in this particular case.

Recuperation of chromic acid from solutions containing cationic impurities seems more promising due to higher efficiency of the transfer process.

Multistage countercurrent rinsing is often used in chromium plating lines. In these rinsing systems all ions dragged out from tanks with plated parts are returned back. Therefore, recuperation of chromic acid free of cationic impurities can be applied not only to plating solutions but also to diluted solutions in rinsing tanks.

A comparative evaluation of above-mentioned methods of separation of chromic acid and cationic impurities is given below.

2. Direct Removal of Metal Cations

A two-chamber cell with cationic membrane (Fig. 1) was used for the removal of cationic impurities from hard-chromium plating solution (250 g/l CrO_3).

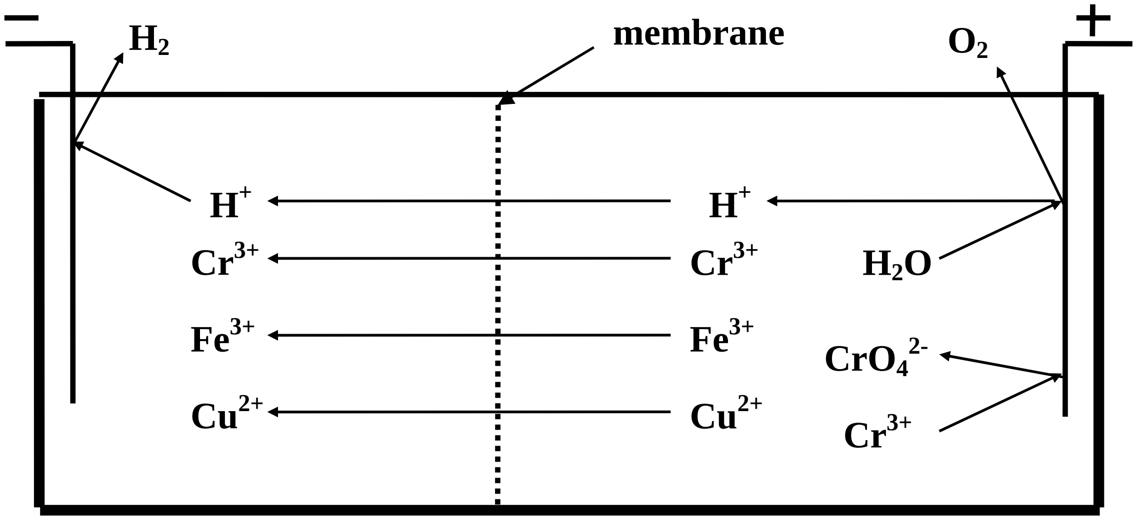

Fig. 1. Two-chamber cell for the purification of chromium plating solution.

Lead anode and stainless steel cathode were used for the purification process. Some part of Cr^{3+} is oxidized at the anode:

$$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e^- \quad (1),$$

and another (much smaller) part passes through the membrane into the auxiliary catholyte solution. Due to very low transport numbers of metal cations in the cationic membrane the rate of their removal is relatively low (Fig. 2).

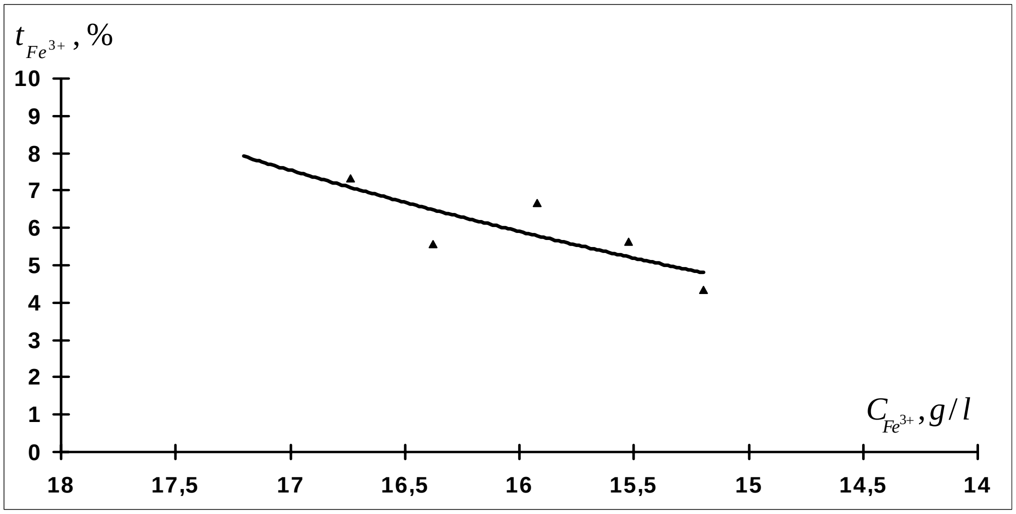

Fig. 2. Effect of the concentration of Fe^{3+} (g/l) in chromium plating solution (250 g/l) on the transport number (in %) of ferric ions through the cationic membrane.

Therefore specific energy consumption for the removal of iron is very high, especially of lower concentrations of the impurity (Fig. 3).

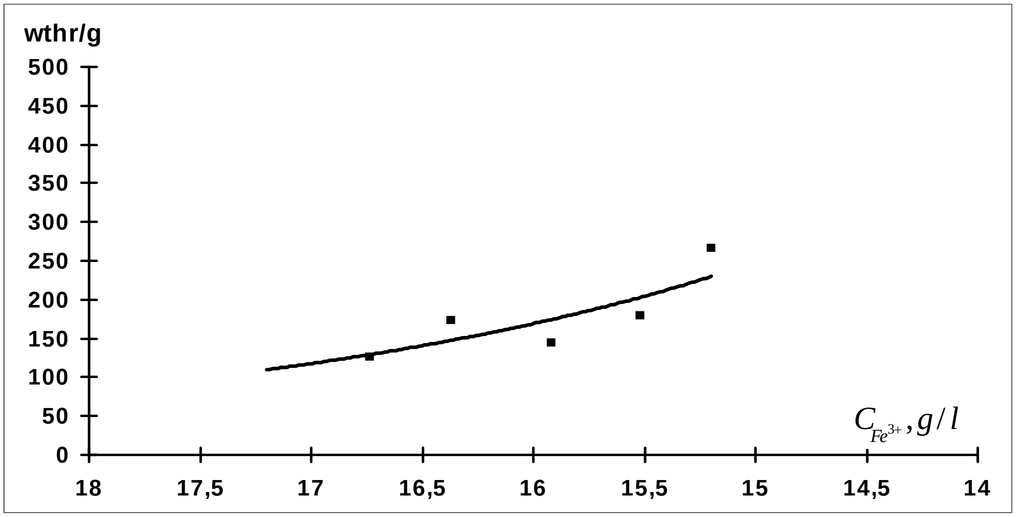

Fig. 3. Specific energy consumption for the removal of 1 g of Fe^{3+} from the chromium plating solution (250 g/l CrO_3).

3.Recuperation of chromic acid from reclaim tanks and spent solutions

Spent chromium plating solutions containing too much iron and other cationic impurities as well as reclaim tanks installed in chromium plating lines are good objects for the application of the electrolytic transfer of chromate ions from solutions containing metal cations. There are two modifications of this process: (1) the cathode is installed directly in the chromate-containing solution (Fig. 4); and (2) the cathode is separated from the chromate-containing solution by the cationic membrane.

3.1. Two-chamber cell

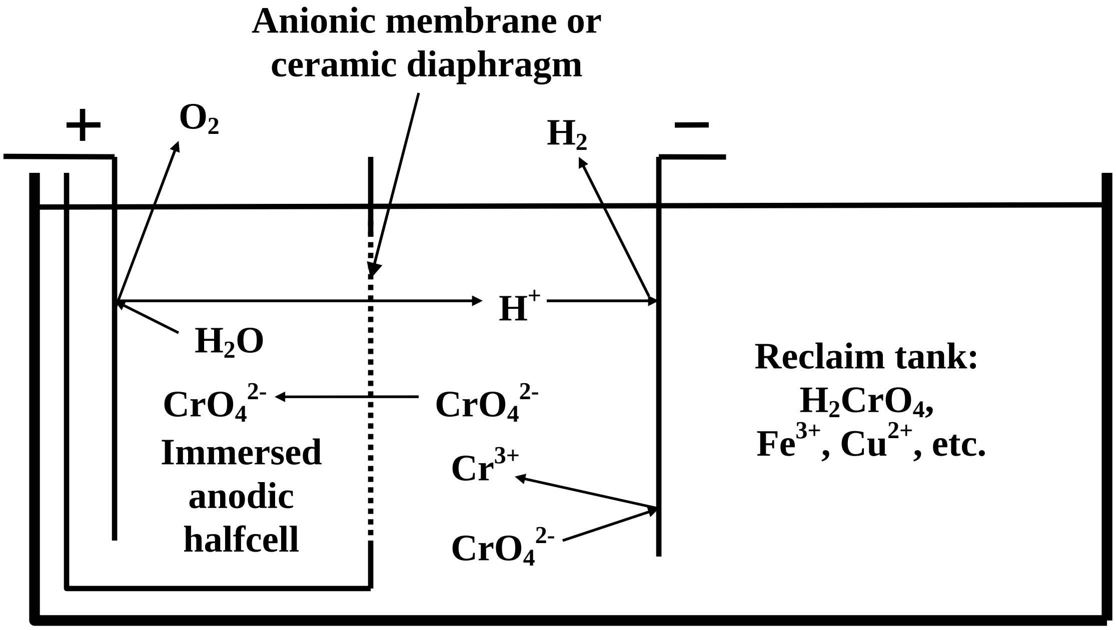

Fig. 4. Reclaim tank installed in the chromium plating line.

Concentration of chromic acid inside the anodic halfcell is increasing in the course of electrolysis. However, the rate of the transfer of chromate ions through the membrane or diaphragm is gradually decreasing due to the diffusion process in the opposite direction. Therefore experimentally measured (so called ”apparent”) transport numbers of chromate ions are decreasing with increasing difference between the concentrations of chromate (expressed as CrO_3) in the anolyte and in the catholyte (Fig. 5). Considerable part of chromate contained in the reclaim tank is reduced at the cathode into Cr^{3+}. Current efficiency of this process, and thus relative loss of hexavalent chromium, depends on the concentration of chromate in the catholyte (Fig. 6).

Apart from the discharge at the cathode hydrogen ions are also consumed in the reduction reaction:

$CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$ (2).

If the input of hydrogen ions by the transfer from the anolyte and with dragged-in plating solution is insufficient to compensate their consumption by the cathodic discharge and reaction (2), the pH value in the reclaim tank will gradually increase resulting in the precipitation of chromate of heavy metals (including chromate salts of trivalent chromium and iron).

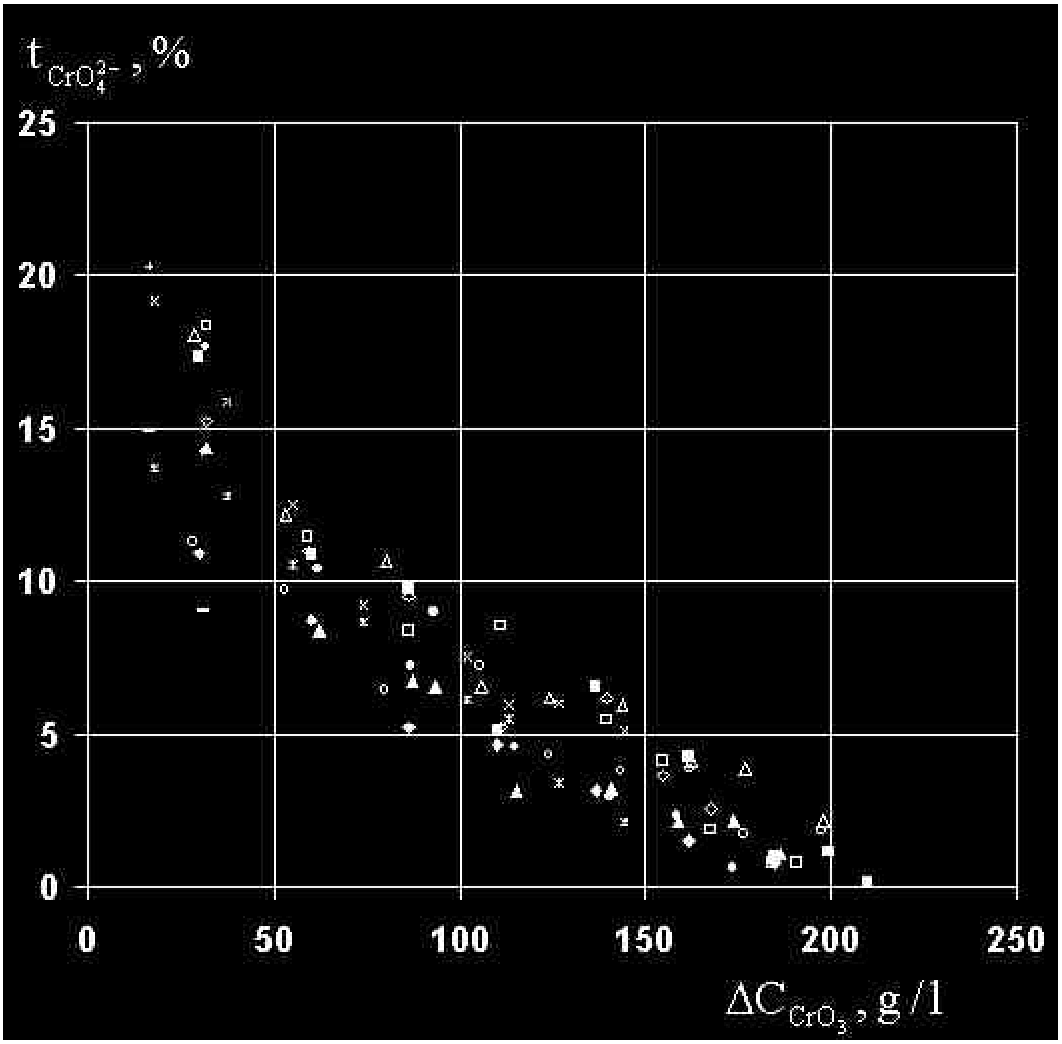

Fig. 5. Effect of the difference between the concentrations of CrO_3 *in the anolyte and in the catholyte on the apparent transport number of chromate ions. Experiments with ceramic diaphragm.*

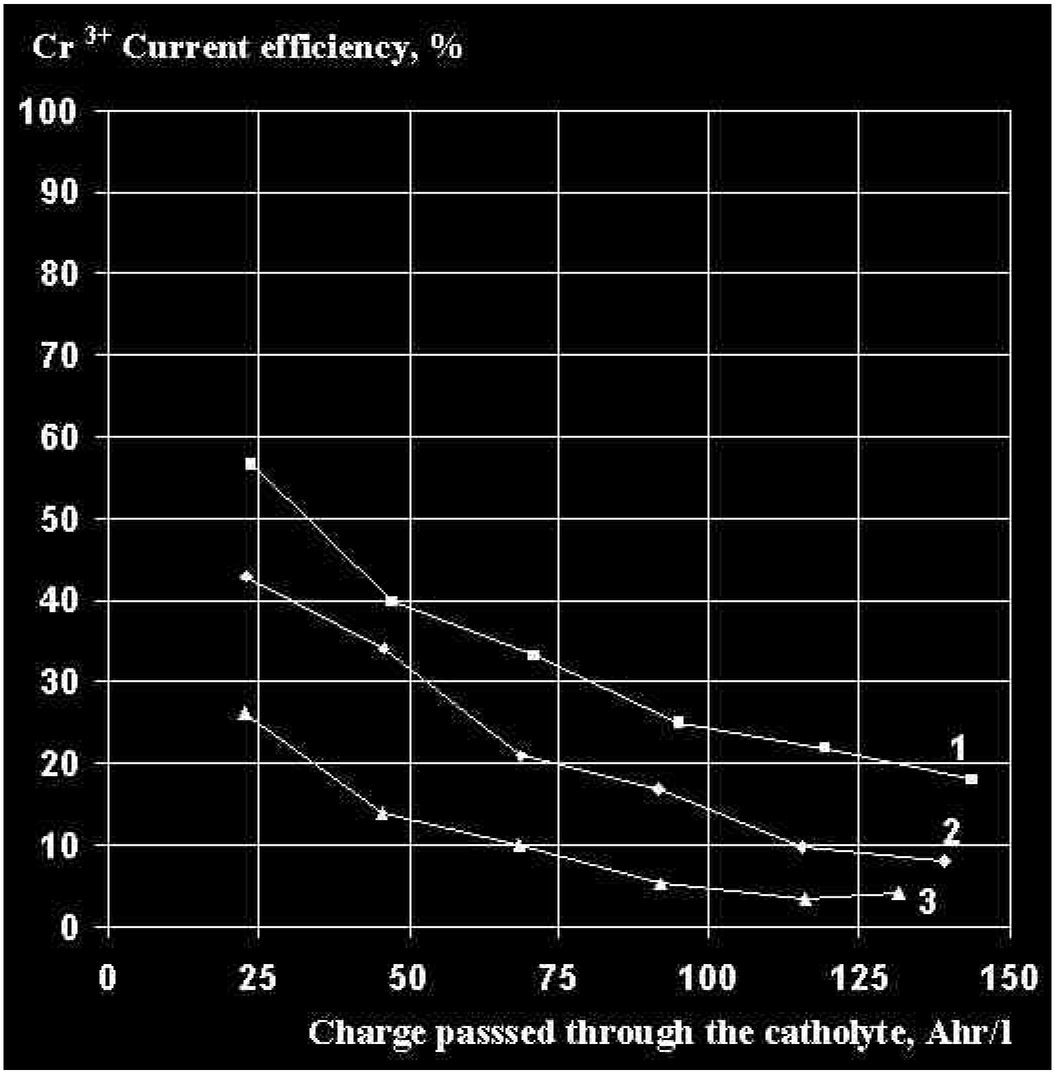

Fig. 6. Current efficiency of Cr^{3+} *as a function of electric charge, passed through the catholyte.*
1, CrO_3 *250 g/l,* H_2SO_4 *2.53 g/l;*
2, CrO_3 *146 g/l,* H_2SO_4 *1.46 g/l;*
3, CrO_3 *50 g/l,* H_2SO_4 *0.50 g/l;*

Taking into account the losses of hexavalent chromium by cathodic reduction and possible precipitation (at higher pH) the recuperation of chromate from reclaim tanks or spent chromium plating solution using two-chamber cells should be considered inefficient economically.

3.2. Three-chamber cell

Three-chamber cell (Fig. 7) eliminates losses of chromate caused by cathodic reduction and by the precipitation of chromates from the catholyte. Data on specific consumption of electric energy in the three-chamber cell are given in Fig. 8.

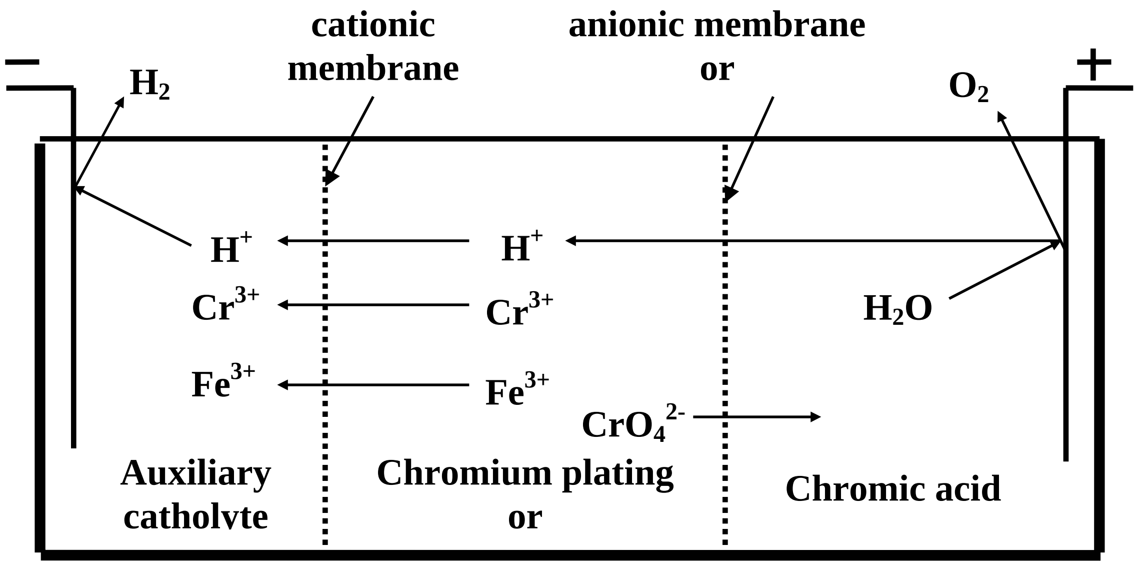

Fig. 7. Three-chamber cell for the recovery of chromic acid from spent chromium plating solution and reclaim tanks in chromium plating lines.

It follows from the data in Fig. 8 that the specific consumption of energy might be considered acceptable (around 15 wthrs/g), if the accumulation of CrO_3 in the anolyte does not exceed its concentration in the spent solution (or reclaim tank) by more than 50 g/l. This means that several stages of membrane electrolysis should be used, if an overall difference between the initial and final concentrations is more than 30-50 g/l (Fig. 9). Concentration of chromic acid in the solution which passed through the intermediate compartments 1 to 7 is gradually decreasing. Concentration of chromic acid in the anodic compartments 1’ to 7’ is gradually increasing. The overall fluid flow values through each series of compartments are established on the basis of desirable CrO_3 concentrations in the solutions outlets in chamber 7 and 7’. If we take as an example the conventional chromium plating solution (CrO_3 250 g/l) which needs regeneration due to excessive bult-up of iron, then we will have average differences in the CrO_3 concentrations between the solution 1’ and 7, 2’ and 6, etc. equal to $250/7 \approx 36$ g/l which seems to be quite acceptable (See Fig. 8).

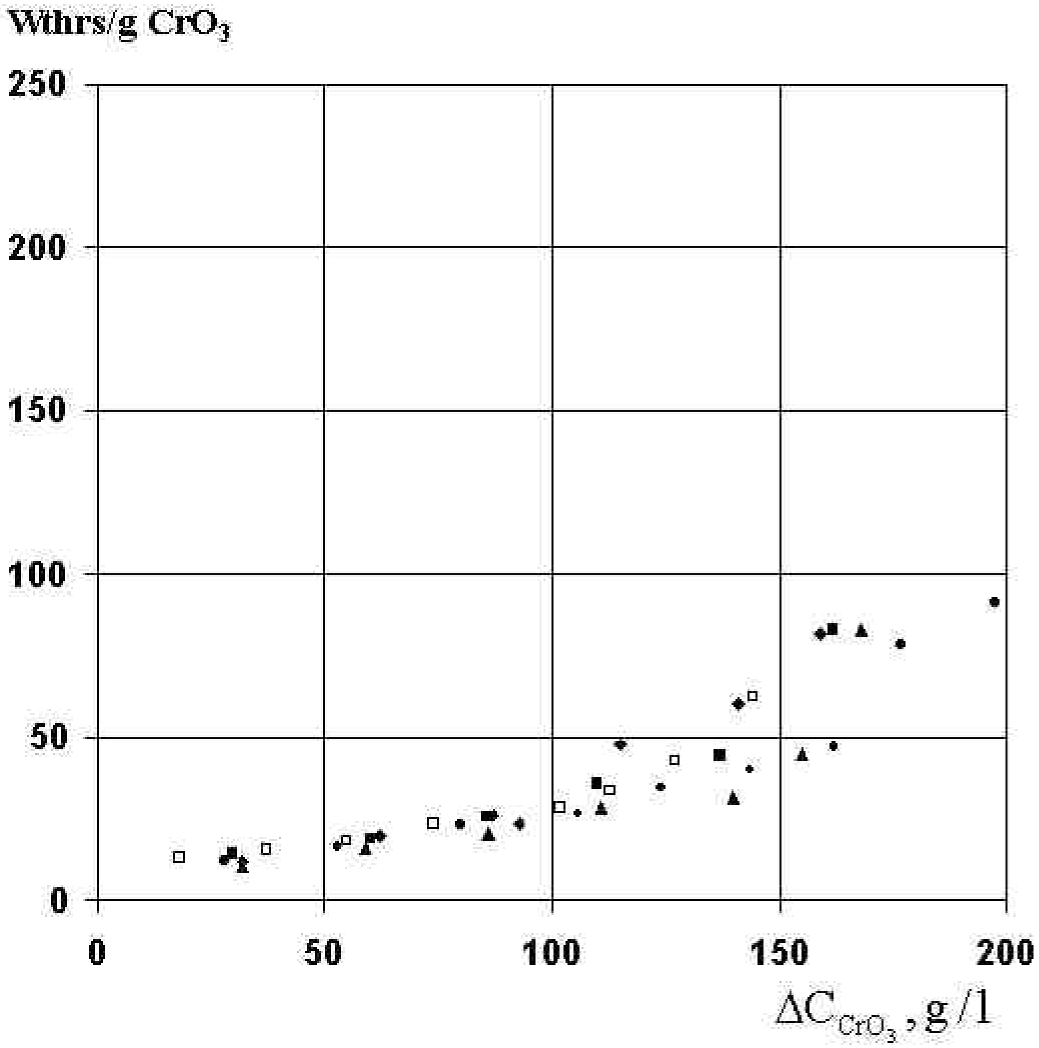

Fig. 8. Specific consumption of electric energy for the recovery of 1g of CrO_3 as a function of the difference between the its concentrations in the anolyte and in the spent solution or reclaim tank.

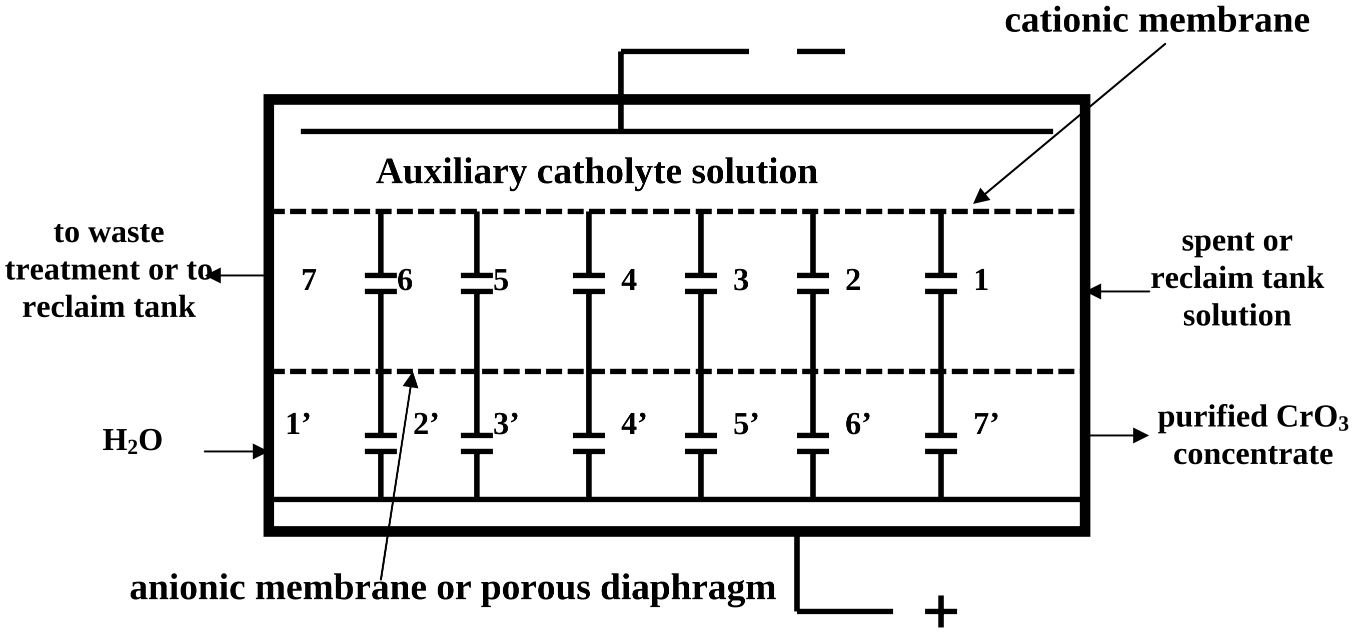

Fig. 9. Seven-stage unit for the recovery of CrO_3 from spent chromium plating solutions or from rinse water contained in the reclaim tank in the chromium plating line.

Summary

Two modifications of membrane electrolysis can be used for the separation of chromic acid and cationic impurities: (1) direct removal of metal cations from solutions, and (2) indirect purification, i.e. recovery of pure chromic acid from contaminated solutions. The second method is especially valuable for the creation of closed-loop chromium plating lines with multistage countercurrent rinses, where addition of concentrated chromic acid (~250 g/l) is made not directly from the first rinsing tank but from the anodic compartment of the electrolytic purification unit.