Regeneration of Chromate-free Zinc Passivating Solutions

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Zinc passivating solutions based on trivalent chromium compounds are used now on a wider scale. Conventional regeneration method (such as removal of zinc ions and reoxidation of trivalent chromium to hexavalent) is not suitable. A three-chamber electrolytic cell with two cationic membranes and the passivating solution in the intermediate compartment allows the removal of excess Zn^{2+} from the passivating solution, to prevent oxidation of Cr^{3+} and to eliminate dumping of the solution.

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Introduction

Zinc pasivating solutions based on trivalent chromium compounds may become an effective substitute for conventional chromate-based solutions. However, like the latter ones they have limited operation time due to gradual built-up of zinc ions. Selective removal of them should extend the operation period and eliminate periodic dumping. Membrane electrolysis has been successfully used for the removal of zinc and other cations from chromate-based solutions [1]. However, anodic oxidation of trivalent chromium into chromate, which is desirable in the case of chromate-based solutions, should be completely excluded in the electrolysis of trivalent-based baths. This means, that the anode should be separated from the passivating solution in the course of the regeeration. Therefore, the regeneration cell should have two cationic membranes.

Experimental Procedure

Regeneration of passivating solution was made in a three-compartment cell with two cationic membranes (Fig. 1),



Fig.1 Three-chamber cell with two cation exchange membranes for the regeneration of Cr(III)-passivating solution.

copper cathode and platinized niobium anode. Cathode and anode compartments were filled with 0.1-1.0 N sulfuric acid before each experiment. Intermediate compartment contained proprietary passivating solution. Recommended pH range is 1.3-1.7 and is adjusted by adding nitric acid. Initial concentration of zinc ions varied from 2 to 11 g/l and for normal operation of the passivating solution this

concentration should not exceed 6 to 8 g/l. Concentrations of zinc and chromium (III) ions in the intermediate and cathode compartments and cathode current efficiency of zinc were determined.

Results and Discussion

Zinc ions which are transfered into the catholyte are discharged at the cathode or are built up in the solution depending on the pH value. It should be noted that the pH is changing in the course of the electrolysis in all three compartments: it is falling down in the catholyte and rising up in the anolyte and in the intermediate compartment. Data on changing pH and Zn concentration in the intermediate and cathode compartments are shown in Figs. 2 and 3.



Fig.2. Concentration of zinc ions, sulfuric acid and pH in the catholyte vs. number of amper-hours passed through 11 of the catholyte. Initial concentration of Zn^{2+} in the intermediate compartment was 10.8 g/l.1, Zn^{2+} ; 2, H_2SO_4 ; 3, pH.



Fig. 3. Concentration of zinc ions in the intermediate compartment vs. number of ampere-hours passed through 11 of the solution in the intermediate compartment.

Since the initial pH value in the catholyte in this experiment was below 1.0 zinc ions transfered from the intermediate compartment were not discharged at the cathode. Therefore, current efficiency (C.E.) for hydrogen discharge was equal to 100%. At the same time the input of hydrogen ions to the catholyte was always less than 100 %:

$$t_{H^{+}} = 1 - \sum t_{i} = 1 - (t_{Z_{n^{2+}}} + t_{SO_{4}^{2^{-}}} + \sum (t_{Cr^{3+}} + t_{Na^{+}} + t_{K^{+}}, \text{ etc.}))$$
(1)

$$t_{H_2} = 1 - t_{SO_4^{2-}} - (t_{Zn^{2+}} + \sum (t_{Cr^{3+}} + t_{Na^+} + t_{K^+}, \text{etc.}))$$
(1a)

Here t_i - are transport numbers of varios ions.

Due to the use of a cationic membranes $t_{SO_4^{2-}}$ was rather small. The content of free sulfuric acid in the catholyte, $m_{H_2SO_4}$, was changing in the following way in the course of the electrolysis:

$$0 > \Delta m_{H_2SO_4} = (Q/2F) \times (t_{H^+} - C.E_{H_2})/100) \text{ moles}$$
(2)

Here $\Delta m_{H_2SO_4}$ is the input of the acid, Q is the electric charge passed, and F is Faraday's number.

Curve 2 in Fig.2. illustrates this process.

The loss of sulfuric acid in the catholyte, $\Delta m_{H_2SO_4}$, exceeds somewhat the built-up of metal salts, $\Delta m_{M_2SO_4}$, dissolved in the catholyte. (The difference between - $\Delta m_{H_2SO_4}$ and $\Delta m_{M_2SO_4}$ is due to the transfer of sulfate ions from the catholyte into the intermediate compertment). In sufficiently long batch regeneration experiments gradual conversion of sulfuric acid into corresponding salts leads to the catholic deposition of zinc (at pH≥2) and finally to the hydrolysis of zinc sulfate (at pH≥6-8) and precipitation of zinc hydroxide (Table). Free alkalies are formed by sodium or potassium ions transfered into the catholyte from the passivating solution, when the disbalance between the input (t_{H^+}) and the consumption ($C.E._{H_2}$) of hydrogen ions has led to a complete loss of free sulfuric acid. So, selective removal from the catholyte of only Zn ions (as metal deposit) in the course of the electrolysis seems desirable in order to minimize the consumption of sulfuric acid and the amount of waste formed. The catholyte will under such conditions (2<pH<5), contain all cations which were transfered from the passivating solution except most of Zn²⁺ and H⁺.

In a special regeneration experiment (see Table) initial concentration of sulfuric acid in the catholyte was lower than in other experiments. Therefore, zinc deposition starts immediately as soon as zinc ions appear in the catholyte. Later the deposition rate and current efficiency become to fall down due to the absence of free acid and the precipitation of zinc hydroxide. After the addition of some acid to the catholyte and dissolution of hydroxide metal deposition has resumed.

Table.
Cathodic current efficiency (C.E.) of zinc. Initial concentration of Zn^{2+} in the intermediate compatment
(spent passivating solution) 11.6 g/l. Initial concentration of sulfuric acid in the catholyte - 0.1 N.

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Ah/l (catholyte)	1.6	2.9	6.9 ^{*)}	22.9	28.3**)	33.6	38.9	46
Cathodic current efficiency, %	6.4	15.7	4.2	1.3	7.3	33.0	13.9	6.1
*) E								

^{*)} Formation of zinc hydroxide

**) Sulfuric acid was added to the catolyte.

Small amounts of trivalent chromium are also transfered into the catholyte from the intermediate compartment. Trivalent chromium can be recovered from the catholyte by precipitation as hydroxide and then returned to the passivating solution.

There is also a problem of electrolytic transfer of anionic components of the passivating solutions into the anolyte through the cationic membrane. Their transport numbers are, of course, very small and can be made still smaller by increasing the total concentration of all kinds of cations in the anolyte. An appropriate ratio of concentrations of an alkaline metal salt and free acid in the anolyte allows to maintain desirable pH value in the intermediate compartment (i.e. in the passivating solution). This ratio will be somewhat lower in a continuously operating regeneration unit and somewhat higher in the case of batch operation, since the acid is consumed in the passivating process.

Summary

Regeneration of zinc passivating solutions based on trivalent chromium can be carried out in a three-chamber electrolytic cell with two cationic membranes. Zinc ions are discharded at the cathode to form metal deposit. The only reagent consumed in the regeneration process is sulfuric acid.

Reference:

[1] S.S. Kruglikov, D.Yu. Turaev. AESF/EPA Conference for Environmental and Process Excellence 2003, p. 81-86