Removal of Cadmium and Cyanide Ions from Rinse Water in Plating Lines.

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An input of both cadmium and cyanide ions into waste water is practically eliminated by using two reclaim tanks equipped with electrolytic membrane half-cells operating continuously. Cadmium is deposited on the cathode in the first tank and is returned into the plating tank by periodic stripping. The anode in the first tank is behind the cationic membrane which prevents the access of cyanide complex to the anode. Cyanide is destroyed in the second reclaim tank by anodic oxidation in the presence of chloride ions. Cationic membrane separates the cathode in this tank and allows to maintain optimum pH value.

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Introduction

Cadmium plating process creates two types of problems related with environment protection. It is necessary to minimize the input of cadmium ions into waste water in presence of ligands, such as cyanide, ammonia, etc. The use of reclaim tanks and the removal of both cadmium and ligands from them may provide an efficient and inexpensive solution. Certain industrial experience has been already accumulated during recent few years. Plating out of cadmium from reclaim tanks and simultaneous anodic oxidation of cyanide are used in a number of plating shops and the purpose of a present paper is to study this process in more detail.

Experimental

Three types off cells were used in the experiments: (A) a non-divided cell (Fig. 1); (B) a two-compartment cell with anionic membrane (Fig. 2); (C) a two-compartment cell with cationic membrane and two cathodes (Fig. 3).

A conventional cyanide cadmium plating solution was diluted by 10 to 25 times in order to simulate rinse water in the reclaim tanks. Chloride (10-40 g/L) was added to the solution in some experiments. Copper cathodes and graphite or platinized titanium anodes were used. Solutions in the cell were periodically analysed and weight of the cathode was determined in the course of the electrolysis.

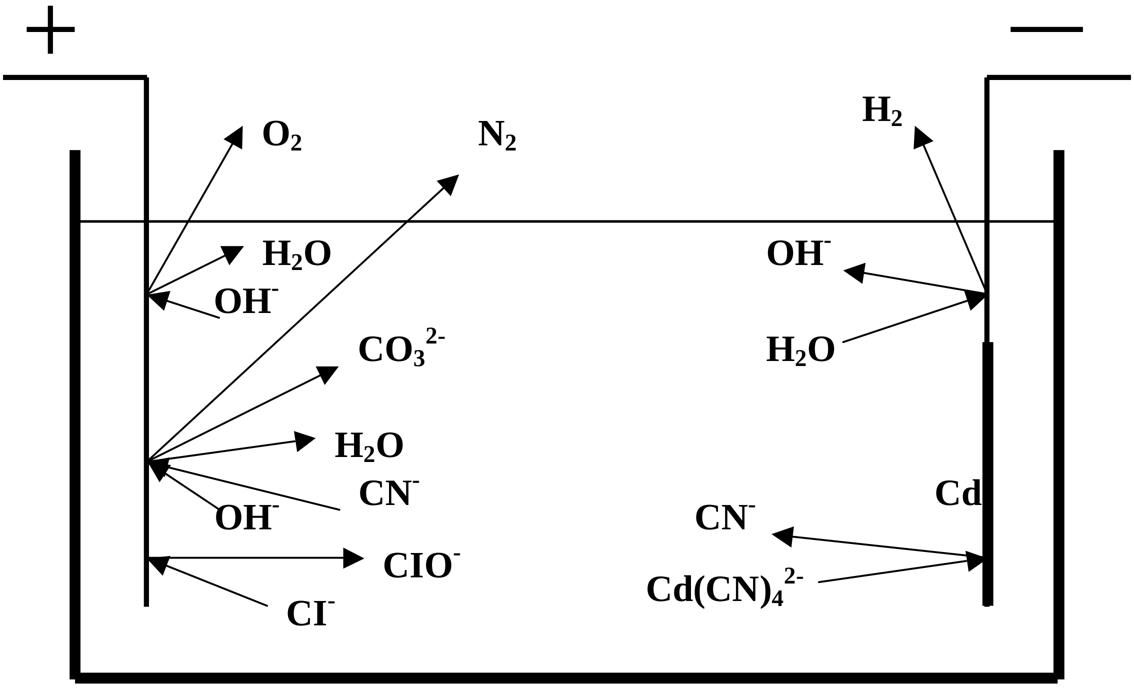

Fig. 1. Non-divided cell (in the presence of Cl⁻).

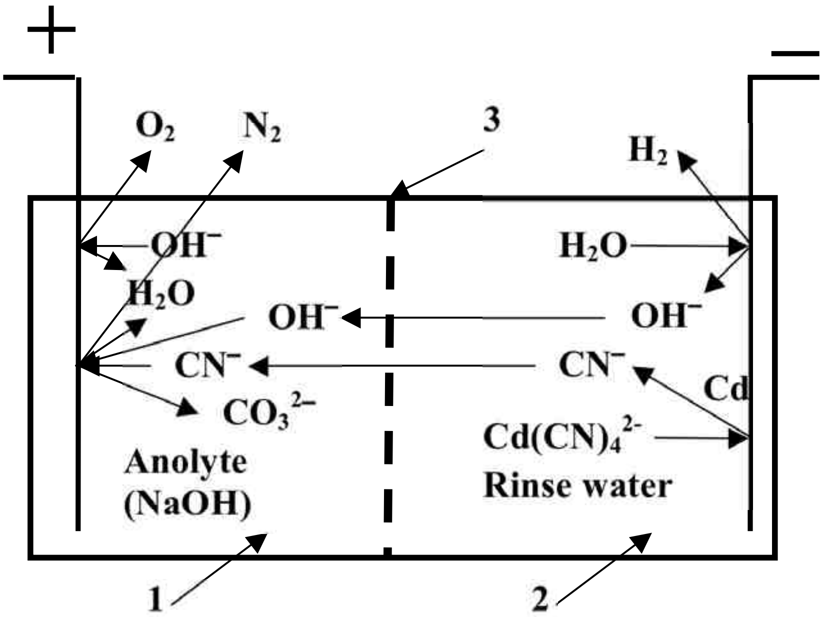

Fig. 2. Two-compartment cell with anionic membrane; 1, anolyte; 2, catholyte (rinse water in the reclaim tank); 3, anionic membrane.

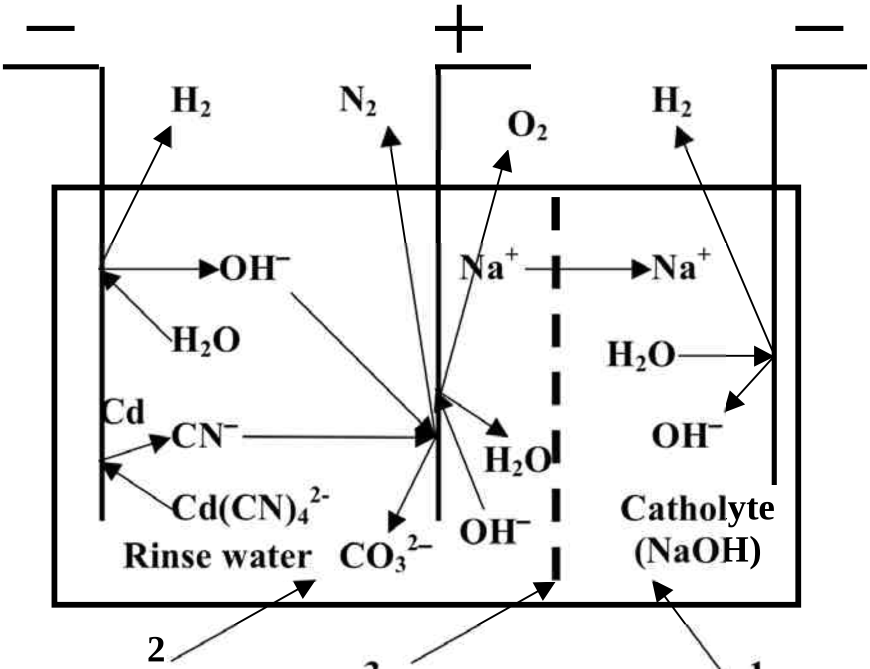

Fig. 3. Two-compartment cell with cationic membrane and two cathodes; 1, catholyte; 2, anolyte (rinse water in the reclaim tank); 3, cationic membrane.

Processes proceeding in the non-divided cell are shown in Fig. 1. Cadmium is deposited at the cathode. On industrial scale the cathode is made of stainless steel and is periodically immersed as an anode into plating tank for the dissolution of cadmium deposit. In the absence of chloride ions following reactions proceed at the electrodes:

At the cathode:

$Cd(CN)_4^{2-} + 2e^- \rightarrow Cd + 4CN^-$ (1)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (2).

At the anode:

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ (3)

$2CN^- + 12\ OH^- \rightarrow 2CO_3^{2-} + N_2 + 6H_2O + 10e^-$ (4).

If the solutions contain chloride ions, they also take part in the electrode reactions:

At the anode (in the alkaline media):

$Cl^- + 2OH^- \rightarrow ClO^- + 2e^- + H_2O$ (5).

At the cathode:

$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ (6).

In addition to reaction 6 hypochlorite ions which are very active can disproportionate into chlorate, ClO_3^- or are oxidized into it at the anode. They can also oxidize cyanide ions:

$5ClO^- + 2OH^- + 2CN^- \rightarrow 2CO_3^{2-} + N_2 + 5Cl^- + H_2O$ (7).

Reaction 7 may accelerate destruction of cyanide as is shown in Tables 1 to 5 and Fig. 4.

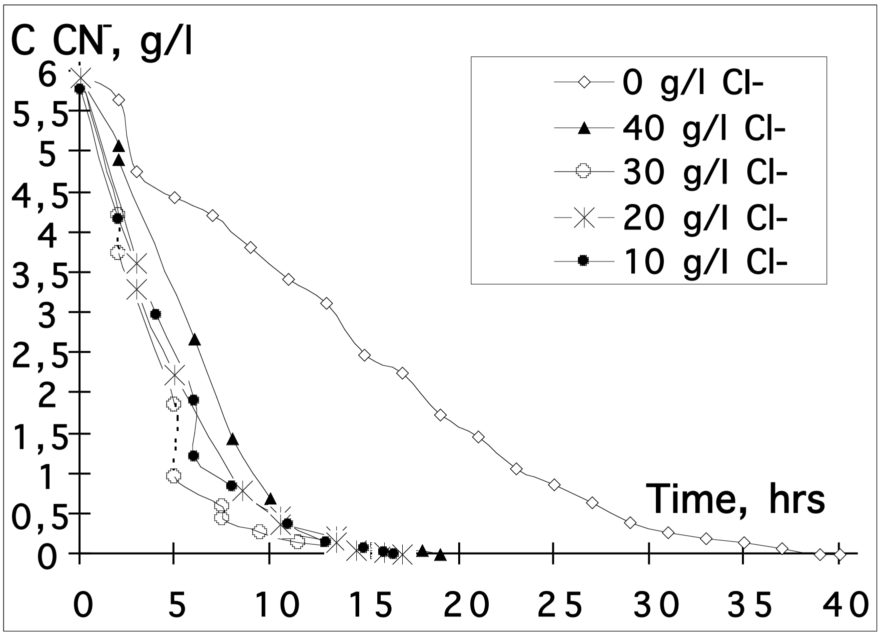

Fig. 4. Concentration of cyanide during the electrolysis in the presence and in the absence of chloride.

Table 1. Removal of cadmium and cyanide during the electrolysis in the absence of chloride.

Time, hrs	pH	CN$^-$, g/L	Δm Cd, g$^{*)}$
0	12.6	5.98	0
2	12.0	5.64	0.124
5	11.75	4.75	0.149
7	10.9	4.44	0.017
9	10.8	4.21	0.049
11	10.8	3.82	0.043
13	10.9	3.41	0.042
15	11.0	3.13	0.016
17	10.98	2.48	0.024
19	11.0	2.24	0.016
21	11.01	1.73	0.012
23	11.1	1.45	0.015
25	10.8	1.06	0.011
27	10.75	0.858	0.009
29	10.7	0.637	0.021
31	10.22	0.4082	0.007
33	10.21	0.2782	0.007
35	10.21	0.2028	0.007
37	10.15	0.1508	0.000
39	9.8	0.0754	0
40	9.4	0	0

$^{*)}$ Δm Cd represent weight of cadmium deposited during particular periods of electrolysis.

Table 2. Removal of cadmium and cyanide during the electrolysis in the presence of 10 g/L CI$^-$.

Time, hrs	pH	CN$^-$, g/L	Δm Cd, g
0	12.4	5.77	0
1	12.5		
2	11.9	4.16	0.264
3	11.5		
4	10.9	2.98	0.128
6	10.3	1.91	0.067
break	10.25	1.22	
8	10.15	0.8528	0.039
11	10.05	0.3718	0.028
13	10.0	0.159	0.013
15	9.5	0.0728	0.026
16	9.45	0.026	0.003
16.5	9.4	0	0.003

Table 3. Removal of cadmium and cyanide during the electrolysis in the presence of 20 g/L Cl^-.

Time, hrs	pH	CN^-, g/L	Δm Cd, g
0	12.3	5.92	0
3	11.1	3.62	0.318
break	10.7	3.30	0.076
5	10.5	2.24	
8.5	10.1	0.8	0.065
10.5	9.5	0.479	0.016
break	9.4	0.373	0.034
13.5	9.23	0.213	
break	9.2	0.159	0.005
14.5	9.1	0.058	
16	9.07	0.0273	0.005
17	8.95	0	0.004

Table 4. Removal of cadmium and cyanide during the electrolysis in the presence of 30 g/L Cl^-.

Time, hrs	pH	CN^-, g/L	Δm Cd, g
0	12.25	5.92	0
1	11.0		
2	10.2	4.21	0.250
break	10.1	3.73	
5	9.7	1.86	0.153
break	9.7	0.9601	
7.5	9.1	0.585	0.066
break	9.05	0.457	
9.5	9.0	0.266	0.042
11.5	8.9	0.1599	0.009
13.5	8.8	0.1076	0.016
15.5	8.7	0.0533	0.007
break	8.65	0.026	
16	8.6	0	0.007

Table 5. Removal of cadmium and cyanide during the electrolysis in the presence of 40 g/L Cl^-.

Time, hrs	pH	CN^-, g/L	Δm Cd, g
0	12	5.92	0
2	11.6	5.08	0.211
break	11.2	4.91	
6	10.2	2.68	0.163
8	9.55	1.43	0.052
10	9.10	0.691	0.033
11	9.05	0.266	0.016
break	9.00	0.266	
13	8.8	0.1812	0.039
15	8.55	0.1066	0.012
17	8.47	0.0533	0.009
break	8.4	0.0533	
18	8.4	0.0442	0.005
19	8.35	0	0

Anode reactions (3) and (4) lead to the consumption of hydroxyle ions. Out of two cathode reactions only (2) compensates this effect, provided it is combined with reaction (3). However all other combinations reduce pH of the solution. For example, a desirable combination of reactions (1) and (4) reduces the content of alkali with the rate of 1.2 moles per Faraday. Even hydrogen evolution reaction (2) cannot compensate losses of alkali in reaction (4).

Actual change in pH value in the course of the electrolysis is shown in Fig. 4.

Fast oxidation of cyanide (even in the absence of chloride) leads to the destruction of cadmium-cyanide complex and precipitation of insoluble non-complex salt:

$Cd(CN)_4^{2-} \rightarrow Cd(CN)_2\downarrow$ + cyanide destruction products (8).

These processes result in the incomplete removal of cadmium from the reclaim tank.

Another problem is gradual change of pH (Fig. 5), which might create dangerous conditions due to volatility of HCN molecules formed at pH ≤ 10. On the other hand, oxidation of cyanide is practically not sensitive to the changes in pH within the range of 10.5 to 11.5 (Fig. 6).

Therefore the next step of experiments was the separation of the anode from cadmium-cyanide solution by anionic membrane (Fig. 2). Sodium hydroxide solution was used as an anolyte (Table 6). Results obtained show that the concentration of cyanide was reduced in the catholyte by only 27 percent from its initial value due to preferential transfer of hydroxide ions through the membrane. Therefore, this method of removal of cyanide from the reclaim tank should be considered as inefficient.

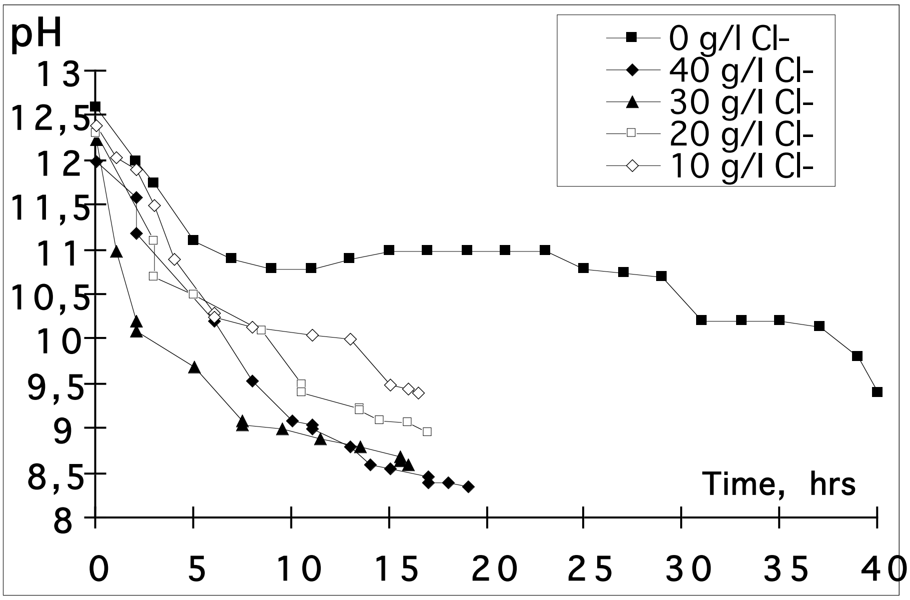

Fig. 5. Values of pH changing in the course of electrolysis.

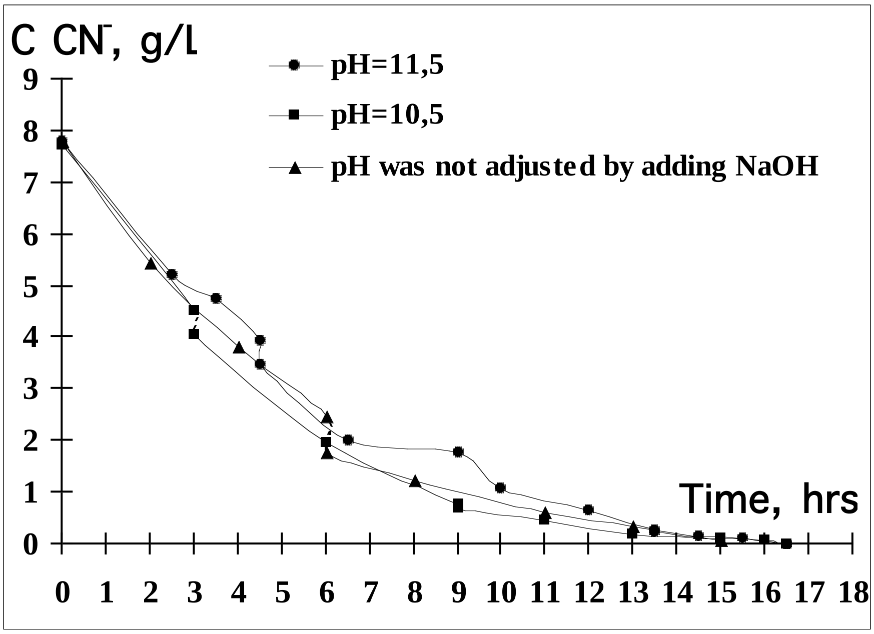

Fig. 6. Concentration of cyanide during the electrolysis at constant and varing pH (Cl⁻ 10 g/L).

Table 6. Values of pH of the catholyte and the anolyte changing in the course of the electrolysis with the anionic membrane.

Time, hrs	0	1	2	3	4	5
Catholyte, pH	12,85	13,05	13,15	13,1	13,2	13,2
Anolyte, pH	13	12,95	12,75	12,5	11,3	9,65

The use of two-compartment cell shown in Fig. 3 with cationic membrane and two cathodes could not prevent neither lowering of pH in the reclaim tank, nor prevent too fast oxidation of cyanide, which leads to partial precipitation of cadmium-cyanide salt. Nevertheless this process is used in a number of plating shops.

Analysis of industrial experience and recent results of the above experiments suggest a new and principally different approach to the problem: the use of two successive reclaim tanks. First one (Fig. 7) is used for the removal of cadmium. It has two anodes, one of them being separated from the bulk solution by cationic membrane. This additional anode reduces the oxidation of cyanide and allows to maintain constant pH is the reclaim tank, which, of course, contains no chloride. The second reclaim tank contains 10-20 g/L of chloride and has no membrane. Major part of cyanide will be oxidized in the second tank.

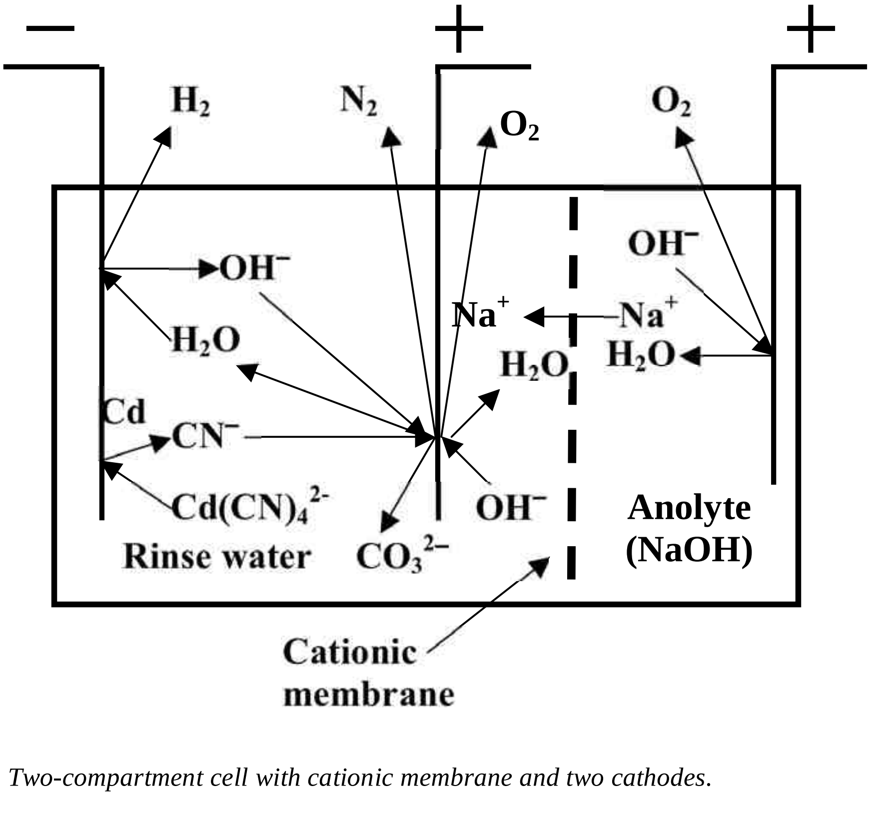

Fig. 7. Two-compartment cell with cationic membrane and two cathodes.

Summary

Results of experimental study allow to improve the existing process of removal cadmium and cyanide from reclaim tanks in plating lines. Simultaneous removal of these contaminants from rinse water is not efficient and two successive reclaim tanks have been proposed.

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