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# Peculiarities of Chemical Extraction of Zinc and Cadmium from Waste Ammonia Electrolytes of Zinc and Cadmium Plating

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**Abstract:** It has been investigated how to recover zinc and cadmium from used ammonia electrolytes for plating zinc and cadmium. It is suggested to use a two-stage process to remove metal (zinc and cadmium) and ammonia from used electrolytes.

**Keywords:** zinc, cadmium, hydroxide, ammonia, electrolyte, sodium phosphate, metal.

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Due to the creation of a significant amount of wastewater containing poisonous impurities of heavy metals, inorganic acids and alkalis, surfactants, and other extremely toxic substances, galvanic manufacturing is one of the most hazardous causes of environmental contamination. New environmental technologies must be used in conjunction with current methods to the development of electroplating.

Galvanic production waste may be less hazardous to the environment in a number of ways, including the development of electrolytes with readily recyclable organic additions and the creation of techniques for purifying wastewater and wash water from manufacturing, particularly from heavy metal ions. Additionally, as ammonia (ammonium ions) contribute to eutrophication of water bodies, the presence of ammonia in effluent from galvanic generation is undesirable.

The method used to extract the zinc affects how much cadmium is produced. Cadmium and zinc are initially reduced combined before the dry extraction of zinc. Cadmium evaporates more readily because it has a lower boiling point than zinc. Consequently, the cadmium-zinc combination evaporates from the reduction tank and comes into contact with oxygen someplace. The resultant cadmium is transformed into cadmium oxide by oxygen before being dissolved in sulfuric acid. By electrolyzing the resultant cadmium sulfate solution with aluminum anodes and lead cathodes, a very pure cadmium electrolyte is produced. Physical properties

One of the most effective anti-corrosion metals is zinc, which is used to make anodes, alloys, and printing plates for zincography (Skalny, 2004). Numerous electrolytes have been created based on zinc and its compounds for the manufacture of zinc coatings. Galvanizing electrolyte efficiency loss is mostly caused by the introduction of hazardous contaminants

into solutions by treated items. The issue of using galvanizing electrolytes and removing essential components from them, particularly zinc, becomes critical as a result (Vinogradov, 1998; Nikulin, 1980; Proskuryakov and Schmidt, 1977).

Ammonia zinc electrolyte, the composition of which is shown in Table 1, is often used in manufacturing, notably at businesses in the Penza region.

**Table 1. The composition of the galvanizing electrolyte**

| Component                      | Concentration, g/l | pH      |
|--------------------------------|--------------------|---------|
| ZnO                            | 13                 | 6,5-7,0 |
| NH <sub>4</sub> Cl             | 260                |         |
| H <sub>3</sub> BO <sub>3</sub> | 25                 |         |

The physical and mechanical characteristics of the metal itself have a significant impact on the area of application of cadmium coatings. Nickel-cadmium batteries, low-melting alloys, and corrosion protection for steel components are the principal uses for cadmium. With a modest overvoltage, cadmium is liberated from solutions of simple salts. Cadmium's application is restricted by its high cost, rarity, and toxicity both as a metal and in its compounds. However, because cadmium coatings are more durable in hostile settings, it is not viable to fully discard them (in sea water, salt solutions, etc.). Additionally, cadmium electrolytes are utilized to safeguard the most important threaded items owing to their great scattering power and flexibility.

There are many techniques for removing cadmium ions from waste and industrial water. Cadmium most frequently precipitates as hydroxide or sulfide. Although the use of sulfides as precipitants necessitates extra wastewater treatment due to sulfur-containing chemicals that might damage water supply systems, precipitation with hydroxides does not offer a high level of purification (Vinogradov, 1998; Zorkina, 2000; Varentsov, 2003; Kruglikov et al. , 2005; Sirotkin et al., 2005; Turaev, Sirotkin, Kruglikov, 2001).

Simple acidic (sulfuric, hydrochloric, and hydroboric) and complicated complex (alkaline cyanide, ammonia, pyrophosphate, and others) cadmium plating electrolytes are typically employed in industry (Applied Electrochemistry, 1984; Vinogradov, 1998).

Table 2 lists the chemical make-up of the most popular cadmium electrolytes used in industry. The research item was chosen to be Electrolyte No. 2. (Applied Electrochemistry, 1984).

Therefore, the quest for an efficient technique for treating wastewater from cadmium, zinc, and ammonium ions is an important challenge as there are no ways for removing base metals and ammonia from such electrolytes.

In order to design a technique for their extraction from used ammonia zinc and cadmium plating electrolytes as well as to examine the physicochemical characteristics of the deposition of zinc, cadmium, and ammonium ions in the form of phosphates.

**Table 2. Industrial cadmium electrolytes**

| Compound                                              | Electrolyte 1 | Electrolyte 2 | Electrolyte 3 |
|-------------------------------------------------------|---------------|---------------|---------------|
| CdSO <sub>4</sub> , g/l                               | 40-60         | 40-50         | -             |
| CdCl <sub>2</sub> , g/l                               | -             | -             | 50-75         |
| (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , g/l | 240-250       | 200-280       | -             |
| NH <sub>4</sub> Cl, g/l                               | -             | 30-40         | 200-280       |
| NaCl, g/l                                             | 500-100       | -             | 30-35         |
| Dispersant NF-B (35%), ml/l                           | -             | -             | -             |
| Dispersant NF-B (35%), ml/l                           | -             | -             | 70-80         |
| Urotropin, g/l                                        | 15-20         | 7-10          | -             |
| Thiourea, g/l                                         | -             | 1-2           | -             |
| Glue joiner, g/l                                      | -             | 4,0-4,5       | -             |
| pH                                                    | -             | -             | 4,0-4,5       |
|                                                       | 4-6           |               |               |
| Deposition mode:                                      |               |               |               |
| temperature, °C                                       | 15-30         | 20-40         | 15-30         |
| cathodic current density, A/dm <sup>2</sup>           | 0,5-1,5       | 0,8-1,2       | 1,5-2,0       |

**Table 3. Concentration of cadmium ions at different volumes of added precipitant.**

| № experience | volume of electrolyte solution, ml. | the volume of the added precipitant solution (0.04M Na <sup>3</sup> PO <sup>4</sup> ), ml. | Residual concentration of cadmium in the filtrate, mg/l. |
|--------------|-------------------------------------|--------------------------------------------------------------------------------------------|----------------------------------------------------------|
| 1            | 10                                  | 50                                                                                         | 25,2960                                                  |
| 2            | 10                                  | 60                                                                                         | 19,0260                                                  |
| 3            | 10                                  | 70                                                                                         | 6,3414                                                   |
| 4            | 10                                  | 80                                                                                         | 2,3416                                                   |
| 5            | 10                                  | 90                                                                                         | 2,2196                                                   |
| 6            | 10                                  | 100                                                                                        | 3,4630                                                   |
| 7            | 10                                  | 110                                                                                        | 1,3240                                                   |
| 8            | 10                                  | 120                                                                                        | 0,7257                                                   |
| 9            | 10                                  | 130                                                                                        | 1,1140                                                   |

Table 3 provides the outcomes of the precipitation of cadmium ions using a 0.043M solution of Na<sub>3</sub> PO<sub>4</sub>. Due to the low concentration of the precipitant, utilizing 0.043 M sodium phosphate solution results in a significant dilution of effluent. In this aspect, the experiment's Na<sub>3</sub> PO<sub>4</sub> solutions were more concentrated. Table 4 displays the outcomes of zinc precipitation from the electrolyte using sodium phosphate solutions of 0.1 M and 0.25 M. The residual zinc content after the precipitation of zinc ions with 1.156 M sodium phosphate solution was 544.52 mg/l. Figure 3 depicts the relationship between the residual zinc concentration and the sodium phosphate solution concentration at the same molar ratio. The study of this dependency reveals that the residual content of zinc in the filtrate rises when a higher concentrated precipitant is used. Figure 4 illustrates how pH affects how completely zinc ions precipitate. The electrolyte was precipitated using a 0.25 M sodium phosphate solution at various pH levels to explore this dependency. At pH 8.7, the residual zinc content was lowest. The solution's zinc content rose as a result of the pH's change to the acidic side.

Following analyzing the data, we can say that there aren't many differences between the residual zinc content in the filtrate between 16°C and 20°C after precipitation with 0.043 M sodium phosphate solution. The residual metal content rose and reached 6.0500 mg/l if the precipitate ages at a temperature of 7°C. This number appears to be related to the production of small crystals that readily pass through the filter rather than a rise in the solubility of the ensuing precipitate, the presence of which is detected by an atomic absorption spectrophotometer.

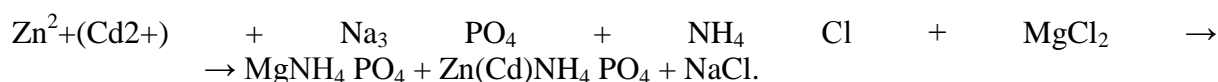
**Table 4. Dependence of the residual concentration of zinc on the amount of precipitant.**

| N <sub>o</sub> experience | Sediment concentration, mol/l | Volume of added precipitant, ml | Zinc content after precipitation, mg/l | pH of the sample after precipitation |
|---------------------------|-------------------------------|---------------------------------|----------------------------------------|--------------------------------------|
| 1                         | 0,1                           | 21,5                            | 12,15                                  | 7,8                                  |
| 2                         | 0,1                           | 23,7                            | 11,35                                  | 7,8                                  |
| 3                         | 0,1                           | 30,0                            | 9,8                                    | 7,8                                  |
| 4                         | 0,1                           | 34,4                            | 8,55                                   | 7,8                                  |
| 5                         | 0,25                          | 8,6                             | 17,22                                  | 7,8                                  |
| 6                         | 0,25                          | 9,4                             | 17,11                                  | 7,8                                  |
| 7                         | 0,25                          | 12,0                            | 18,7                                   | 7,8                                  |
| 8                         | 0,25                          | 13,8                            | 15,5                                   | 7,8                                  |

As previously mentioned, adding 50 ml of 0.043 M sodium phosphate solution to 10 ml of electrolyte produced the lowest concentration of zinc ions, which was 0.3100 mg/l. This concentration is higher than the MPC for industrial wastewater, which is 0.075 mg/l, but much lower than the MPC for zinc in drinking water, which is 5 mg/l (Vinogradov, 1998; Decree of the head of the Penza city administration dated April 3, 2003 No. 662). As a result, dilution or extra treatment are required for effluents with such a high zinc ion level.

Experiments 7, 8, and 9 (see Table 3) were performed with increased concentrations of the precipitant in order to decrease the additional volumes of the precipitant needed to remove cadmium ions from the electrolyte solution.

The information in the table indicates that a drop in the effectiveness of cadmium extraction results from an increase in the precipitant concentration at similar molar ratios. Thus, precipitating the electrolyte with a 0.043 M Na<sub>3</sub>PO<sub>4</sub> solution removes cadmium ions from the electrolyte in the most thorough manner possible. The smallest residual concentration obtained, however (0.7257 mg/l), still exceeds the maximum permissible concentration (MPC) of cadmium in effluent from galvanic production (1 g/l) (Resolution of the head of the Penza city administration dated 03.04.2003 No. 662). The composition of magnesium (zinc, cadmium) ammonium phosphate was examined in the context of this work to determine if it could be isolated from metal residues (zinc and cadmium) and ammonium cations:



The cadmium electrolyte or its filtrate was simultaneously precipitated with a 1.052 M solution of MgCl<sub>2</sub> and a solution of Na<sub>3</sub>PO<sub>4</sub> at different concentrations to extract the ammonium ions (Kreshkov, 1965).

With simultaneous precipitation of 1.052 M MgCl<sub>2</sub> and 0.25 M Na<sub>3</sub>PO<sub>4</sub> in the ratio of 13 volumes of filtrate: 5 volumes of MgCl<sub>2</sub> solution: 21 volumes of Na<sub>3</sub>PO<sub>4</sub> solution, the most thorough extraction of ammonia from the filtrate—previously obtained by precipitating the

electrolyte with a 0.043 M  $\text{Na}_3\text{PO}_4$  solution (experiment No. 8, Table 3—was achieved. In this instance, the remaining ammonium ion concentration was 87.5 mg/L. This resulted in a nearly 3200-fold decrease in the concentration of ammonium ions. The MPC, 13.5 mg/l, is still exceeded by the remaining ammonium ion concentration (Resolution of the head of the Penza city administration dated 03.04.2003 No. 662).

When utilizing precipitants in the ratio of the volume of the filtrate to the volume of 1.156 M  $\text{Na}_3\text{PO}_4$  and the volume of 1.052 M  $\text{MgCl}_2$  1.3:1:1, a thick curd mass formed when the concentration of sodium phosphate was increased further to 1.156 M. Cadmium concentration in the product after drying is no greater than 0.6 mg/kg.

After the first precipitation, the filtrate was concurrently poured with 1.156 M sodium phosphate solution and 1.052 M magnesium chloride solution in order to separate the ammonia from the zinc electrolyte. The creation of a thick curd mass, which may be shaped and dried in the air during production, was seen with the addition of a one and a half excess of both precipitants (the ratio of the volume of the filtrate to the volumes of 1.156 M  $\text{Na}_3\text{PO}_4$  and 1.052 M  $\text{MgCl}_2$ , 1:1.1:1.2). The finished product is well prepared for usage as a complex fertilizer rich in trace elements after drying (Zn, Mg, B).

A new two-stage approach for extracting metal (zinc and cadmium) and ammonia from used electrolytes may be suggested as a result of the investigation. Zinc (cadmium) is removed from the electrolyte in the first stage, and the filtrate is then treated with solutions of 1.052  $\text{MgCl}_2$  and 1.156 M  $\text{Na}_3\text{PO}_4$  in the second stage. The final mass is formed and let dry in the air. The suggested approach has a number of benefits, including not requiring expensive reagents or installations, being straightforward and very simple to apply, being waste-free and ecologically friendly, and allowing you to put valuable non-ferrous metal back into production.

## Conclusion

The most thorough separation of zinc is accomplished by precipitating it with a 0.043 M solution of sodium phosphate in a 1:5 electrolyte to precipitant volume ratio at pH 7.8 and temperatures between 16°C and 20°C. The precipitation of a 0.043 M sodium phosphate solution at a ratio of 1:12 electrolyte volume to precipitant volume at a temperature of 16–20 °C and a pH of 7.6 results in the lowest residual concentration of cadmium. The use of solutions of 1.052 M  $\text{MgCl}_2$  and 1.156 M  $\text{Na}_3\text{PO}_4$  resulted in a 3200-fold decrease in the amount of ammonium ions in the filtrate. It is suggested to use a two-stage process to remove metal (zinc and cadmium) and ammonia from used electrolytes.

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