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WASTE TREATMENT OF TWO ELECTROPLATING SOLUTIONS OF Cu AND Zn BY MIXING AND PRECIPITATION

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ABSTRACT

Our studies suggest a cheap and simple way to decontaminate two ligand-containing rinsing waters of metal finishing. Both copper diphosphate and acidic zinc ammonium containing rinsing wastewater may be decontaminated by mixing, which results in precipitation of solid solution of potassium, ammonium, copper, and zinc diphosphates. About 80–99.5% of environmentally hazardous substances, viz. zinc, copper, and diphosphate are removed from the solution. Chemical and phase composition of the precipitate was examined. We have also suggested several possible ways to utilize the precipitate. This way of decontamination requires no expensive reagents since only a small amount of H_2SO_4 is required for pH adjustment.

Key Words: Diphosphate; Copper; Zinc; Ammonium; Electroplating; Rinsing water; Decontamination; Precipitation; X-ray diffraction; Phase composition

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INTRODUCTION

The use of solutions of ionized metal-containing ligands is neglected everywhere in industries because of the complicated and expensive waste treatment. Diphosphate copper and acidic zinc (containing ammonium chloride) electroplating solutions have been used in electroplating due to exceptional properties of coatings obtained by using these solutions.

For metal removal from complexing agent containing solutions and for their reuse in industry, various methods have been used:

1. The oxidative destruction of ligands: after a complete oxidation of ligands, heavy metals may be removed by common hydroxide precipitation.[1] The electrochemical method of decontamination is also widely used. The ligands are destroyed anodically and heavy metals are deposited on the cathode. Combined photolytic and electrolytic cell system is recommended for copper and ethylenediaminetetraacetic acid (EDTA) containing industrial effluent decontamination.[2]

2. Chemical precipitation: the possibility to precipitate metals in the form of insoluble metal hydroxides in complexing agent containing solutions depends on the complex stability constant (β_n) and hydroxide solubility (S), which can be described by the equation:

$$\mathrm{ML}_n = \beta_n S L^n/[\mathrm{OH}^-]^m$$

where ML_n is the metal complex residual concentration after precipitation, L is the ligand concentration, n is the number of ligand molecules in complex, and m is the valence of metal ion.

Similarly, when other barely soluble compounds are precipitated, the efficiency of removal is determined by the complex stability constant and the solubility of the barely soluble compound. Inorganic and organic sulfides were widely recommended for removal of heavy metal ions from ligand-containing solutions, 10–20 years ago.

In practice it is difficult to achieve DCL by hydroxide precipitation, nevertheless, it is achieved for ammonia, Cu-diphosphate, and Fe-EDTA solutions. However, citric and tartaric acids in the alkaline solutions coprecipitate with metal hydroxide in excess of metal salt.[3] When Ni(II) concentration in the solution is twice as high as that of Ni(II)–citrate complex, the residual Ni(II) and citrate concentrations are very low. The amorphous precipitate is then formed. Both metal and ligand precipitate without destroying the ligand and their reuse in industry is possible. Tartrate and citrate easily precipitate in excess of Cu(II) in the acidic solutions.[4,5] The precipitates are crystalline and easily filtered. Similarly, glycine may be removed from spent electroless plating solutions in the form of barely soluble crystalline *cis*-$\mathrm{Cu(gly)_2{\cdot}H_2O}$ and *trans*-$\mathrm{Cu(gly)_2{\cdot}2H_2O}$.[6]

3. Solvent extraction,[7] ion exchange,[8] cementation,[9] membrane separation,[10] reverse osmosis[11] are also used.

Most of the heavy metal ions form various barely soluble and complex diphosphates. Two main factors which affect chemical composition of the compounds are the molar ratio of diphosphate ions to metal ions (*n*) and the pH.

The protonization constants of diphosphate ions are as follows according to Ref.[12]:

$$P_2O_7^{4-} + H^+ \rightleftharpoons HP_2O_7^{3-} \quad \log K_1 = 8.66$$

$$HP_2O_7^{3-} + H^+ \rightleftharpoons H_2P_2O_7^{2-} \quad \log K_{12} = 6.12$$

$$H_2P_2O_7^{2-} + H^+ \rightleftharpoons H_3P_2O_7^{-} \quad \log K_{13} = 2.03$$

$$H_3P_2O_7^{-} + H^+ \rightleftharpoons H_4P_2O_7 \quad \log K_{14} = 1.52$$

As early as 1949 Rogers and Reynolds reported that copper in concentrated solutions (as well as in copper-diphosphate plating baths) is complexed in two anions $CuP_2O_7^{2-}$ and $Cu(P_2O_7)_2^{6-}$, and the latter is the predominant one. The ratio $|CuP_2O_7^{2-}|/|Cu(P_2O_7)_2^{6-}|$ increases with dilution and $CuP_2O_7^{2-}$ predominates in extremely diluted solutions.[13] These results were confirmed later by other investigators[14,15] and a number of references. As long as the pH of the copper-diphosphate plating bath is in the range 7.5–9.0, the major portion of uncomplexed diphosphate ions are in the form of $P_2O_7^{4-}$ and $HP_2O_7^{3-}$. In slightly acidic (pH 5.3–7.0) solutions, complex $Cu(HP_2O_7)(P_2O_7)^{5-}$ ions are formed. If $pH < 5.3$ then $Cu(HP_2O_7)_2^{4-}$ is formed; however, these results are arbitrary, as precipitate is formed, which interferes with the investigation.[16]

It is known that barely soluble phases $Cu_2P_2O_7{\cdot}5H_2O$, $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$, $Cu_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$, $Zn_2P_2O_7{\cdot}5H_2O$, $Zn_3K_2(P_2O_7)_2{\cdot}3H_2O$, $ZnK_2P_2O_7{\cdot}2H_2O$, $ZnK_6(P_2O_7)_2{\cdot}10H_2O$, $Zn_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$, $Zn(NH_4)_2P_2O_7{\cdot}H_2O$, $Zn(NH_4)_6(P_2O_7)_2{\cdot}6H_2O$, $Zn(NH_4)_2H_4(P_2O_7)_2{\cdot}2H_2O$ may form depending on *n* and pH, when solutions of $CuSO_4$ or $ZnSO_4$ are mixed with $K_4P_2O_7$ or $(NH_4)_4P_2O_7$.[17–23]

The usual procedure employed for copper-diphosphate decontamination involves addition of Fe(II), Fe(III), Ca, Mg, Mn(II), which binds diphosphate and precipitates copper in the form of insoluble salts or $Cu(OH)_2$.[24] The DCL for copper in the United States and other western countries (in Lithuania as well) is 1 ppm as a rule and a large amount of Me^{n+} should be added ($Me^{n+}/Cu \geq 4$) and large amounts of voluminous sludge are formed. The process of precipitation is thought to involve sorption and hydrolysis. Copper-diphosphate complexes can be destroyed by adding a large amount of NaOH (to $pH \geq 12.4$), which results in gelatinous $Cu(OH)_2$ precipitation.[25] The industrial wastewaters containing diphosphate copper plating rinsing waters can be decontaminated by pH adjustment and ion-exchange or membrane technology.[26]

We have suggested the decontamination of copper diphosphate by adding $FeCl_3$, which results in the formation of $Fe_4(P_2O_7)_3 \cdot x\,H_2O$.[27] After that, free copper ions may be decontaminated by the usual precipitation in the form of $Cu(OH)_2$ using alkali. This method requires much less diphosphate-binding reagents and produces a smaller amount of galvanic sludge.

Another possible way of decontamination of diluted solutions of copper diphosphate is to add a hardly decontaminating solution, which contains other metal ions and a ligand. If metal ions bind to an excess of diphosphate, then copper and another metal are precipitated in the form of diphosphates. Thus acidic ammonium containing zinc-plating solution may be used industrially to bind the excess of diphosphate.

EXPERIMENTAL

Experiments on the decontamination were carried out at 18 ± 2°C using the following solutions containing [g/L (M)]:

Modeling copper-plating solution: $CuSO_4 \cdot 5H_2O$ 100 (0.40), $K_4P_2O_7$ 250 (0.76).

Industrial copper-plating solution *Limeda GMP*: $CuSO_4 \cdot 5H_2O$ 102 (0.41), $K_4P_2O_7$ 478 (1.45), KNO_3 5 (0.05), KH_2PO_4 10 (0.07), ammonia 25% 5 mL/L (0.03), additive *Limeda GMP-1* 2.5 mL/L, additive *Limeda GMP-2* 0.25 mL/L.

Modeling zinc-plating solution: $ZnCl_2$ 100 (0.73), NH_4Cl 180 (3.36).

Industrial zinc-plating solution *Likonda ZNSR*: $ZnCl_2$ 40 (0.29), NH_4Cl 200 (3.74), additives *Likonda ZnSR-A* 50 (mL/L), *Likonda ZnSR-B* 5 (mL/L).

3 M H_2SO_4 or 3 M KOH solutions were used to adjust the pH. $Cu_2P_2O_7 \cdot 5H_2O$ and $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ were synthesized as described in Ref. [17], $n = 0.4$ and 1.0, respectively.

$Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$ was synthesized as described in Ref.[18], $n = 1.0$. The solution was allowed to settle for 24 hr. The actual way of preparation, described in Ref.[18], suggested the settling of the solution for 4 hr. However, our x-ray diffraction (XRD) analysis of precipitates showed that 4 hr are not sufficient to reach the equilibrium state. Twenty-four hours are supposed to be enough because the results of XRD after 24 hr are identical with the results obtained after 6 days.

$Zn_2P_2O_7{\cdot}5H_2O$ and $Zn_3K_2(P_2O_7)_2{\cdot}3H_2O$ were synthesized as described in Ref.[19], $n = 0.4$ and 1.0, respectively. $Zn_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$ was synthesized as described in Ref.[21], $n = 0.74$.

In order to stimulate the save rinse tank solution model, the modeling copper diphosphate solution was diluted to a copper concentration of 5 g/L (79 m*M*). We used an industrial copper diphosphate solution, which was diluted to a copper concentration of 0.2 g/L (3.1 m*M*) in the experiment of cascade set solution simulation. An appropriate amount of model (2.9–19 mL in the case of save rinse tank solution simulation) or industrial (0.9–2.4 mL in the case of cascade set solution simulation) zinc-plating solution was added to 50 mL of diluted copper phosphate solution. After that, the pH was adjusted using 3 *M* H_2SO_4 or 3 *M* KOH (in the cases when $m \geq 2$). The solution was stirred constantly by a magnetic stirrer during the mixing of solutions and 20 min after the mixing. After 24 hr, the solution was filtered using a *Filtrak* filter (Germany) "a slow filtering for finest deposits," a Buchner funnel, and a vacuum-jet pump. Samples were conserved by adjusting pH to ~ 2 by adding H_2SO_4.

Ammonium concentration was determined by a reaction using Nesslers reagent and by masking heavy metals with Rochelle salt.[28]

Residual Cu, Zn, K, and P concentrations in the solution were determined by emission spectroscopy using a direct current argon plasma emission spectrometer *SpectraSpan VI* (Beckmann Instruments, Inc. USA). Standard solutions were prepared from monoelement stock solutions containing 1000 mg/L of Cu, Zn, K, or P. Measurements were carried out using Cu 224.700 nm, Zn 206.200 nm, K 404.140 nm, and P 253.565 nm spectral lines.

The precipitate was rinsed several times and dried at 30°C up to constant weight. About 0.1 g of precipitate was accurately weighed and dissolved in 50 mL 0.7 *M* H_2SO_4. Concentrations of Cu, Zn, K, and P were determined by emission spectroscopy, and concentration of NH_4^+ was determined by the reaction with Nesslers reagent.

The XRD patterns of the precipitate were measured using Cu Kα radiation selected by a secondary graphite monochromator. A continuous scan mode was used in the range $5° \leq 2\theta \leq 60°$ with a scan rate of $1°\ 2\theta\,\mathrm{min}^{-1}$.

RESULTS AND DISCUSSION

At first, we were looking for optimal conditions for copper, zinc, and diphosphate precipitation. We have tried different ratios of ammonium-containing zinc-plating solution and copper diphosphate solution, and various pH (Fig. 1).

Our results show that residual copper concentration (Fig. 1a and b) is the lowest at $m = 1.5$ and pH 3.5–4.5; $m = (|Cu^{2+}| + |Zn^{2+}|)/|P_2O_7^{4-}|$, and residual

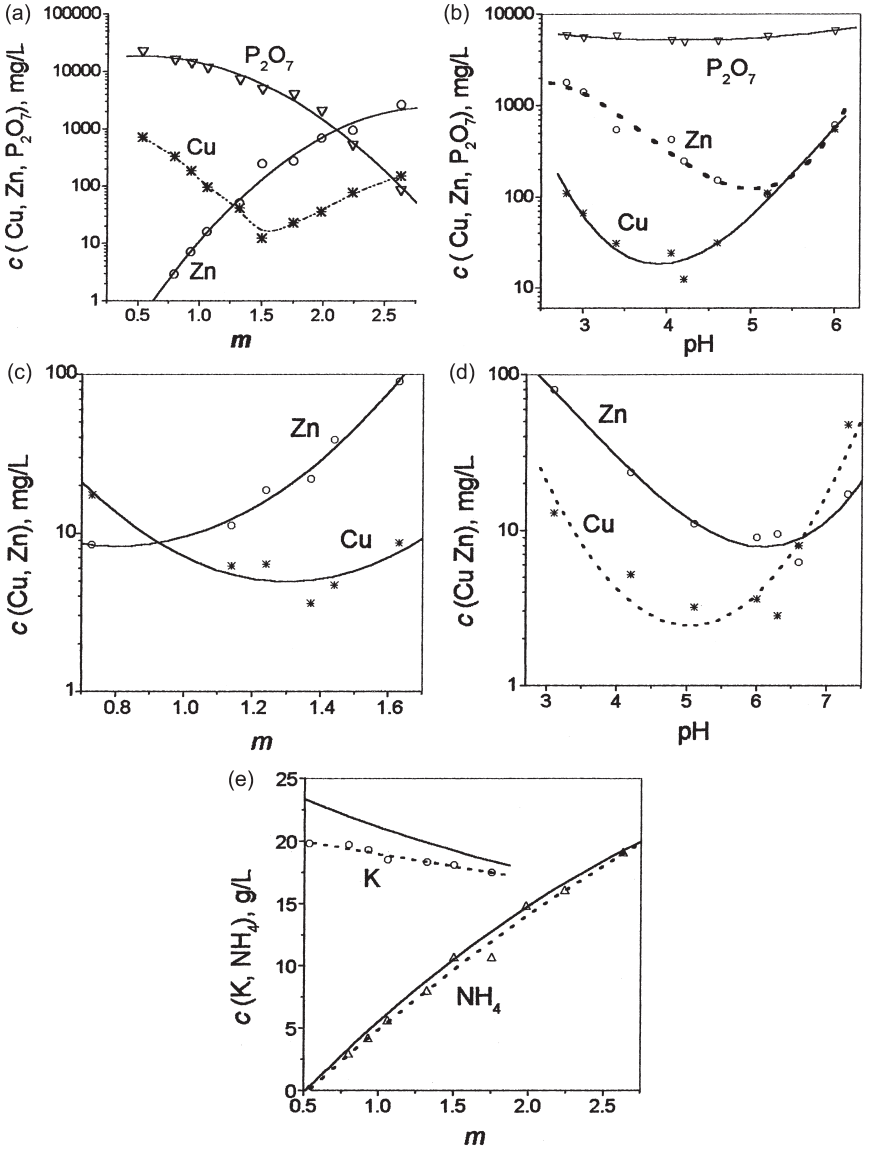

Figure 1. Dependence of residual concentrations *c* Cu, *c* Zn and *c* P_2O_7 (*a*, *b*, *c*, *d*), *c* K and *c* NH_4 (*e*) on *m* (*a*, *c*, *e*) and on pH at $m = 1.5$ (*b*, *d*). Modeling zinc-plating solution was added to the modeling diphosphate copper-plating solution diluted to *c* Cu = 5 g/L (*a*, *b*, *e*). Plant zinc-plating solution was added to the plant diphosphate copper-plating solution diluted to *c* Cu = 0.2 g/L (*c*, *d*). Straight lines in (*e*)—*c* K and *c* NH_4 in initial mixture of solutions.

zinc concentration is the lowest at pH 4.5–5.5. For example, if pH is 4.2 and $m = 1.5$, residual c Cu = 13 mg/L, c Zn = 250 mg/L, c $P_2O_7^4 = 4950$ mg/L. Therefore, in this case, 99.7% of copper, 97% of zinc, and 81% of diphosphate are removed. Experiments with a diluted industrial copper-plating solution (Fig. 1c and d) gave similar results but the residual c Cu and c Zn were significantly lower, and the minimal concentrations shifted to higher pH values: pH 4–6 for copper and pH 5–7 for zinc owing to significantly lower concentrations of $NH_4^+(NH_3)$ in the reaction mixture.

The removal of K^+ and NH_4^+ by precipitation was also studied (Fig. 1e). The higher the m value, less amount of K^+ is removed from the solution. A fair portion of NH_4^+ was only removed, moreover, the determination of that NH_4^+ using Nesslers reagent had significant standard deviation $\geq 10\%$.

We determined the phase and the chemical composition of precipitates. In the system under study, copper and zinc diphosphates of the following composition: $Cu_2P_2O_7{\cdot}5H_2O$, $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$, $Cu_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$, $Zn_2P_2O_7{\cdot}5H_2O$, $Zn_3K_2(P_2O_7)_2{\cdot}3H_2O$, $Zn_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$[17–23] may be precipitated. These salts were synthesized as described in the "Experimental" section.

$Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$, $Cu_3(NH_4)_2(P_2O_7){\cdot}3H_2O$, $Zn_3K_2(P_2O_7)_2{\cdot}3H_2O$, and $Zn_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$ salts have a monoclinic unit cell and are isomorphous. These salts have various unit cell parameters due to different atomic radii of Cu and Zn. It may be seen from the d values of the diffraction peak (011) of these phases. The d value increases from 8.86 Å for $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ up to 9.13 Å for $Zn_3K_2(P_2O_7)_2{\cdot}3H_2O$ and from 8.995 Å for $Cu_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$ up to 9.20 Å for $Zn_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$. The precipitate contains almost pure $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (Fig. 2a) when there is no Zn in the solution. Increase in zinc concentration and m of the solution leads to an increase in the d value of the diffraction peak (011) and to the variations of d values of other peaks [Figs. 2b and c and 3; $d_{(011)} \sim f(m)$]. But the precipitate contains only one diphosphate phase when $m \leq 1.5$. This may be caused by replacement of some portion of Cu ions in $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ crystals by Zn ions. Copper and zinc ions take part in formation of the same diphosphate crystal during precipitation in the solution containing Zn and Cu. But according to the XRD data two diphosphate phases are never formed in this case. The same result could be achieved by replacement of K^+ by NH_4^+ in diphosphate crystals.

Peaks of the $Zn_2P_2O_7{\cdot}5H_2O$ phase appear in XRD patterns of the precipitate when $m \geq 1.75$. The amount of this phase increases with an increase in m (Fig. 4). The d values of the peaks in XRD patterns slightly differ from the data obtained using $Zn_2P_2O_7{\cdot}5H_2O$ synthesized by us and the data given in powder diffraction file No. 7-87. This difference may be explained in the same manner as above, i.e., some portions of Zn atoms are replaced by Cu atoms.

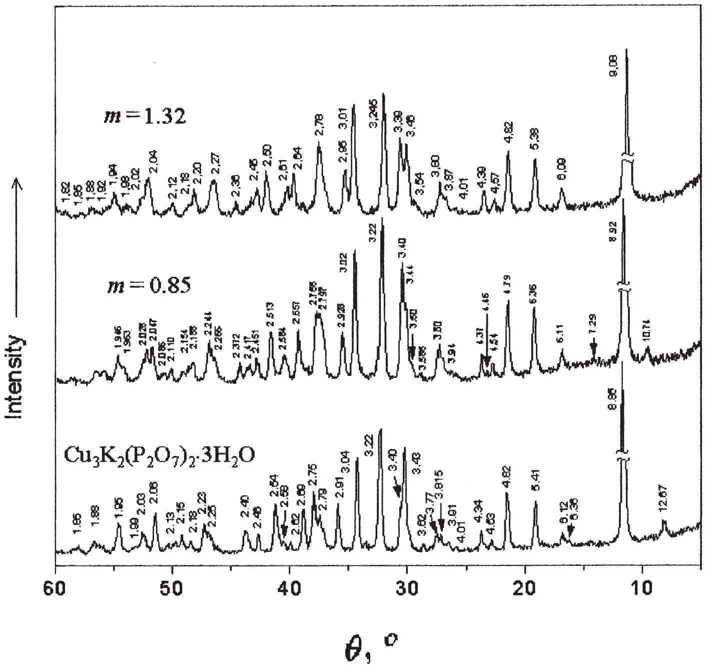

Figure 2. XRD pattern of $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ and the precipitate from solution with $m = 0.85$ and 1.32.

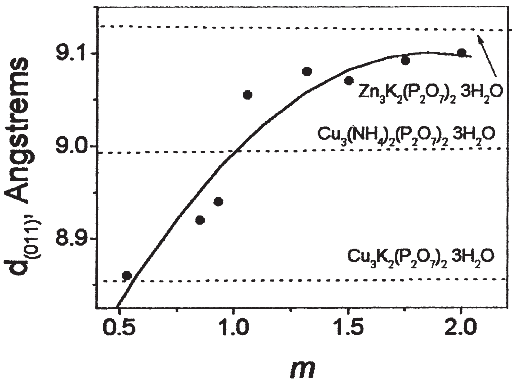

Figure 3. XRD peak (011) $d_{(011)}$ value as a function of m. Dashed lines show $d_{(011)}$ values for corresponding diphosphate phases.

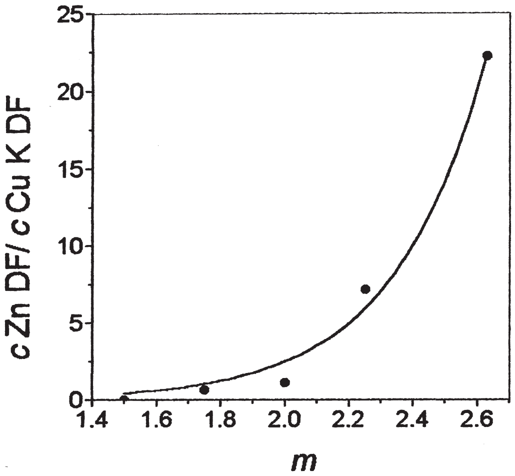

Figure 4. Dependence of the ratio *c* Zn DF/*c* Cu K DF with *m* of the solution. Zn DF means $Zn_2(Cu)P_2O_7{\cdot}5H_2O$ and Cu K DF—$Cu_3(Zn)K_2(NH_4)\ (P_2O_7)_2{\cdot}3H_2O$.

Analysis of chemical composition of the precipitate correlates with the data obtained by XRD and provides an important additional information (Fig. 5). As we have expected, the increase in m results in an exponential decrease in $|Cu|$ and an exponential increase in $|Zn|$. When $m = 0.53\text{–}1.5$, m_{pr} is about 1.5, and increase in m to the value 2.25–2.63 results in $m_{pr} \simeq 2$. $|Cu + Zn|$ increases in the same manner. Alternatively, $|P_2O_7|$ significantly decreases when $m > 1.5$. These observations correlate well with the XRD data. When $m > 1.5$, $Me^{II}_2P_2O_7{\cdot}5H_2O$ ($m_{pr} = 2$) precipitates instead of $Me^{II}_3Me^{I}_2(P_2O_7)_2{\cdot}3H_2O$ ($m_{pr} = 1.5$).

When m increases from 0.8 to 1.5 at pH 4.2, the molar ratio $|K^+|/|NH_4^+|$ in the precipitate decreases (Fig. 5b) because the molar ratio $|K^+|/|NH_4^+|$ in the solution decreases as well. However, a further increase in m results in a slow increase in this ratio. This may be accounted for greater quantities of KOH added to the solution to get a constant pH 4.2 when $m \geq 2$. The overall amount of potassium and ammonium in the precipitate remains nearly the same. But it decreases until m reaches 1.5. The XRD analysis suggests that it occurs because more zinc precipitates in the form of $Zn_2P_2O_7{\cdot}5H_2O$.

The XRD patterns suggest that in the pH range from 2.8 to 6.0 at $m = 1.5$, phase composition of the precipitate is nearly the same. Chemical composition analysis of the precipitate showed that an increase in the pH results in an insignificant increase in $c\ NH_4^+$ and insignificant decrease in $c\ K^+$ (Fig. 5c).

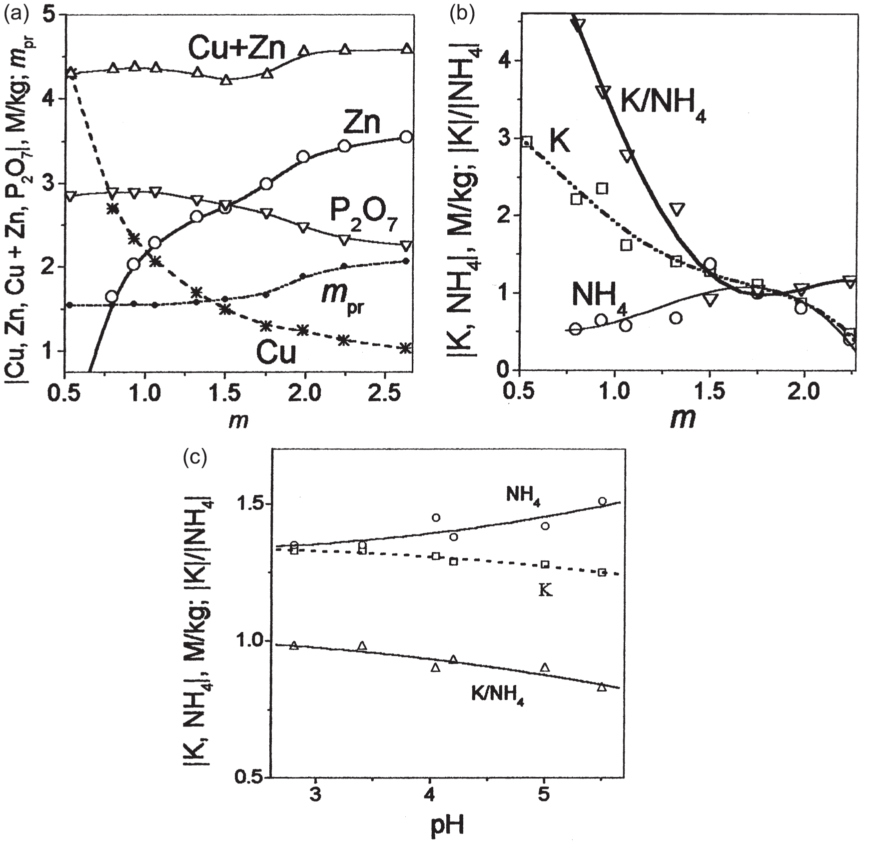

Figure 5. Dependence of concentrations *c* Cu, *c* Zn and *c* P_2O_7 (*a*), *c* K and *c* NH_4 (*b*) in precipitate on *m* at pH 4.2 and on pH at $m = 1.5$ (*c*). Modeling zinc-plating solution was added to the modeling diphosphate copper-plating solution diluted to c Cu $= 5\,g/L$.

Complex process of precipitate formation during the interaction of diluted copper- and zinc-plating solutions can be approximately described by the following equations:

$$\begin{aligned} &a\mathrm{Cu(P_2O_7)_2^{6-}} + b\mathrm{CuP_2O_7^{2-}} + c\mathrm{Cu(HP_2O_7)(P_2O_7)^{5-}} + d\mathrm{Zn^{2+}} \\ &\quad + e\mathrm{K^+} + f\mathrm{NH_4^+} + x\mathrm{P_2O_7^{4-}} + y\mathrm{HP_2O_7^{3-}} + 3\mathrm{H_2O} \\ &\quad \rightleftharpoons \mathrm{Cu}_{a+b+c}\mathrm{Zn}_d\mathrm{K}_e(\mathrm{NH_4})_f(\mathrm{P_2O_7})_2\cdot 3\mathrm{H_2O}\downarrow + (c+y)\mathrm{H^+}, \end{aligned} \tag{1}$$

where $a + b + c + d = 3$, $e + f = 2$, when $m \leq 1.5$

$$a\mathrm{Cu(P_2O_7)_2^{6-}} + b\mathrm{CuP_2O_7^{2-}} + c\mathrm{Cu(HP_2O_7)(P_2O_7)^{5-}} + d\mathrm{Zn^{2+}} + x\mathrm{P_2O_7^{4-}} + y\mathrm{HP_2O_7^{3-}} + 5\mathrm{H_2O} \rightleftharpoons \mathrm{Cu}_{a+b+c}\mathrm{Zn}_d\mathrm{P_2O_7{\cdot}5H_2O}\downarrow + (b+y)\mathrm{H^+}, \tag{2}$$

where $a + b + c + d = 2$, when $m > 1.5$.

Two possible ways for utilization of the precipitate may be proposed:

1. It may be used as a microfertilizer, as it contains two important microelements, such as zinc and copper.
2. Both zinc and copper may be electrolytically recuperated as brass.

For the recuperation experiment, 10 g of dry precipitate obtained from a diluted industrial solution at pH 5.5 and $m = 1.7$, and 30 g of $K_4P_2O_7$ were dissolved in 100 mL of distilled water. The solution contained 5.6 g/L of copper and 16.0 g/L of zinc, pH 9.6. Electrolysis was carried out in a simple electrolyzer with two flat stainless steel anodes and a copper cathode for 5 hr at $i_c = 1\,\mathrm{A\,dm^{-2}}$. The color of the deposit changed from copper-like red at the beginning of the process, then to brass-like yellow, and finally to a pale yellow. As a result of electrolysis the pH decreased to 8.7, c Cu to 0.2 g/L and c Zn to 11.2 g/L. Ten grams of the precipitate were dissolved in the same residual solution and electrolysis using the same cathode was repeated. The deposit was visually the same.

This preliminary investigation shows that such a process may be easily realized in industry. Naturally, this particular investigation in laboratory must be carried out before its industrial implementation.

CONCLUSION

A new cheap and simple method of decontamination of hardly decontaminating zinc- and copper-plating wastewaters is suggested. The main part of heavy metals and diphosphate ions may be removed after mixing both rinsing waters in optimal ratio and adjusting the pH in the form of fine crystalline, easy-to-filtrate, utilizable precipitate of solid solution of diphosphates. This type of approach may also be used to decontaminate other ligand-containing wastewaters, and further investigations are needed to find other cost-effective, reliable, and simple methods of decontamination of several environmentally hazardous wastewaters.

NOMENCLATURE

c	concentration
n	$\|P_2O_7{}^4\|/\|Me^{n+}\|$
DCL	discharge consent level
m	$(\|Cu^{2+}\| + \|Zn^{2+}\|)/\|P_2O_7^{4-}\|$ in initial mixture of solution
m_{pr}	$(\|Cu^{2+}\| + \|Zn^{2+}\|)/\|P_2O_7^{4-}\|$ in precipitate

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