



## **THE INTERACTION OF TWO LIGAND CONTAINING ELECTROPLATING SOLUTIONS. FINAL DECONTAMINATION**

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### **ABSTRACT**

We suggested previously a cheap and simple way to decontaminate two ligand-containing rinsing waters of metal finishing. Both copper diphosphate containing rinsing wastewater and acidic zinc ammonium containing rinsing wastewater may be decontaminated by mixing with each other, which results in precipitation of solid solutions of copper-zinc-potassium-ammonium diphosphates. This way of decontamination requires no expensive reagents since only a small amount of H<sub>2</sub>SO<sub>4</sub> is needed for pH adjustment. 80-99.5 % of environmentally dangerous substances, viz. zinc, copper and diphosphate, are removed from the mixture. However, Cu<sup>2+</sup> and Zn<sup>2+</sup> amounts in filtrates significantly exceed discharge consent level (DCL). Moreover, high concentrations of undesirable diphosphate and ammonium ions, which cause the eutrophication of natural water reservoirs, are present in the filtrates. Depending on the waste water composition of the specific plant and the environment protection requirements the goals of the decontamination may be as follows: 1.) To remove Cu<sup>2+</sup> and Zn<sup>2+</sup> ions below DCL, 2.) To remove Cu<sup>2+</sup> and Zn<sup>2+</sup> ions below DCL and additionally to lower the amount of phosphates, 3.) To remove Cu<sup>2+</sup> and Zn<sup>2+</sup> ions below DCL and additionally to lower the amount of phosphates and ammonium.

Our investigation has shown, that goal 1 can be easily and cheaply achieved in industry by using lime, goal 2 – by using lime and spent steel etching solution or phosphogypsum. Goal 3 was achieved by precipitating barely soluble fine crystalline MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O. It has been determined, that at optimal conditions as much as 95% of NH<sub>4</sub><sup>+</sup> ions are precipitated, both residual *c* Cu<sup>2+</sup> and *c* Zn<sup>2+</sup> < DCL, and the concentration of soluble phosphates is reduced 5-40 fold.

Keywords: diphosphate, copper, zinc, ammonium, electroplating, rinsing water, decontamination

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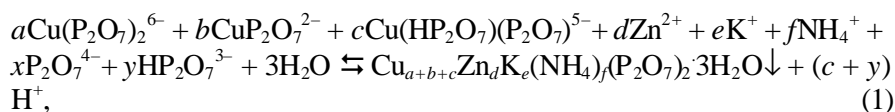
## INTRODUCTION

We have suggested a cheap and simple way to decontaminate two ligand-containing rinsing waters of metal finishing [1]. Copper diphosphate containing rinsing wastewater and acidic zinc ammonium containing rinsing wastewater, both may be decontaminated by mixing, which results in precipitation of solid solutions of copper-zinc-potassium-ammonium diphosphates. This way of decontamination requires no expensive reagents since only a small amount of  $\text{H}_2\text{SO}_4$  is needed for pH adjustment. 80-99.5 % of environmentally dangerous substances, viz. zinc, copper and diphosphate, are removed from the mixture.

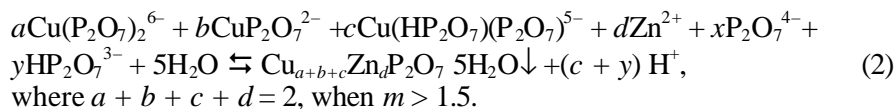
As far back as 1949 Rogers and Reynolds reported, that copper in concentrated solutions (as well as in copper-diphosphate plating baths) is complexed in two anions  $\text{CuP}_2\text{O}_7^{2-}$  and  $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ , and the latter is the predominant one. The ratio  $|\text{CuP}_2\text{O}_7^{2-}|/|\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}|$  increases with dilution and  $\text{CuP}_2\text{O}_7^{2-}$  predominates in extremely diluted solutions [2]. Later these results were confirmed by the other investigators [3, 4 and a diversity of references]. As far as the pH of copper-diphosphate plating bath is in the range 7.5-9.0, the major portion of uncomplexed diphosphate ions is in the form of  $\text{P}_2\text{O}_7^{4-}$  and  $\text{HP}_2\text{O}_7^{3-}$  according the protonisation constants of diphosphate ions [5]. In slightly acidic (pH 5.3÷7.0) solutions, complex  $\text{Cu}(\text{HP}_2\text{O}_7)(\text{P}_2\text{O}_7)^{5-}$  ions form. If  $\text{pH} < 5.3$  then  $\text{Cu}(\text{HP}_2\text{O}_7)_2^{4-}$  forms, however, these results are arbitrary, as precipitate forms interfere with the investigation [6].

Barely soluble phases  $\text{Cu}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ ,  $\text{Cu}_3\text{K}_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cu}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ ,  $\text{Zn}_3\text{K}_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{ZnK}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $\text{ZnK}_6(\text{P}_2\text{O}_7)_2 \cdot 10\text{H}_2\text{O}$ ,  $\text{Zn}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ ,  $\text{Zn}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NH}_4)_2\text{H}_4(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$  may form depending on  $n$  ( $n = |\text{P}_2\text{O}_7^{4-}|/|\text{Me}^{n+}|$ ) and pH, when solutions of  $\text{CuSO}_4$  or  $\text{ZnSO}_4$  are mixed with  $\text{K}_4\text{P}_2\text{O}_7$  or  $(\text{NH}_4)_4\text{P}_2\text{O}_7$  [7-13]. In the system under study, copper and zinc diphosphates of the following composition:  $\text{Cu}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ ,  $\text{Cu}_3\text{K}_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cu}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ ,  $\text{Zn}_3\text{K}_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$  may be precipitated [7-13]. But according to the XRD data the precipitate contains only one diphosphate phase when  $m \leq 1.5$  ( $m = (|\text{Cu}^{2+}| + |\text{Zn}^{2+}|)/|\text{P}_2\text{O}_7^{4-}|$  in initial mixture of solution). This may be caused by replacement of some portion of  $\text{Cu}^{2+}$  and  $\text{K}^+$  ions in  $\text{Cu}_3\text{K}_2(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$  crystals by  $\text{Zn}^{2+}$  and  $\text{NH}_4^+$  ions. Peaks of the  $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$  phase appear in XRD patterns of the precipitate when  $m \geq 1.75$ . The amount of this phase increases with increase in  $m$ , and no peaks of  $\text{Cu}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$  are observed. It may be explained in the same way as above: a fraction of Zn atoms is replaced by Cu atoms in  $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$  crystals.

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



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



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

However,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  amounts in filtrates significantly exceed discharge consent level (DCL), which is  $1 \text{ mg dm}^{-3}$  in Lithuania [14] (in EU countries and the USA likewise).

Moreover, high concentrations of undesirable diphosphate and ammonium ions, which cause the eutrophication of natural water reservoirs, are present in the filtrates. The ammonium present in the wastewaters is a potent inhibitor of algal photosynthesis and interferes in the stabilization process of the oxygenation in swamps and lagoons. Furthermore, ammonia is toxic to fish, even in very low concentrations [15-17]. It is recommended that wastewater should not contain more than  $0.02 \text{ mg dm}^{-3}$  of free ammonia and this is taken as reference for the dump wastewater [18].

An increasing  $\text{Ca}^{2+}$  ion concentration reduces toxic effects of ammonium ions, however, toxicity of zinc and ammonium ions has a cumulative effect. The toxicity of ammonium ions also increases at higher pH [17].

Phosphorus stimulates the growth of algae in the natural water resources, which receive the wastewater [19]. Phosphorus is frequently the limiting factor for algae growth, and in much smaller concentrations, than that of nitrogen, is a very potent growth stimulator.

Depending on the waste water composition from the specific plant and the environment protection requirements the goals of the decontamination may be as follows:

1. To remove  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions below DCL.
2. To remove  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions below DCL and additionally to reduce the amount of phosphates.
3. To remove  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions below DCL and additionally to reduce the amount of phosphates and ammonium.

Goals 1 and 2 were achieved by adding cheap and environmentally low dangerous  $\text{CaO}$ , phosphogypsum (*FG*) and  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Fe}^{2+}$  compound solutions:  $\text{MgSO}_4$ ,  $\text{CaCl}_2$  and spent steel etching solution (*SSES*).

$\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  form a number of simple and double low soluble salts with diphosphate ions, including monoclinic  $\text{Me}_3^{\text{II}}\text{Me}_2^{\text{I}}(\text{P}_2\text{O}_7)_2 \cdot x\text{H}_2\text{O}$  diphosphate ( $\text{Me}^{\text{I}} = \text{K}^+, \text{NH}_4^+$ ) [20-26]. After adding the  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  compounds we can expect an effective  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  precipitation due to the solid solution formation. Precipitation of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions is also facilitated by decreased concentration of diphosphate ions (due to

precipitation of  $Mg^{2+}$  and  $Ca^{2+}$  diphosphates).  $Fe^{2+}$  ions form barely soluble diphosphates as well, however, they are not described in references.

*FG* is a by-product of fertilizer industry. Four tons of *FG* produced for every ton of phosphoric acid. Despite the fact, that *FG* contains up to 98% of calcium sulphate  $CaSO_4 \cdot 2H_2O$  (gypsum), its usage is quite complicated because of specific chemical composition and structure. For example, Stock Joint Lifosa in Kedainiai (Lithuania) has literally hills of *FG* (nearby 20 millions of tons). This *FG* contains, %: 31-37 CaO, 44-54  $SO_3$ , 0.5-1.5  $R_2O_3$ , 0.24-0.32  $Na_2O$ , 0.04-0.08  $K_2O$ , 0.91-2.86 total  $P_2O_5$ , 0.14-0.48 total F; density 750-800  $kg\ m^{-3}$ , specific area 260-290  $m^2\ kg^{-1}$ . *FG* particles mostly are rhomboidal, 5-500  $\mu m$  long, 1-50  $\mu m$  wide, 0,05-0,5  $\mu m$  thick crystals of  $CaSO_4 \cdot 2H_2O$  [27].

*FG* is suitable for the removal of  $Sr^{2+}$  and  $Pb^{2+}$  from the wastewaters, as it was determined by [28]. In Western countries and the USA one of the important industrial problems is flue gas desulphurisation (FGD) gypsum utilization, because huge amounts of FGD gypsum are generated during decontamination of power plant exhaust gases. However, only a small fraction of FGD gypsum is utilised, which is a similar situation to that of *FG* [29].

Goal 3 was achieved by precipitation of barely soluble fine crystalline  $MgNH_4PO_4 \cdot 6H_2O$ . It is known that potassium and heavy metal ions are included effectively into forming crystals [30, 31].

Plants, which remove phosphorus biologically from wastewaters, use anaerobic digesters for sludge treatment. The sidestreams from the sludge dewatering equipment contain high phosphorus concentrations.  $MgNH_4PO_4 \cdot 6H_2O$  (*struvite*) precipitation (MAP process) is used for sewage water treatment in Japan. Phosnix process developed by Unitika Ltd. has been operating at full scale at several sites in Japan since 1987. A similar process is used by Kurita Water Industries [19]. About 94 % of phosphates are precipitated in the form of *struvite* by addition of  $Mg(OH)_2$  or  $MgCl_2$ . Since concentration of ammonium ions is much higher, this process removes as little as 6% of it, but it is mainly removed by anaerobic process. Both companies are continuously investigating and optimising *struvite* precipitation process and improving equipment (e.g. [32, 33]). Unitika Ltd. offers *struvite* under the name "Green MAP II", and it has been promoted as an "environmentally friendly special fertilizer for forest regeneration of artificially created slopes" as well as a "plant friendly long lasting type gardening fertiliser" at a price of ~270 US\$/t [34]. Apparently, however, MAP process is used only in Japan, and might be used in Australia in close future [34]. In case of municipal sewage, a high concentration of ammonium ions suppresses microorganisms in the biological treatment plants, and therefore, it is favourable to remove it by precipitation as  $MgNH_4PO_4 \cdot 6H_2O$  [35, 36].

Conditions of precipitation of  $MgNH_4PO_4 \cdot 6H_2O$  and its properties are well known, (e.g. [37, 38]), because it is used for determination of

magnesium and phosphorus in ores and minerals [39-41]. Potassium and heavy metal ions co-precipitated to some extent, and, therefore, the analysis is performed in the solutions, when heavy metals have already been removed. If the concentration of potassium is significant, precipitate is dissolved, and then precipitated again. In our case, in order to compensate the co-precipitation of potassium, it would be necessary to slightly increase the amount of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$ . Co-precipitation of heavy metal ions (in this case  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) should be sufficient to remove them down to the concentration below DCL.

$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , as well as the other alkaline-earth metal phosphates is suitable for removal of heavy metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ) from aqueous solutions. The efficiency of the phosphates in removal of  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$  ions has been shown to decrease in the following sequence:  $\text{Mg}_3(\text{PO}_4)_2 > \text{MgNH}_4\text{PO}_4 > \text{Ca}_3(\text{PO}_4)_2 > \text{CaHPO}_4 > \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  which is inverse to their hydrolytic stability series. The maximal capacity decreases for  $\text{Pb}^{2+}$  from 22.8 mg-eq/g of  $\text{Mg}_3(\text{PO}_4)_2$  to 0.6-9.6 mg-eq/g of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . Similar results are attained for  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  [42-44].

## MATERIALS/METHODS/PROCEDURES

Experiments on the decontamination were carried out at  $18 \pm 2^\circ\text{C}$ .

Decontaminating filtrate was prepared by adding of modelling zinc-plating solution (containing  $\text{ZnCl}_2$  100 g  $\text{dm}^{-3}$ ,  $\text{NH}_4\text{Cl}$  180 g  $\text{dm}^{-3}$ ) to the modelling diphosphate copper-plating solution (containing  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  100 g  $\text{dm}^{-3}$ ,  $\text{K}_4\text{P}_2\text{O}_7$  250 g  $\text{dm}^{-3}$ ), diluted to a copper concentration of 5 g  $\text{dm}^{-3}$  at  $m = 1.4$ , pH 4.5. The filtrate contained (mg  $\text{dm}^{-3}$ ):  $\text{Cu}^{2+} - 24$ ,  $\text{Zn}^{2+} - 73$ ,  $\text{P}_2\text{O}_7^{4-} - 3560$ ,  $\text{NH}_4^+ - 9500$ .

In our research, we have used the following solutions: 2 M  $\text{MgSO}_4$ , 1 M  $\text{CaCl}_2$ , *SSES*, containing 2.72 M  $\text{FeSO}_4$  and 0.11 M  $\text{H}_2\text{SO}_4$ .

An appropriate amount of  $\text{MgSO}_4$ , or  $\text{CaCl}_2$  solutions, or *SSES* was added to the 50  $\text{cm}^3$  filtrate. After that, the pH was adjusted using 3 M and 0.5 M  $\text{NaOH}$ . The solution was stirred constantly by a magnetic stirrer during the pH adjusting and 15 minutes after that. After 24 hours, the solution was filtered using a *Filtrak* filter paper "a slow filtering for finest deposits" in a Buchner funnel with the help of a vacuum-jet pump. Samples were conserved by adjusting pH to  $\sim 2$  by adding  $\text{HCl}$ . Analogous, decontamination was investigated using  $\text{CaO}$  powder. In the cases when decontamination using  $\text{CaO}$  and *FG* was investigated, in the first stage  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions were removed below DCL by adding  $\text{CaO}$  to pH 7.0, 10 g of *FG* was added to the 100  $\text{cm}^3$  of filtrate, and the pH was adjusted by adding  $\text{CaO}$ . pH of the mixture was declining slowly, and it was corrected every 15 min during first two hours, and every 30 min afterwards.

All the reagents used were either "chemically pure" or "pure for analysis" (made in Russia).

Residual  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{n+}$  and P(V) concentrations in solution were determined by emission spectroscopy applying a direct current argon plasma emission spectrometer Beckman SpectraSpan VI. Standard solutions were prepared from monoelement stock solutions containing  $1000 \text{ mg dm}^{-3}$   $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$  and P(V). Measurements were carried out using Cu 224.700 nm, Zn 206.200 nm, Fe 259.940 nm and P 253.565 nm spectral lines.

Ammonium was determined using the reaction with the Nesler reagent by masking heavy metals with Rochelle salt [45].

X-ray diffraction (XRD) patterns of precipitate were measured using Cu  $K_{\alpha}$  radiation selected by a secondary graphite monochromator. A continuous scan mode was used in the range of  $5^{\circ} \leq 2\theta \leq 60^{\circ}$  with a scan rate of  $1^{\circ} 2\theta \text{ min}^{-1}$ .

## RESULTS AND DISCUSSION

At first, we were looking for optimal conditions for copper, zinc and diphosphate precipitation. We tried various pH and different  $m$  at optimum pH for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  precipitation after mixing with  $\text{MgSO}_4$ ,  $\text{CaCl}_2$  solution and *SSES*. Our results showed that by adding  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  solutions, the residual concentrations either of both  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  or one of them are higher than DCL at any pH and  $m$  (Fig. 1 a, b, e, f). However, *SSES* effectively removed  $\text{P}_2\text{O}_7^{4-}$  ions and  $c \text{P}_2\text{O}_7^{4-} < 1 \text{ mg dm}^{-3}$  were easily achieved. Residual  $c \text{Cu}^{2+}$  and  $c \text{Zn}^{2+}$  both are below DCL at pH 6.6-7.4 or  $m > 1.15$  (pH 6.8) after mixing with  $\text{CaCl}_2$  solution (Fig. 1 c, d). Since CaO acts as a pH adjusting agent and a source of  $\text{Ca}^{2+}$  ions, after mixing with CaO powder both the residual  $c \text{Cu}^{2+}$  and  $c \text{Zn}^{2+}$  are lower than DCL at pH 6.3-7.7 (Fig. 2). Thus, goal 1 can be easily and cheaply achieved in industry by using lime.

CaO is particularly effective for the removal of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , and *SSES* is effective for removal of diphosphate. Initially, we tried to achieve goal 2 using mixture of *SSES* and CaO, however, we failed to obtain consistent reproducible results, apparently because of formation of colloidal solutions. It turned out, that the better way to achieve the goal 2 is the precipitation by two steps: at first to remove  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  below DCL by adding of CaO to pH 7.0-7.5 and after filtration remove residual diphosphate by adding *SSES* to molar ratio  $[\text{Fe}^{2+}] : |\text{P}_2\text{O}_7^{4-}| \approx 2$  and adjusting pH to 8.5-9.0 by adding CaO. The residual  $\text{P}_2\text{O}_7^{4-}$  and  $\text{Fe}^{n+}$  concentrations are below  $1 \text{ mg dm}^{-3}$ , what is important for many European countries where  $\text{Fe}^{n+}$  concentration in wastewaters is severely restricted.

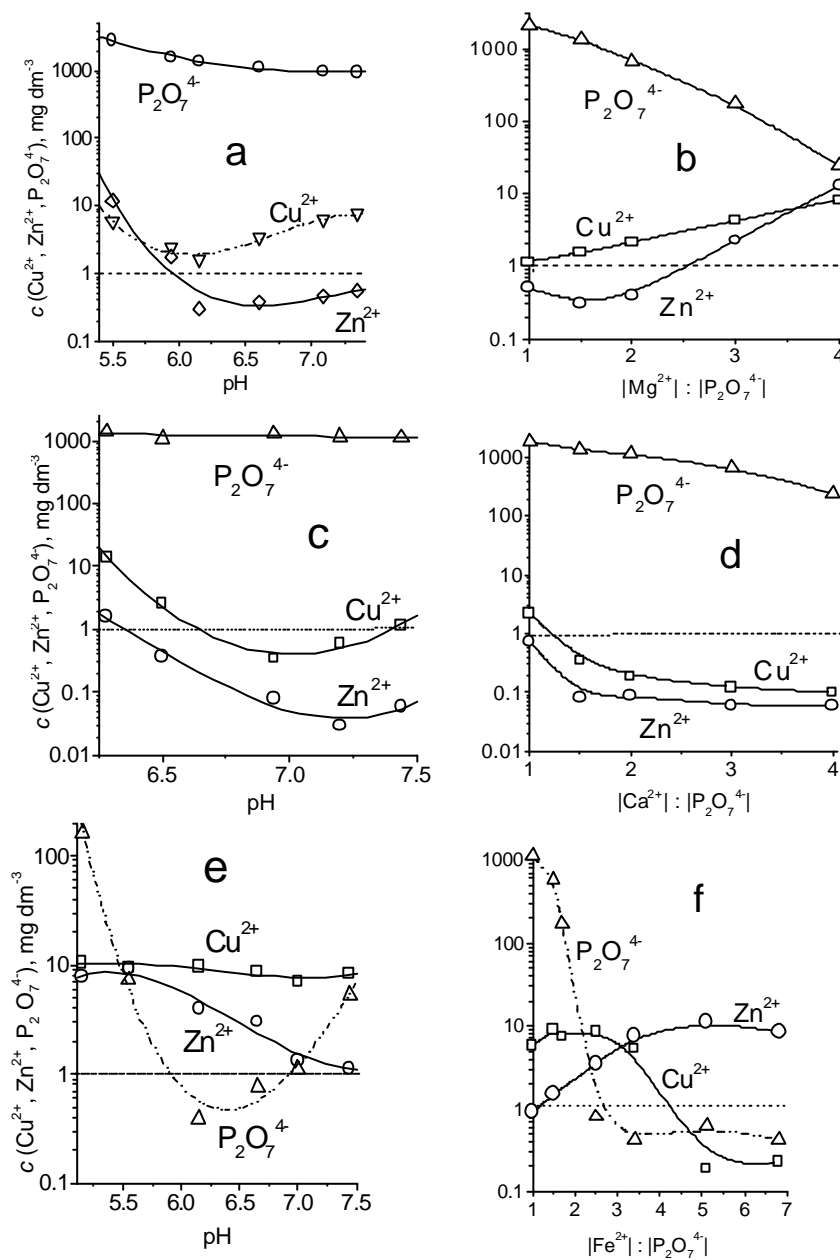


Fig. 1. Dependence of residual concentrations of Cu<sup>2+</sup>, Zn<sup>2+</sup> and P<sub>2</sub>O<sub>7</sub><sup>4-</sup> ions on pH at |Mg<sup>2+</sup> (a) or Ca<sup>2+</sup> (c)| : |P<sub>2</sub>O<sub>7</sub><sup>4-</sup>| (*m*) = 1.5 or Fe<sup>2+</sup> (e) *m* = 2.5 and on *m* at pH 6.1 (b), 6.8 (d) and 6.5 (f). Decontaminated filtrate contained (mg dm<sup>-3</sup>): Cu<sup>2+</sup> – 24, Zn<sup>2+</sup> – 73, P<sub>2</sub>O<sub>7</sub><sup>4-</sup> – 3560, NH<sub>4</sub><sup>+</sup> – 9500; pH 4.5.

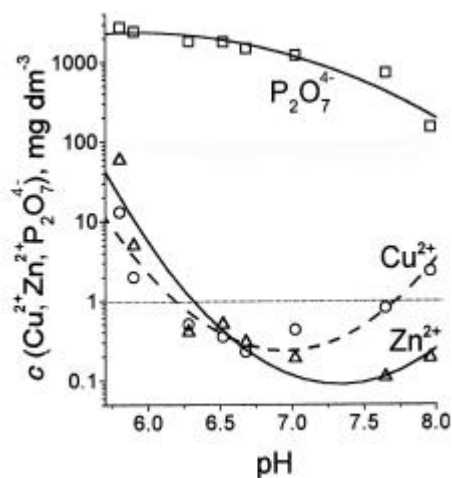


Fig. 2. Dependence of residual concentrations of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{P}_2\text{O}_7^{4-}$  ions on pH by its adjusting with CaO powder). Decontaminated filtrate contained ( $\text{mg dm}^{-3}$ ):  $\text{Cu}^{2+}$  – 24,  $\text{Zn}^{2+}$  – 73,  $\text{P}_2\text{O}_7^{4-}$  – 3560,  $\text{NH}_4^+$  – 9500; pH 4.5.

Similarly, using *FG*, at first  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  were removed below DCL by adding of CaO and then the filtrate was mixed continuously with *FG* (10 % suspension). The results showed (Fig. 3), that dyphosphate ions could be effectively removed from the filtrate down to residual concentrations 1.5-3  $\text{mg dm}^{-3}$  by mixing with *FG* suspension 4-6 h at pH 7.3-7.7. In this case the precipitate may be simply utilised as a long lasting type phosphorus fertilizer.

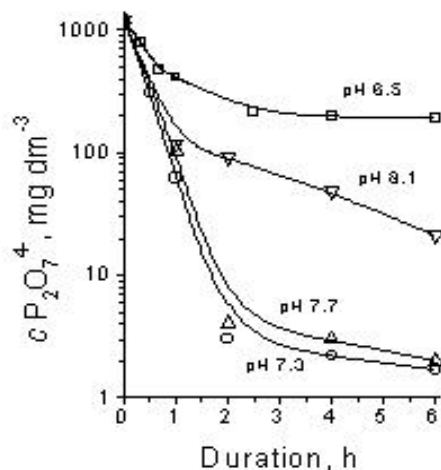


Fig. 3. Dependence of residual concentrations of  $\text{P}_2\text{O}_7^{4-}$  ions on the duration of mixing with phosphogypsum (10 % suspension). Decontaminated filtrate contained ( $\text{mg dm}^{-3}$ ):  $\text{P}_2\text{O}_7^{4-}$  – 1210,  $\text{Cu}^{2+}$  – 0.5,  $\text{Zn}^{2+}$  – 0.1,  $\text{NH}_4^+$  – 9500; pH 7.5.



Task 3 was achieved by precipitating of barely soluble fine crystalline  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ .  $\text{MgSO}_4$  and  $\text{Na}_3\text{PO}_4$  solutions were added to achieve the molar ratio  $|\text{Mg}^{2+}| : |\text{NH}_4^+| : |\text{PO}_4^{3-}| = 1.5 : 1 : 1.25$ . It has been determined (Fig. 4) that at the optimum pH 7-8, 95-97 %  $\text{NH}_4$  ions is precipitated, both the residual  $c \text{Cu}^{2+}$  and  $c \text{Zn}^{2+}$  lower than DCL, and the concentration of soluble phosphates decreases 5-40 times. The effectiveness of decontamination was studied at optimal pH 7.5 at the molar ratios  $|\text{Mg}^{2+}| : |\text{NH}_4^+| : |\text{PO}_4^{3-}| = 1:1:1$  and  $2:1:1.5$  (Table 1).

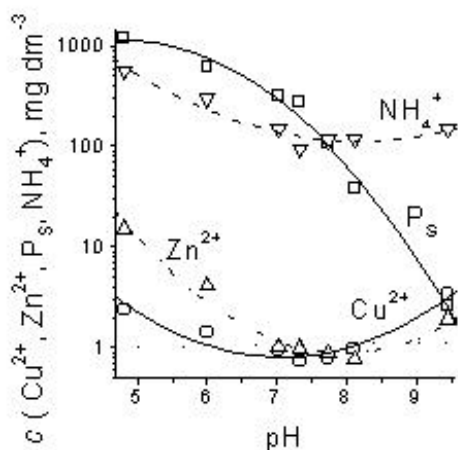


Fig. 4. Dependence of residual concentrations of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{P}_s$  and  $\text{NH}_4^+$  on pH after mixing with  $\text{MgSO}_4$  and  $\text{Na}_3\text{PO}_4$  solutions to molar ratio  $|\text{Mg}^{2+}| : |\text{NH}_4^+| : |\text{PO}_4^{3-}| = 1.5 : 1 : 1.25$ . Decontaminated filtrate contained ( $\text{mg dm}^{-3}$ ):  $\text{Cu}^{2+} - 24$ ,  $\text{Zn}^{2+} - 73$ ,  $\text{P}_2\text{O}_7^{4-} - 3560$ ,  $\text{NH}_4^+ - 9500$ ; pH 4.5.

Tab. 1. Dependence of residual  $c \text{Cu}^{2+}$ ,  $c \text{Zn}^{2+}$ ,  $c \text{P}_s$  and content of  $\text{K}^+$  in the precipitate on molar ratio  $|\text{Mg}^{2+}| : |\text{NH}_4^+| : |\text{PO}_4^{3-}|$  in the initial mixture of solutions. Decontaminated filtrate contained ( $\text{mg dm}^{-3}$ ):  $\text{Cu}^{2+} - 24$ ,  $\text{Zn}^{2+} - 73$ ,  $\text{P}_2\text{O}_7^{4-} - 3560$ ,  $\text{NH}_4^+ - 9500$ ; pH 4.5.

$ \text{Mg}^{2+}  :  \text{NH}_4^+  :  \text{PO}_4^{3-} $	Residual concentrations, $\text{mg dm}^{-3}$			$\text{K}^+$ , % in precipitate
	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{P}_s$	
1 : 1 : 1	0.98	0.28	613	1.10
1.5 : 1 : 1.25	0.78	0.86	109	1.82
2 : 1 : 1.5	0.70	1.21	58	1.91

The content of  $\text{K}^+$  in air-dried precipitate was determined and XRD analysis of precipitate was performed. The results have shown that optimum molar ratio is  $|\text{Mg}^{2+}| : |\text{NH}_4^+| : |\text{PO}_4^{3-}| \sim 1.5:1:1.25$ . At the molar ratio  $|\text{Mg}^{2+}| : |\text{NH}_4^+| : |\text{PO}_4^{3-}| = 1:1:1$  the content of  $\text{P}_{\text{soluble}} (\text{P}_s)$  in filtrate is too high and at  $|\text{Mg}^{2+}| : |\text{NH}_4^+| : |\text{PO}_4^{3-}| = 2:1:1.5$  residual  $c \text{Zn}^{2+}$  is higher than DCL. The

content of  $K^+$  in the precipitate formed at the ratio  $[Mg^{2+}] : [NH_4^+] : [PO_4^{3-}] = 1.5:1:1.25$  significantly increases compared with that in the precipitate formed at  $[Mg^{2+}] : [NH_4^+] : [PO_4^{3-}] = 1:1:1$  and remains approximately the same when the ratio increased up to  $[Mg^{2+}] : [NH_4^+] : [PO_4^{3-}]$  ratio from 1.5:1:1.25 to 2 :1:1.5.

The diffractograms of the three precipitates are almost the same, and correspond to the compound  $MgNH_4PO_4 \cdot 6H_2O$ . When  $[Mg^{2+}, (PO_4)^{3-}] : [NH_4^+] > 1$ , barely soluble  $Mg_3(PO_4)_2 \cdot 22H_2O$  and  $Mg_3(PO_4)_2 \cdot 8H_2O$  should form additionally [37, 38]. The absence of the peaks in the diffractograms shows that they are in amorphous state.

Preliminary research has shown, that goal 3 can be successful achieved by using extractive phosphoric acid (intermediate product in fertilizer industry; SJ Lifosa (Kedainiai, Lithuania) sells it for ~ 250 US\$/t  $P_2O_5$ ) as a phosphate source and  $MgO \geq 98\%$  purity), produced from Lithuanian dolomite in SJ Achema (Jonava, Lithuania) pilot set, as a magnesium source and a pH adjuster.

### CONCLUSIONS

Final decontamination of the filtrates obtained after interaction of two ligand- containing (copper diphosphate and zinc ammonium) electroplating solutions was investigated. We tried to achieve it by cheap and simple means. It was determined that  $Cu^{2+}$  and  $Zn^{2+}$  ions may be removed below DCL in industry using lime. After that, the amount of diphosphate may be removed to concentrations lower than  $1 \text{ mg dm}^{-3}$  by addition of spent steel etching solution (SSES)  $\alpha$  to  $1.5\text{-}3 \text{ mg dm}^{-3}$  by continuous mixing with phosphogypsum. Lime as pH adjuster in both cases may be used. It is possible to remove  $Cu^{2+}$  and  $Zn^{2+}$  ions below DCL and additionally to lower the amount of phosphates (5-40 fold) and ammonium (~ 95 %) by precipitation of barely soluble fine crystalline  $MgNH_4PO_4 \cdot 6H_2O$  (*struvite*). Extractive phosphoric acid (an intermediate product of fertilizer industry) may be used as phosphate source.

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