PREVENTION OF THE ANTHROPOGENIC POLLUTION OF NATURAL WATER IN THE NEAR-BORDER REGIONS

YaremaTevtul[1], Sonia Gutt[2]

"Yurii Fedkovich "Chernivtsi National University[1], Kotsiubinsky St., 2, Chernivtsi 58012, Ukraine.
E-mail: yatevtul@chnu.cv.ua
„ Ştefan cel Mare " University of Suceava, Faculty of Food Engineering,
Str. Universitatii, no. 13, 720229, Suceava, Romania,, e-mail: gutts@usv.ro

Abstract: *Various methods of prevention of the natural water pollution have been reviewed. Some results related to development of the ecologically safe technologies for the metals and alloys surface treatment have also been reported. Original equipment for the ecologically safe technological processes is described. It is shown how to carry out various resource saving processes of chemical and electrochemical treatment of metals and dielectrics.*

Keywords: *water pollution, ecologically safe technologies, electrochemical treatment.*

Anthropogenic pollution of the near-border waters is under constant and strict attention of many government and non-government ecological organizations. This is caused by a high threat of such pollution, which can easily move between the neighbor countries. Quality of drinking and irrigation water and even soils can significantly decrease because of this pollution causing health deterioration caused by polluted food. Therefore, monitoring of the surface natural water quality has become rather important issue. However, prevention of its pollution is even more important. This problem can be solved only through development of the ecologically safe technological processes.

There are several classes of the sewage waters depending on the pollutants nature and here we concentrate on the heavy metals containing sewage waters analysis. They are being mainly discharges by the plants with surface treatment of metals, alloys or dielectrics such as chemical and electrochemical etching and polishing, dielectric metallization, electrochemical dimensional processing etc.

This paper deals with pollution, with iron, nickel, copper, cobalt, zinc, chromium, cadmium and manganese ions.

Iron pollution level has been determined for the Siret river water in 1993-2006 and maximal concentration of the iron ions was 0, 7 mg/l at the border with Romania and 0, 6 mg/l within Storozhinets. Maximal level of the iron content in the river of Prut was 6,9 mg/l within Kolomyya, 0,54 mg/l within Nepolokivtsi and 0,7 mg/l within Magala. Maximal permissible concentration (MPC) of Fe(III) ions for the drinking or domestic use waters is 0,5 mg/l however technological regime for some electronic, semiconductor industries, artificial and synthetic fibers establish even more strict requirements. Iron content (converted into Fe (II) concentration) in the technological water should be kept under 0, 05 mg/l.

Toxic action of Fe (II) sulfate reveals in qualmishness, arterial pressure fall and blood fibrillation worsening. Heavy poisoning can cause death from liver lesions, jaundice, metabolic acidosis and shock. Excessive content of the iron compounds in the food can become a way of poisoning. Therefore, taking into account possible ions migration, maximal iron content in the food should be kept under 0,42 % and sewage irrigation water should not contain more than 15-70 mg/l of the iron compounds [1].

Dangerous waste formed at the near-border production plants can potentially emit such kind of pollution. It is known that total amount of such waste has grown in 2003-2005. Amount of the first danger class waste has grown from 11, 5 to 25,2 t; second class – from 62,7 to 310,0 t; third class – from 9,2 to 122,8 t [2]. Rather significant amounts of the dangerous materials containing heavy metals have been collected at various waste disposal areas and dumps by the end of 2005. So, total amount of iron in these waste materials can be assessed as 38,3 t; nickel and its compounds – 0,5 t; lead and compounds – 13,8 t; copper and compounds – 0,4 t; chromium and compounds – 9,1 t.

Ratio between recycled and primary technological waters also influence on the natural water pollution level. This general ratio has decreased in the Chernivtsi region from 34 % (2003) to 29 % (2005). Local ratio has decreased in the near-boundary Storozhinets district from 60 % to 52 % (same years). Amount of the primary technological water has decreased for the same period of time from 19,7 to 22,1 mil. m^3. This information can be evidence of reducing environment protection activity and increasing primary water usage at the local production plants.

Our investigation of the surface water pollution levels in the rivers of Prut and Danube basin within city of Chernivtsi in 1996 proved no MPC exceeding for the compounds of lead, copper, nickel, chromium and cadmium. Maximal exceeding for the compounds of manganese was 3,5 times over its MPC level [3].

There are several known methods of the nonferrous metal ions extraction from the waste technological solution. Below we shall consider some of them.

Reagent-based extraction of the nonferrous metal ions as an insoluble compound is one of the most widely used methods. This method is cheap since it requires rather inexpensive calcium hydroxide. However, it provides no real opportunity to have the nonferrous metal compounds recycled. Processing a mixture of the wastewater from different production stages we would receive a mixture of the various hydroxides and have no chance to develop an ecologically safe extraction technology. No economically worthwhile method can be applied to extract an individual hydroxide or other individual metal compound from the hydroxides mixture. Land disposal of such mixture is just a squandering and low-effective using of expensive chemical compounds. Moreover, some illegal land disposals of the nonferrous metal waste can be found and these spots can cause rather significant pollution of soils and surface water layers. Finally all metal pollutants contaminate food and cause toxic action to the local population.

Only separate formation of poorly soluble compounds of the nonferrous metals such as hydroxides, carbonates or double salts can provide opportunity to develop an ecologically safe technology to extract them. This extraction technology should work with separate stages of the galvanic productions. Only this operation mode can ensure formation of individual hydroxides or other compounds that can be economically worthwhile recycled.

Electrochemical reduction of the nonferrous metal ions from electrochemical wastewater or exhausted electrolytes is also under strict attention [4, 5]. This method provides opportunity to extract some amount of the nonferrous metals in the form of pure compact or metal powder deposits. This advantage can be used to utilize such deposits as electrolysis anodes, catalysts, active paste for the chemical current sources etc. Insoluble anode materials should be used in this extraction technology. This requirement sets some limitation on this technology usage area. For instance, gaseous chlorine will be formed and emitted during such electrolysis if rather high chloride concentration is present in the solution. Of course, this process is very dangerous and is absolutely unacceptable for the ecologically safe extraction technology. This restriction confines the electrochemical reduction technology usage by chloride free solutions only.

Electrodialysis and electrocoagulation technologies aren't fully compatible with environment safety requirements as well. These technologies cause formation of highly concentrated waste solutions or slurries, which also require proper and rather difficult utilization. Same problem affects ion exchange, adsorption and extraction methods. They also cause formation significant amounts of waste solutions after regeneration of the ion-exchange agents.

Therefore, one can see that a problem of development of environment friendly metal and dielectric surface treatment technology is very topical today.

Extraction of Fe(II) ions through their oxidation to Fe(III) by the air oxygen followed by formation of Fe(III) hydroxide is given in [4]. However, usage of this method is rather narrow. Highly concentrated acid solutions are traditionally used for the steel details surface etching and rust removing. Excessive acid should be neutralized before Fe (III) oxide can form. Additional neutralization stage raises total cost of the metal extraction technology.

Development of environmental friendly technology of the metals and dielectrics nickeling is also a matter of great interest. Such nickel-covered details are widely spread in various electronics, machinery and home appliances production technologies. Nickeling solutions are short-living and unsuitable for the content correction. That is why nickeling technology causes everyday formation of vast amounts of waste solutions containing up to 30 g/l of the nickel salts. As we mentioned above, chemical extraction methods are not economically worthwhile since they cause expensive nickel losses.

We have investigated an opportunity to develop ecologically friendly chemical nickeling technology, which includes complete nickel recycling. We also analyzed advantages and disadvantages of electrochemical nickel extraction from waste chemical nickeling solution versus reagent-catalytic extraction method. Chemical nickeling and reagent-catalytic nickel extraction often run under electrochemical mechanism. That is why we investigated electrochemical characteristics of these processes on platinum and nickel electrodes. The latter electrode was selected because in fact any nickeling or nickel-covering process takes place on the nickel electrode. First nickel layer quickly covers any electrode material surface and further process runs on the nickel surface. Simultaneous phosphorus deposition during nickeling has also been taken into account. However, hereafter we shall use a term "nickel extraction" since this is the main aim of our investigation and, on other hand, it is known that the phosphorus content remains relatively small.

Solution 1 containing 30 g/l of nickel chloride five-water crystalline hydrate, 3 g/l of sodium hypophosphite mono-water crystalline hydrate, 50 g/l of sodium acetate three-water crystalline hydrate with pH=6.0 was used to investigate characteristics of the electrochemical nickel extraction. Voltammetry investigation was held at 293-333 K with platinum or freshly covered nickel-phosphorus electrodes. It has been found that the limit current of the voltammetry curve (VAC) linearly depends on the potential increase rate. Since coefficient A in $I_{\lim} = A + B \cdot v^{\frac{1}{2}}$ is not equal to zero throughout all investigated potential increase rates region we can conclude that the electrode process rate can be controlled by both stages of ions diffusion or electron transferring.

We have determined coefficients of equations $\varphi = A + B\ln(I / I_{\lim} - I)$ and $\varphi = A + B\ln(I_{\lim} - I)$, which can be used to describe a linear parts of VAC [6]. Comparing values of the coefficients A and B to some parameters of the electrode process we found that the first equation is more suitable for the VAC linear parts description. The middle point potential of VAC ($\varphi_{1/2}$) was found dependent on the electrode material: a value of $\varphi_{1/2}$ for the platinum electrode is more negative comparing to the nickel one.

An influence of the solution pH value on $\varphi_{1/2}$ has been investigated for the process of nickel reduction from the solution 2 (30 g/l of nickel chloride five-water crystalline hydrate, 10 g/l of sodium hypophosphite mono-water crystalline hydrate, 50 g/l of sodium acetate three-water crystalline hydrate; pH=5,0). $\varphi_{1/2}$ Value was found growing from -0,900 to -0,200 V in the temperatures range 293 – 333 K and at the potential increase rates $5 \cdot 10^{-2} - 5 \cdot 10^{-1}$ V/s and pH value increase from 2,0 to 6,0. Therefore, we can conclude that increasing the pH value we can achieve lower energy consumption for the metal ions reduction.

Activation energy for the nickel deposition on the platinum electrode is 70 kJ/mole higher than the energy for deposition on the nickel electrode. This difference corresponds to $\varphi_{1/2}$ values obtained for these electrodes. This effect can be caused by different nature of the nickel nucleus, which form on the electrode surface. Three-dimensional nickel nuclei are being formed on the platinum electrode surface while in case of nickel electrode fresh nickel deposits on existing nickel crystals.

Voltammetric investigation data were used to predict nickel extraction conditions for the solution containing 25 g/l of nickel sulfate seven-water crystalline hydrate, 20 g/l of sodium hypophosphite mono-water crystalline hydrate and 10 g/l of sodium acetate three-water crystalline hydrate. Maximal electrolytic nickel extraction effectiveness can lower metal content down to 1 g/l. Further extraction is inexpedient since current-output drops to 10 % at the current density of 15 A/dm^2.

Chemical deposition of the nickel hydroxide is the second stage of extraction. System clarification rate is rather important parameter to characterize this stage. This parameter was measured as a time change (t, minutes) of the clarified liquid layer ratio (H, %). Maximal clarification of a 140 mm liquid layer was achieved in 120 min. Dependence of H on t can be shown through equation $H(1) = 6{,}70 + 3{,}55 \cdot t - 5{,}04 \cdot 10^{-2} \cdot t^2 + 2{,}26 \cdot 10^{-4} \cdot t^3$ with a pair correlation coefficient 0,99. Nickel hydroxide sedimentation rate can be a limit stage for the process of nickel extraction from waste solutions. Surface active compounds are used traditionally in order to speed up this process. However, this is unsuitable for our method because surfactant can be captured in the nickel hydroxide powder, which would complicate its further reuse.

We investigated influence of the constant magnetic field on the nickel hydroxide sedimentation rate. A magnet with the magnetic induction value of 47 T was used in this experiment. It was found that dependence of H on t for the system under such magnetic field can be shown through equation $H(2) = 17{,}04+5{,}34t-0{,}12t^2+8{,}5\cdot10^{-4}t^3$ with a pair correlation coefficient 0,99. Second term in the equations for H (1) and H(2) can be interpreted as an increment of the clarified liquid width. Comparing these values for H(1) and H(2) (3,55 and 5,34) we can conclude that effect of the constant magnetic field actually results in faster nickel hydroxide sedimentation. Nickel hydroxide sediment is recommended to reuse for the fresh chemical nickeling solution preparation.

Therefore, above results become a foundation for development of the ecologically friendly chemical nickeling technology. This technology ensures extraction of the nickel ions as compact or powdered metal nickel or nickel hydroxide. Metal nickel can be reused as anodic material for the electrochemical nickeling and nickel hydroxide can be reused as a source material for the chemical or electrochemical nickeling solutions preparation.

This technology has been put into real usage at one light machinery plant in Chernivtsi. That was the single Ukrainian installation for a differentiated extraction of the nonferrous metal ions from galvanic wastewater and exhausted electrolytes. The installation ensured separate extraction of nickel, copper and other ions instead of extraction their unreusable mixture. Extraction technology involved floatation processing of the hydroxides dredge followed by thermoprocessing. This operation resulted in formation of the metal oxides, which were grinded and then used as pigments for the outside painting works. Such a technology can be characterized both positively and negatively. On one hand, it slows down speed and amount of the natural water and soil contamination by the heavy metal ions from galvanic wastewater, which is the positive result. However, this advantage is rather uncertain because the wind erosion and acid rains can gradually release metal ions from the painted plaster and result in deferred air, surface water and soil contamination.

We have also proposed a reagent-catalytic method of the nickel ions extraction from exhausted chemical nickeling solution. This method is grounded on the hypothesis of auto-catalytic nature and electrochemical mechanism of the nickel ions reduction. Finding appropriate conditions for the solution instabilization followed by active reduction of the nickel ions within the liquid phase was one of the fundamental problems to develop this method of extraction. We supposed that nickel reduction runs according to the scheme: $Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+$ [7]. pH and temperature can significantly influence rate of this process. Its induction period can be very long if no catalyst is added. The exhausted solutions containing 6,8 g/l of the nickel chloride six-water crystalline hydrate was used at this stage. All investigations were carried out at the temperature 333-343 K and pH value of 6,0-7,0. Nickel hydroxide starts to form if pH level exceeds 7,0 and this process significantly slows down formation of the metal nickel powder. An optimal conditions for the metal nickel formation was determined: T = 338-343 K and pH = 6,5-7,0. Keeping these conditions and using the metal nickel powder as a catalyst-initiator one can bring the nickel ions concentration below its maximal permissible level for the fish-growing water bodies (0,01 mg/l) within 30 min [8]. This result can be interpreted as a "complete" nickel extraction from the solution. The above results were used in a patented method of the nickel ions extraction from exhausted solutions for the chemical nickeling [9].

Counteraction anthropogenic contamination of the natural water with iron compounds is also a very important problem. Almost any surface processing of the steel details other iron alloys results in formation of exhausted solutions and washing waters contaminated with iron ions.

Possible reuse of exhausted solution after SP10 steel etching has been investigated. Freshly made etching solution 1 contains 90 g/l of sulfuric and 50 g/l of hydrochloric acid. Maximal content of the iron ions in the exhausted solution was 35,1 g/l. Exhausted solution 2 (containing 10,7 g/l of the iron ions) has been aerated in order to oxidize Fe(II) ions to Fe(III) with further transformation into Fe(III) hydroxide. However, this operation was found ineffective because of too high residual concentration of the acids. Only adding 140 g/l of sodium hydroxide we could achieve formation of the Fe(III) hydroxide sediment. Follow up thermoprocessing of this sediment can transform it into a pigment or an adsorbent suitable for hydrogen sulfide adsorption. On other hand, large amount of sodium hydroxide makes this method economically inexpedient.

We have completed the volammetry investigation of the iron ions reduction from exhausted etching solution. Two characteristic parts were identified on the VACs. The first is located within the potential range from 0 to -200 mV (all potential values are given here and after in relation to the saturated chloride-silver reference electrode potential). It can correspond to the transformation of Fe(II) into Fe(III). The second is located within the potential range -350 – -800 mV and probably corresponds to the Fe(II) reduction process. An influence of aeration on the VAC character was investigated for the solution 2. Shifting of the platinum electrode stationary potential towards more positive values can be caused by decrease in concentration of Fe(II) aqueous ions and corresponding increase in concentration of Fe(III) aqueous ions. Besides that, a transformation of hexaaqueous complex $Fe(H_2O)_6^{3+}$ into tetrachloride complex $FeCl_4^-$ is also possible in the presence of chloride ions. Voltammetric data were used to predict an optimal condition for electrochemical ironing. Electrochemical ironing of various details is quite widely spread operation at many plants. Hardness of the electrochemically deposited iron layer is close to the hardened steel, that is why electrochemical ironing is used regularly to fix worn out details and mechanisms. Frailness of electrochemical iron deposits is lower than chromium and speed of the iron layer growing can achieve up to 0,5 mm/hour.

Exhausted etching solutions for SP10 steel in some ways are similar to the special ironing compositions. That is why we carried out an amperostatic iron deposition from exhausted etching solution 3 with iron ions content of 35,1 g/l.

Special membrane electrolytic cell [10] was used for this operation. Anolyte and catholyte were separated with an ion-exchange membrane MK-40. 10 % solution of sodium sulfate was used as anolyte while the exhausted etching solution was used as catholyte. It was found that relatively light-colored, dense and well-bonded iron deposits can be formed at the current density of 0,65 – 1,0 A/dm^2. Less dense but still light-colored and well-bounded deposits can be formed at the current density of 2.0 – 5,0 A/dm^2. Finally, powdered iron deposits are being formed if the current density is 10,0 – 20,0 A/dm^2. Therefore, exhausted chloride-sulfate etching solutions for the steel SP10 can be used for fixing the steel details through the electrochemical ironing. On other hand, powdered iron sediments can be utilized as catalysts. The exhausted solutions can also be reused for preparation of the mixed sulfate-chloride ironing electrolyte [11].

Copper and its alloys are widely used at many electrical and electronics plants. Any copper detail should be preliminary processed using chemical and electrochemical methods such as etching, polishing, surface dimensional processing etc. Copper plating of the steel details surface is also a common stage preceding deposition of protective or decorative coating. Exhausted solutions and wastewaters after these operations have high content of copper ions. Extraction of copper as poorly soluble Cu(II) hydroxide or carbonate can not completely resolve this problem. Atmospheric precipitations, especially acid rains can act on the galvanic slurries and convert these compounds into the soluble ones, which would contaminate natural waters and soils. Therefore, we need to develop the slurry-free technologies in order to prevent such contamination. Regeneration of the exhausted copper solutions is one of possible ways to achieve this aim.

We have completed a series of investigations of the chloride copper etching solutions regeneration. So, electrochemical parameters of the copper ions extraction from the exhausted etching solution containing 75,17 g/l of copper ions have been investigated [12]. Source etching solutions composition was (g/l): $CuCl_2 2H_2O$ – 180; HCl – 10,5; KCl – 275. Following experimental methods were applied in the framework of this investigation: voltammetry, iodometry, galvanostatic copper deposition. It is shown that increase in the copper content causes decrease in the Cu reduction start potential. Copper concentration does not influence a value of the copper deposit formation limit current though. This value is controlled by the rate of electroactive ions diffusion towards an electrode surface. Analysis of the VAC coefficients proves relatively high rate of the complex ions dissociation at the electrode surface. This process does not influence the total rate of the electrode process.

Electrochemical regeneration of the exhausted electrolyte is recommended as a part of the ecologically safe technology of the copper details etching. This stage requires two- or three-chamber electrolytic cells where the anodic and cathodic areas are separated with ion-exchange membrane [10]. Exhausted chloride solutions of the copper etching should be placed in the cathode part while aqueous solution of sodium sulfate with the insoluble ORTA anode should be placed in the anodic one. This design of the electrolytic cell prevents any chlorine emission. Dense and well-attached copper coating can be formed at the current density of 3,3-10,0 A/dm^2. Higher current densities cause formation of poorly attached and powered copper. Copper extraction should last until very low initial copper content in the solution is reached. Then it can be reused for new copper etching. Copper etching rate in the recycled solution was found the same as in the freshly-made one. Therefore, development of this regeneration scheme and putting it into real production schemes would ensure ecologically friendly process of the copper etching, which prevents contamination of the environment with copper.

We can conclude that the present data and scientific results can ensure formation and development of the ecologically friendly processes for the chemical treatment of some metals, alloys and dielectrics.

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