DEVELOPMENT OF AN INTEGRATED TECHNOLOGY FOR TREATMENT OF NICKEL-CONTAINING WASTEWATER: REGENERATION OF EXHAUSTED NICKEL ELECTROPLATING SOLUTIONS

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Abstract
A cost-efficient integrated technology was proposed for treatment of low and high concentration wastewater flows of nickel electroplating installations with a closed water circuit scheme. An option was substantiated to regenerate exhausted electrolyte solutions by sorption and oxidation removal of impurities. The proposed method allows to remove organic compounds from a solution and remove traces of iron selectively by fine silica gel as an adsorbent and hydrogen peroxide as an oxidising agent. Optimal treatment parameters have been identified to ensure complete iron removal from the exhausted electrolyte solution by silica gel: heating the solution at 70^0C for 20 minutes. The method allows to regenerate exhausted electrolyte solutions, recycling a valuable metal and preventing environmental contamination by highly toxic concentrated solutions. We propose the technology for introduction at electroplating facilities of Ukraine.

Introduction
Electroplating facilities belong to common technological units of many industrial plants. Nickel electroplating operations are used extensively: the amount of nickel coatings in industry is the second only to zinc coatings. Nickel is a highly toxic and expensive metal, as a result, the problem of a cost-efficient technology for nickel recovery from wastewater flows of closed circuit water supply systems of electroplating facilities is fairly relevant.(1)

Depending on levels of heavy metals in wastewater flows of nickel electroplating facilities, there are two types of wastewater: diluted (rinsing) and concentrated ones (exhausted electrolyte). The authors have developed a range of comprehensive technologies for treatment of nickel-containing rinsing water, tailored to specifics of individual production facilities. The technologies are designed to recover the expensive metal and reuse water for production purposes. We also developed hydrodynamic models of wastewater treatment, that allowed us to estimate operational parameters of installations reliably.

The share of exhausted electrolyte solutions in the overall wastewater flow of nickel electroplating facilities reach only 2-3%, however, the exhausted electrolyte contains high concentrations of heavy metals and other pollutants (several hundreds times higher comparatively to their levels in rinsing water). Emergency discharges of exhausted electrolyte, that happen at Ukrainian industrial facilities, pose high environmental risks and cause irreversible losses of expensive nickel. So far, the problem of reliable treatment of such solutions and regeneration of the electrolyte was not resolved. Generally, electroplating facilities add small volumes of exhausted electrolyte to rinsing water flows for their further treatment. Such treatment scheme does not allow to regenerate electrolyte solutions,

moreover it is not a cost-efficient one, because equivalent costs of treatment of concentrated solutions are always lower comparatively to diluted ones. Existing methods of neutralisation of exhausted nickel electrolytes are mainly based on use of basic neutralising reagents. (2) Sediments of low soluble nickel compounds, obtained under neutralisation, may be processed with application of technologies we have developed earlier.(3)

Methods
However, we believe that the most efficient option for neutralisation of exhausted electrolyte is associated with its regeneration by extraction of impurities. The regeneration allows to reuse the electrolyte and to reduce substantively the amount of reagents otherwise necessary to produce a new electroplating solution. The need to replace the electrolyte solution monthly is caused by steadily accumulating impurities (mainly organic compounds and heavy metal ions). The organic impurities are mainly represented by residual polishing fluids at items to be electroplated and destruction products of additives, that are added to the electrolyte to improve quality of nickel coatings. These impurities can be efficiently extracted by the sorption technique (4): exhausted electrolyte is mixed with grained activated carbon (2 g/l), the solution is agitated for 3 hours by high pressure air with subsequent sedimentation for at least 12 hours. The technique allows to reduce organic contents in the electrolyte down to 5 mg/l. In order to remove organic compounds completely, one needs to apply further oxidation of the treated electrolyte (by potassium permanganate or hydrogen peroxide).Nickel coatings are usually applied to steel items, as a result, the electrolyte solution steadily accumulates iron impurities, mainly as Fe^{2+} ions. If iron levels exceed 0.1 g/l, the electrolyte becomes exhausted due to high brittleness and pitting of nickel coatings.

Analysis of published sources suggests the lack of efficient methods to remove traces of iron from concentrated nickel-containing solutions. Published sources provide information on methods that allow to remove iron at levels in excess of 1 g/l (2). In the current study we explored options to regenerate nickel electrolyte by selective removal of iron at lower concentrations. The studies were conducted with use of model solutions of exhausted nickel electrolyte. To simulate the exhausted electrolyte, we added iron (II) sulphate to the standard mat nickel electroplating electrolyte of the following composition (g/l): $NiSO_4$ - 100, $NiCl_2$ - 15, H_3BO_3 - 35, Na_2SO_4 - 30 (to get iron levels in the solution of 0.1 g/l) at pH = 5.

It is well known, that iron can be selectively removed from solutions of other heavy metal ions as iron (III) hydroxide (4). $Fe(OH)_3$ has a very low SP comparatively to hydroxides of other heavy metals ($SP_{Fe(OH)_3}$ = 3,8 · 10^{-38}), as a result, Fe^{3+} ions can be almost completely removed from the model electrolyte solutions at pH=4. As the exhausted nickel electrolyte has pH ≈ 5, we may expect that iron (III) in the solution will be almost completely hydrolysed to $Fe(OH)_3$. However, iron in the exhausted electrolyte is present as iron (II) ions. Therefore, we needed to develop a method for selective iron removal, by its oxidation to Fe^{3+}, hydrolytic sedimentation and eventual removal.

We selected hydrogen peroxide as the oxidising agent. Comparatively to some other oxidising agents, hydrogen peroxide has some advantages for application in this particular case (appropriate Red/Ox potential, lack of potential polluting cations, etc.). Moreover, hydrogen peroxide may be generated electrolytically on-site, at an electroplating facility.

The hydrolytic removal of iron from the electrolyte is associated with some intrinsic difficulties, because $Fe(OH)_3$ tends to form dispersions of nanometer-scale particles. As a result, it is fairly difficult to remove $Fe(OH)_3$ either by filtration, or by sedimentation. To

resolve the problem, we proposed to add silica gel to the electrolyte for co-sedimentation. Fe^{2+} ions can be adsorbed at silica gel surface at pH=5, according to the following scheme:

$$\equiv Si - OH + Fe^{2+} \leftrightarrow \equiv Si - O)_x Fe^{2-x} + H^+,$$
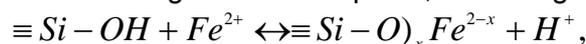
here $\equiv Si - OH$ means silanol groups at the surface of silica gel particles.

Then, immobilised ions Fe^{2+} are oxidised to Fe^{3+} according to the following scheme:

$$\equiv Si - O)_x Fe^{2-x} + H_2O_2 + H_2O \rightarrow \equiv Si - OH + Fe(OH)_3 + H^+.$$
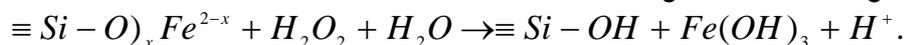
The scheme shows that oxidation of Fe^{2+} ions results in regeneration of silanol groups, therefore causing shift of the equilibrium in the first reactions to formation of reaction products (thus enhancing the degree of iron removal).

The process of iron removal from the exhausted electrolyte was studied in 1 l flask, equipped with a mixer, using the following sequence of steps. We added necessary amounts of 30% solution of hydrogen peroxide and L 40/100 silica gel (grains of 0.1 mm) to 500 ml of the model solution. Depending on experimental conditions, we mixed the components in the flask for 10-40 minutes at 50–90^{0}C. After cooling, we decanted the sediment and filtered the solution through Shott 40 filter. The filtrate was found to contain no dispersed particles (by Tindal cone probe). Residual iron levels in the electrolyte were measured photometrically: Fe^{2+} - by phenantroline probe, Fe^{3+} - by acetylsalycilate probe.

Results
In order to study the iron removal process, we conducted a series of experiments. Amounts of added silica gel varied from 0 to 100 g, while molar ratios of hydrogen peroxide and iron varied from 0.1 to 2. As Figure.2 shows, at molar ratio $H_2O_2 / Fe \geq 1,5$ (i.e. at three-fold excess of the oxidising agent), almost 100% oxidation of iron was achieved.

Figure 1: Levels of trivalent iron (W) vs molar ratio of hydrogen peroxide to iron (n) in the model electrolyte solution.
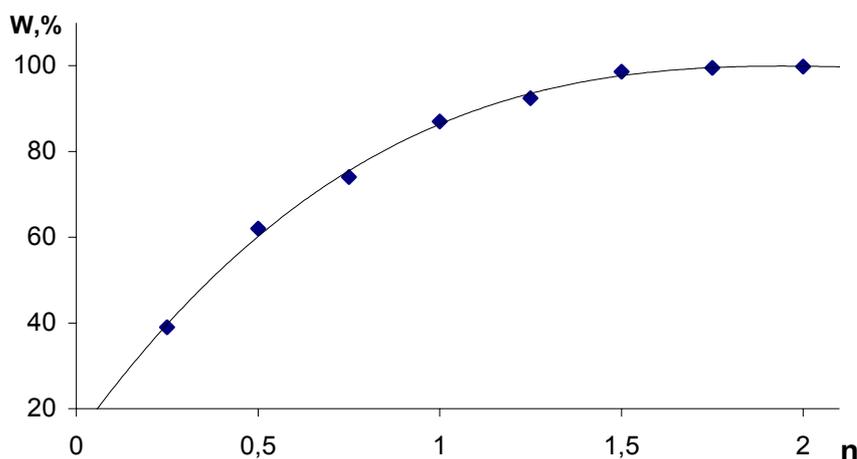
As can be seen at Figure 1, introduction of silica gel allows to improve the degree of iron removal substantially. Without application of silica gel, the degree of separation of iron (III) hydroxide does not exceed 15%. When we added more than 5 g of silica gel to the electrolyte solution and treated it according to the above method, the residual levels of both

Fe^{2+} ions and Fe^{3+} compounds did not exceed the detection limits. The experimental results confirm our assumption that nucleation and formation of solid phase of $Fe(OH)_3$ occur at the surface of silica gel.

Figure 2: Iron content (W) in the model solution vs. amounts of added silica gel (M) (t = 70^{0}C, τ = 20 min)
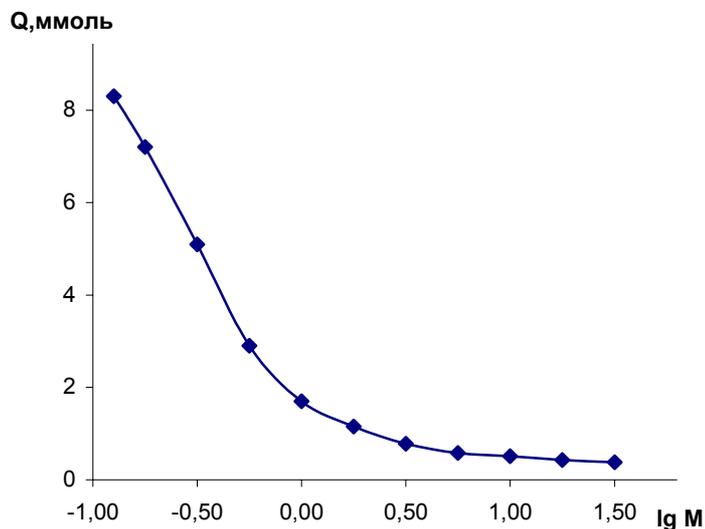
Analysing the dependence at Figure 4, one can identify optimal conditions for complete iron removal from the exhausted electrolyte - treatment of the electrolyte at 70^{0}C for 20 minutes, according to the above methods. It is important to note that such temperature can be easily applied at an industrial nickel electroplating facility (it does not exceed temperatures of standard nickel electrolyte solutions).

Figure 3: Time of complete iron removal from the model electrolyte solution vs. temperature (at silica gel dose of 10 g/l).
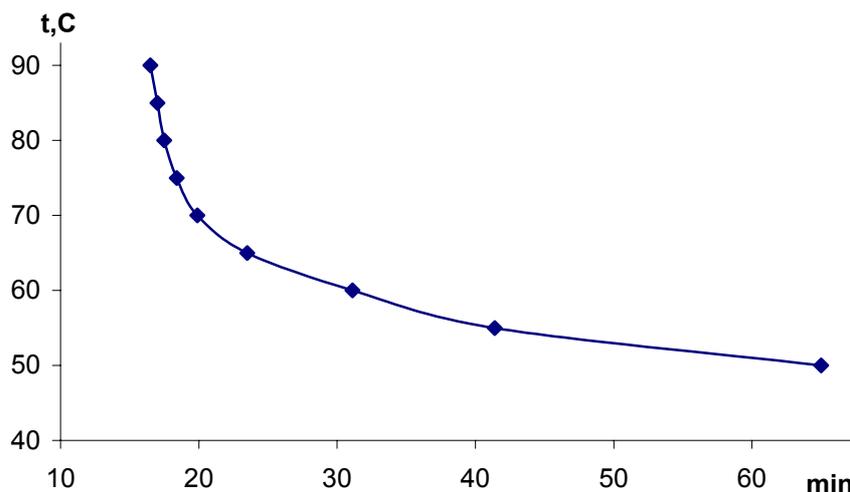
Conclusions

Therefore, the research allowed us to prove a possibility of selective iron removal from concentrated nickel-containing solutions by addition of fine grained silica gel into a solution under treatment. Application of hydrogen peroxide for iron oxidation in the method developed allows also to remove traces of organic substances. The method allows to improve the hydrolytic removal of iron from exhausted nickel electrolytes and can be recommended for introduction at electroplating facilities of Ukraine. Application of the method allows to regenerate exhausted electrolytes much easier, moreover, the process allows to recover expensive nickel and prevent environmental contamination by highly toxic concentrated solutions.

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