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STUDY OF THE POSSIBILITY OF METALS EXTRACTING FROM PICKLE LIQUORS

O. P. Filippova, E. S. Sergeev

Olga P. Filippova, Doctor of Technical Sciences, Professor**; Egor S. Sergeev,** Postgraduate student
Yaroslavl State Technical University, Yaroslavl, Russia, filippovaop@ystu.ru, egorsergeev45@mail.ru

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Abstract. *Nowadays, there is an increase in the amount of waste containing heavy metals, which has a negative impact on the environment and humans. This article deals with the process of extracting copper and other valuable components from jewellery waste using magnesium turnings - a waste product of the machine-building industry. This method makes it possible to utilise three different waste products at once, which is economically and ecologically attractive.*

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Introduction

Jewellery is one of the oldest forms of art. Today, jewellery production is growing rapidly, but, like any production, it is also harmful to the environment. Mainly, this is due to the mandatory preparation of the product surface for the decorative coating, as the oily and oxidic layers of the product prevent diffusion, so reducing the quality of the coating on the surface of the product.

One of the most common surface preparation methods is the chemical one, which includes surface degreasing (removal of the oily layer), pickling (removal of the oxide layer) and surface washing (removal of the pickle and pickling products).

In addition to preparation, the pickling process is also used to produce decorative elements. This is possible as the pickling process is simple, chemical reagents can penetrate into inaccessible areas, and there is no dust, noise, etc. [1].

The main environmental pollution problem of the jewellery industry is the emergence of pickling liquors (PL), mainly acid solutions (most commonly sulphuric acid) [2, 3] as the declining of quality of the pickling. The high aggressiveness of the pickling liquors results in loss of metal (both the product itself and the applied one), as well as the presence of harmful acid vapours during their manufacturing and storage.

Today, PL are combined with other wastewater and neutralised by calcium oxide in the wastewater treatment plants. This produces lime mud (up to 5,000 t/year) and waste water (up to 12,000 m^3/year). This wastewater is diluted hundreds of times before being discharged into the collector because of its high calcium chloride content (up to 100 g/dm ^{3}). In turn, lime mud is not demanded and companies have to pay fines for storing it [4].

PL contain sulphuric acid, hydrochloric acid and nitric acid as well as metal ions such as ferrous iron, aluminium, copper, nickel, trivalent chromium and zinc, etc. Precious metals may also occur in pickling liquors. Therefore precious metal refining is needed. Refining (Fig. 1) is the process of purifying extracted precious metals from impurities and associated components, improving precious metals to meeting of state quality standards and specifications both the Russian and international standards [5].

Fig. 1. Refining of precious metals from pickling liquors

Fig. 2. The Kostroma jewellery plant pickling liquor

The aim of our work is to investigate the composition and properties of the pickling liquors and the possibility of copper extraction by using magnesium turnings (waste of the Rybinsk aircraft plant "ODK-Saturn", Rybynsk, the Yaroslavl region, Russia).

The object of the study are pickling liquors of the Kostroma jewellery plant (Kostroma, Russia) on Fig. 2 and the waste of the Rybinsk aircraft plant "ODK-Saturn"(Rybynsk, the Yaroslavl region, Russia).

Main body

The problem with PL, as with any waste, is the volatility of their composition. Therefore, its constant laboratory monitoring is necessary. The chemical composition of the PL by the Kostroma jewellery factory, obtained in a laboratory study, is shown in Table 1.

Table 1. Composition of the Kostroma jewellery factory PL

Name	Fe	Cu	Ni	Zn	Al
Value	5.56	85.0	4.892	1.529	0.13
Size	g/dm^3	g/dm^3	g/dm^3	g/dm^3	g/dm^3

Note: The pH of this solution is 1.98.

By Table 1, the PL under study contains significant quantity of copper. Copper salts are very toxic to humans and cause functional disorders of the nervous system, kidney and liver disorders, skin and mucous membrane irritation, etc. Copper is also an enzyme poison [6]. This requires its extraction from the PL.

The separation of copper is recommended to be conducted in several stages, the first one is the addition of barium chloride solution to the initial PL:

$$H_2SO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + 2HCL \quad (1)$$

$$Ba^{2+} + SO_4{}^{2-} \rightarrow BaSO_4\downarrow \quad (2)$$

The heavier $BaSO_4$ precipitate removes the mechanical impurities from the solution. About 30 g of barium sulphate precipitate is obtained from 100 cm^3 of the PL solution.

The precipitate is filtered off and magnesium turnings, which are the ODK-Saturn plant waste product, are added to the resulting solution. The composition of the magnesium alloy is 89-92% magnesium, 7-9% aluminum, 0.1-0.5% manganese and 0.2-0.8% zinc. Up to 30% magnesium hydroxide is formed during the storage of the turnings. An experiment was conducted with turnings of different sizes (Fig. 3).

а *б*

Fig. 3. Magnesium turnings: *a* – wool; *b* – heavy

When magnesium turnings are added to the PL, a violent reaction takes place, followed by precipitation (3) and release of gas (4). The colour of the solution changes significantly, from emerald green to blue one. The following reactions proceed:

$$MeАн + Mg \rightarrow MgАн + Me\downarrow, \quad (3)$$

where Me – Al^{3+}, Zn^{2+}, Cr^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+}; Ан – SO_4^{2-}, NO_3^-, Cl^-.

The precipitating metals are on the right of magnesium in the electrochemical series of the metals. A substitution reaction takes place and the resulting precipitate is grey-green [7].

Hydrogen release (Fig. 4) occurs throughout the surface of the magnesium turnings, which are gradually decomposed entering the solution:

$$Mg + HАн \rightarrow MgАн + H_2\uparrow, \quad (4)$$

where Ан – SO_4^{2-}, NO_3^-, Cl^-.

Experiments show, the reaction proceeds more readily if the turnings have been already dissolved in the solution than if they are added to the solution in series.

Fig. 4. Hydrogen release process across the entire surface of the magnesium turning

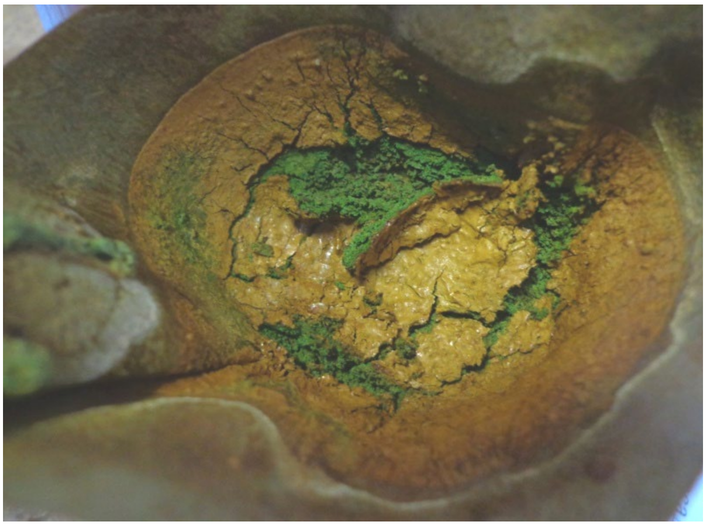

Fig. 5. Precipitate after reaction with turning

The experiment was conducted with wool and heavy turning. Experiments show, the reaction temperature reaches 110 °C with wool turning and 95 °C with heavy one. The reaction with wool turning proceeds faster and more violent than with heavy one, which is due to the larger surface area of the interaction between the magnesium and the solution. The amount of magnesium turning dissolved in the solution is 1 g of turning per 10 cm^3 of solution.

The mass of copper and other metal precipitate obtained is 40 g per 100 cm^3 of solution. Up to 400 g of precipitation can be obtained per 1 dm^3 of solution. During the exothermic reaction, the initial solution evaporates and a viscous, heavy precipitate forms (Fig. 5).

After filtration of the precipitate, the solution is blue and its pH = 7.8. In order to light it, a 0.1 H solution of NaOH alkali was added to the blue solution in ratio 1:1. The precipitate was filtered off and the pH is 8.6.

There was a hypothesis of using the steel road during the process of separating copper from PL. A steel rod with the mass of 7.0202 g put into 30 cm^3 of PL and a chemical reaction took place on its surface (reaction time of about 3 days). When the reaction over, the rod partly dissolved and its mass became 4.5757 g. The mass of the precipitate obtained was 2.5859 g, which is almost equal to the mass of the dissolved part of the rod.

The idea of this method is that as the steel rod is put into the PL, reactions (5), (6) such as those described above (3), (4) take place. However, the iron in the steel, which reacts with the solution, is to the right of magnesium in the electrochemical series of metals. In this case, the reactions are

$$\text{MeАн} + \text{Fe} \rightarrow \text{FeАн} + \text{Me} \downarrow, \qquad (5)$$

where Me – Ni^{2+}, Cu^{2+}, Pb^{2+}; Ан – SO_4^{2-}, NO_3^-, Cl^-.

All the metals in the electrochemical series of metals to the right of iron precipitate in the solution: nickel, lead, copper, etc.

The release of hydrogen is also observed:

$$\text{Fe} + \text{HАн} \rightarrow \text{FeАн} + H_2 \uparrow, \qquad (6)$$

where Ан – SO_4^{2-}, NO_3^-, Cl^-.

During these reactions the colour of the solution is stable, a brown precipitate is deposited (Fig. 6). When calculating the mass ratio of the precipitate to the volume of the solution the following data were obtained: in 1 dm^3 of PL 86.197 g of precipitate is formed. The weight of the precipitate per 1 dm^3 of solution is 86 g. The precipitate contains Ni, Sn, Pb, Cu, Ag, Au.

Fig. 6. Precipitate after reaction with steel rod

In order to validate the results obtained on the composition of the PL, spectral emission analysis on copper and steel plates was performed using the SPECTROMAXx apparatus .

The operating principle of this device is evaporating of the sample material as a result of a spark tracking. The atoms and ions released are excited and emit light. This light is routed into optical systems and measured by using an electronic light-sensitive detector (CCD) converting the light into an electrical discharge. The calibration data is stored in the device's memory in advance. The measured values are compared with that and converted to concentrations.

The obtained data on the composition of the PL are presented in Table 2.

Table 2. Metal content of PL on copper and steel plates

Metal	On the copper plate, %	On the steel plate, %
Cu	-	>20.02
Zn	0.8212	>0.036
Pb	0.4825	>0.132
Sn	0.4616	>0.288
Fe	1.4332	-
Ni	2.6275	2.97
Au	0.0619	-
Cr	0.0208	0.018
Ag	0.0473	-
Co	0.1755	0.1067
Al	0.0702	0.059

Conclusions

By the experiments, PL contains many precious metals (copper, nickel, zinc, etc.); their extraction can solve some economic problems, as well as the problem of heavy metal pollution of the environment.

The method of copper precipitation with magnesium turning (a waste product of the ODK-Saturn metallurgical plant) can be applied practically. However, along with copper, other metals also precipitate; many of them are valued commercially, e.g. zinc, tin, nickel etc. This method makes it possible to utilise three different waste products at once, which is economically and ecologically attractive.

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