Electrochemical utilization of disperse copper-iron waste

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The possibility of processing contaminated copper powder with an iron content of 1.6–12.2% by the electrochemical refining method has been studied. This powder is formed during the processing of copper-containing salt waste of galvanic production by exchange reaction and does not find the application. It is shown that during electro-refining of the contaminated copper powder in the sulfate electrolyte, high-purity cathode copper corresponding to the Cu-ECP grade can be obtained. Technological recommendations for the implementation of the process are proposed, in particular, a method of depassivating a titanium current lead to a copper powder.

It was found that along with the anodic dissolution of copper and iron from the powder, the iron component is chemically dissolved due to the copper exchange reaction. In experiments with model solutions, the effect of Fe(III) ions in the electrolyte on the rate of chemical and electrochemical reactions was studied. It was found that the negative effect of Fe(III) ions on the cathode deposition of copper can be reduced with an additive NaF into the electrolyte and increasing the cathode current density.

Keywords: electrochemical copper refining, processing of copper powder waste.

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Электрохимическая утилизация дисперсных медно-железных отходов

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Исследована возможность переработки медного порошка, загрязнённого железом (1.6–12.2%) методом электрохимического рафинирования. Данный порошок образуется при переработке медсодержащих солевых отходов гальванических производств методом цементации и не находит применения. Показано, что при электрорафинировании загрязнённого медного порошка в сернокислом электролите может быть получена катодная медь высокой чистоты, соответствующая марке М0к. Предложены технологические рекомендации для осуществления процесса, в частности, способ депассивации титанового токоподвода к медному порошку.

Выяснено, что наряду с анодным растворением меди и железа из порошка протекает химическое растворение железной составляющей за счёт цементации меди. В опытах с модельными растворами изучено влияние ионов Fe(III) в электролите на скорость окислительных и электрохимических реакций. Выявлено, что негативное влияние ионов Fe(III) на процесс катодного осаждения меди может быть уменьшено введением в электролит NaF и увеличением катодной плотности тока.

Ключевые слова: электрохимическое рафинирование меди, переработка медных отходов.
Growing consumption of toxic heavy metals (HM) and their compounds by the industry leads to high emission of them into the environment. Excessive HM concentrations cause significant disruption in living organism on cellular, tissue, population levels. The key feature of HM is that they do not degrade, and cannot be removed from environment via biological or chemical transformations [1].

Copper is one of such toxicants. It is considered that copper has low toxicity to humans, which is evidenced by rather high Threshold Limit Value (TLV) – 1 mg/L in drinking value [2]. According to World Health Organization, “The risk from copper deficiency insignificantly higher, compared to excessive intake of it”. However, recent studies suggest that increased copper concentration in food causes damage to central nervous system and internal organs for people affected by Wilson’s disease [3], and worsening Alzheimer’s disease symptoms [4]. Researchers tie development of Indian child liver cirrhosis with high copper concentrations in food, namely in milk which is stored in copper containers [5]. Series of studies indicates carcinogenic effect of copper, showing correlation between occupations in copper processing and occurrence of oncolgical diseases [6].

Effect of copper on other organism is more severe. According to Russian Sanitary Rules and Regulations, allowed copper concentration in drinking water (1 mg/L) is ten times higher than for which toxic effect was observed in laboratory tests on animals [7]. An aqueous organism is more sensitive to copper contamination. For fish, the concentration at which lethality of population is observed is 0.002 mg/L [8]. As such copper TLV for fish farms is 0.001 mg/L [9]. Despite relative toxicity to humans, copper-containing waste possess ecological hazard, especially aqueous organisms.

Due to high specific surface area, copper power promptly transforms into mobile forms upon contact with soil or water when compared to compact metal. Metallic copper is subjected to oxidation and transforms into soluble form only if air is present, as these processes involve oxygen and carbon dioxide. As such, the process is most intense in upper layer of soil. Upon exposure to atmosphere, a stable film composed of CuCO₃ · Cu(OH)₂ is formed on surface of copper which inhibits further oxidation. Studies suggest that copper dissolution is mainly governed by organic complexing [10]. The stable film reacts with formation of soluble chelate compounds which allows for further oxidation of metal. The dissolution is most prominent in soils with pH of 4.5–5.5 [11]. Thus copper powder transforms in bioavailable form rather fast. Toxic effect of copper powder was confirmed in model animal experiments [12].

An example if high HM content waste is the waste of galvanic plants. In this case, the importance of this problem is further reinforced by the value of metals in waste, namely copper.

In Russia, aside from spent high copper technological solutions, galvanic plants annually produce about 12000 ton of copper-containing residue [13] and wastewater with an estimated copper content of 815 ton [8].

A comment way of removing copper from such waste is cementation. The copper is transformed into soluble form (if necessary), and then it is electrochemically displaced from solution with more active metal, usually iron. As technological process, cementation is fast and is easy to conduct.

During cementation of copper with iron, the dissolution of iron takes place in anodic regions and copper deposition on the cathodic region. As such, the mass of cement metal decreases while copper layer grows. This results in formation of copper powder with some residual iron (CPRI). In practice, the copper is usually cemented with scrapped sheet iron from metal can plants, which was treated to remove tin or iron shavings.

Due to significant difference in standard electrode potentials of iron (-0.44 V) and copper (+0.337 V) [14], copper displacement with iron can occur to almost completion, which allows for successful use of cementation for processing of copper-containing solutions. However, high degree of copper removal requires some excess of cementing metal. The copper content in cement precipitates range from 10 to 95% (usually 55–80%) [15], i.e. the formed CPRI can contain up to 45% iron.

Such processing of copper-containing waste allows to transform salt waste into metal powder, which doesn’t low hazard class of the waste, but allows to change it into compact form, convenient for storage and transportation. Processing of 1 m³ of spent sulfuric acid copper electroplating electrolyte results in at least 5 dm³ of copper powder. All of this lead to widespread use of this method and some researchers describe it as promising for processing of copper-containing waste [16].

In Kirov region, processing of copper-containing waste by cementation is conducted by OJSC “Cuprit”. They primarily process spent sulfuric copper electroplating electrolytes and
residue from etching of printed circuit boards in copper-ammonia solution. In 2018, company process more than 50000 m³ of technological solutions, which corresponds to few tons of CPRI.

CPRI produced at OJSC “Cuprit”, has particle seize of 0.1–0.5 mm (80%) to 0.5–1.3 mm (20%), iron content of 1.6 to 12.2% and does not correspond to requirements of Russian National Standard GOST 4960-2009 “Electrolytic copper powder”. CPRI finds no further use, due high iron content complicates processing into pure copper. Iron impurity complicates single stage electrorefining (ER) or powder into high purity cathodic copper. Presence of iron in anodic material leads to side chemical and electrochemical reactions complicating the process. Use multistage purification with fire refining (FR) as pre-treatment stage is not economically viable, due to complex equipment and intolerance to small and medium batches. There are methods to utilize CPRI as filler in construction concrete [17], however, inclusion of toxic powder in construction material can result in ecological hazard. Copper is also a valuable metal, so using it as filler is not economically viable.

As such large volumes of CPRI are accumulated within companies that process copper-containing waste, which calls for method that would allow for economically viable processing of copper powder into high purity copper.

Aim of the work is to study the possibility of processing CPRI into high purity copper through electrorefining, by using CRPI as anode. When developing the technology it is necessary to minimize effect of iron dissolving into electrolyte and account for disperse electrode. Such an experimental work was conducted to evaluate quantities influence of iron in electrolyte on refining process.

**Modern studies on processing of copper waste**

Traditional process of copper waste consist of two stages: fire and electrorefining.

During fire refining (FR), copper is melted and purged with air to oxidize impurities. It is possible due to solubility of copper oxides in liquid copper and their oxidative properties towards the majority of impurities, oxides of which have poor solubility in molten copper. After removal of impurities, copper oxides can be easily reduced by products of wood dry distillation. Copper waste and scrap for FR usually contain up to 4% of impurities, with processed copper having purity of 99.2–99.4% [18].

In [19], FR was used to process copper waste with high nickel content. It is proposed to introduce silicon additives to copper melt, which results in higher purity copper during electrorefining (ER). No similar studies were conducted for waste with high iron content.

In paper [20] describes study on RF of residue containing 40% Fe, 1–2% Cu and 1–2% Zn. Combination of carbothermic method and microwave irradiation allowed for reduction of iron to metal and removal of zinc in form of oxide.

Paper [21] studies purification of copper melt from the tin and lead importing during vacuum melting followed by directed crystallization. However, such elements as Fe, Cr, and Co, cannot be removed by evaporation during vacuum melting.

Paper [22] describes the effectiveness of FR with addition of Cu, P, which allows to obtain purer copper. Haque method can be considered as FR variant, which lies in purification of copper wire scrap from insulating material via treatment in induction furnaces [23].

ER is used for making of high purity copper. After FR, copper to for ER is cast into metal plates that are loaded into electrolytic baths as the anode. Electrolysis is conducted in electrolyte containing sulfuric acid and copper sulfate. Impurities that are more negative than copper dissolve into electrolyte but are not reduced at cathode, more positive impurities remain at anode as residue.

In regards to ER, existing works are directed towards optimization and modeling of the process, but not towards expanding its application. Theoretical and experimental studies of free convection and electrolyte layer separation are studied [24]; automatic regulation of copper ER process in [25]. In [26], modeling of ion flows during ER was studied, and the mathematical model of ion movement was developed. Paper [27] devoted to modeling ion behavior and reasons behind anode passivation. Utilization of arsenic which can occur in ER residue is touched in [28, 29].

For extraction of copper from salt waste, it is proposed to tans from copper into CuO, followed by the dissolution of oxide in sulfuric acid and electroextraction with gradual [30].

Considering that problem of processing copper-based waste with the iron content of 10% and more are not studied in recent works, aim of the work was to study possibility of processing CPRI into high purity copper by means of ER using CPRI as anode.
Material and method

Base electrolyte (BE) used in experiments was electrolyte that is widely for electrefining of copper, g/L: CuSO₄ · 5H₂O – 150, H₂SO₄ – 200 [31, 32], prepared using analytical grade reagents. Analytical grade Fe₂(SO₄)₃ · 9H₂O was used as iron source for model solutions.

Corrosion rate and current yield (CY) during electrolysis were measured gravimetrically. A setup was used to measure CY, in which stabilized power source, electrolysis cell, copper coulometer and milliammeter connected in series. Copperplate was used as cathode.

Qualitative analysis of simultaneous reactions of cathodic reduction of Cu²⁺ and Fe³⁺ was conducted using potentiodynamic method (potentiostat P-30, PC-Pack software was used to record cathodic curves).

X-ray fluorescence (XRF) analyst (EDX-720 Shimadzu) was used to study the composition of CPRI, dynamics of iron content in electrolyte during prolonged electrolysis, purity of refined copper.

Results and discussion

During electrolysis, CPRI can anodically dissolve forming Cu²⁺ and Fe²⁺ ions. Divalent iron ions cannot be reduced at copper cathode, due to standard potential of

\[
\text{Fe}^{2+} + 2e^{-} = \text{Fe} \quad (1)
\]

equal to -0.44 V, which is significantly more negative than that of

\[
\text{Cu}^{2+} + 2e^{-} = \text{Cu} \quad (2)
\]

equal to +0.337 V [14]. However, when Fe³⁺ appear in solution, they can be reduced at the cathode:

\[
\text{Fe}^{3+} + e^{-} = \text{Fe}^{2+} \quad (3)
\]

This is because rather positive standard potential of reaction (3) equal to + 0.771 V [14]. Formation of Fe³⁺ is possible due to diffusion of oxygen into electrolyte, result ion into reaction

\[
4 \text{Fe}^{2+} + O_2 + 4 H^+ = 4 \text{Fe}^{3+} + 2 \text{H}_2\text{O} \quad (4)
\]

Presence of Fe³⁺ in electrolyte reduces cathodic current yield (CY), and increasing anodic CY due to reaction

\[
\text{Cu} + 2 \text{Fe}^{3+} = \text{Cu}^{2+} + 2 \text{Fe}^{2+} \quad (5)
\]

if powder is kept in electrolyte without current supply, both its copper (reaction (5)) and iron part dissolve,

\[
\text{Fe} + 2 \text{Fe}^{3+} = 3 \text{Fe}^{2+} \quad (6)
\]

However, prior to formation of Fe³⁺, when powder is introduced to solution its iron part reacts with Cu³⁺, H⁺ ions:

\[
\text{Fe} + \text{Cu}^{2+} = \text{Fe}^{2+} + \text{Cu} \quad (7)
\]

\[
\text{Fe} + 2 \text{H}^+ = \text{Fe}^{2+} + \text{H}_2 \quad (8)
\]

To model simultaneous occurrence of anodic dissolution of iron and copper experiments were conducted with addition iron (DC01 steel by European ranging) and Cu-ECP copper plates connected in parallel as anodes. Individual ammeters were connected in circuits of copper and iron anodes. Cathodic current density 1 A/dm², electrolysis time – 0.5 h, total current – 90 mA (set with rectifier). Iron anode was submerged in BE under load and removed also under load. This was done to avoid errors due to reaction of metallic iron with electrolyte without current since cementation can occur during this time (reaction 7).

Iron anode removed under load had red color. This indicated that chemical dissolution due to cementation occur simultaneously with anodic dissolution.

Ratios between anodic and cathodic currents were 14.2; 5.57; 3.46; 3.29 and 3.29 after 1, 3, 10, 20 and 30 min of electrolysis respectively. This is due to high reactivity of iron (more negative potential than copper). Decrease in current ratio is explained by shielding of iron surface due to cement copper.

To evaluate ratio between iron consumed by cementation and anodic dissolution, the anode was weighted before and after electrolysis, and also after removal of cement copper from the sample. The cement copper was removed using fast acting solution, g/L: CrO₃ – 200, (NH₄)₂SO₄ – 80 [33]. It was previously established to not dissolve iron.

Consider weight anodically dissolved copper and weight increase on coulometer cathode CY for anodic dissolution of copper and iron is 22.6 and 77.4% respectively. Total weight loss of iron allowed to calculated ration between anodically dissolved and cemented iron (78.5 and 21.5%).

The occurrence of cementation during anodic dissolution of CPRI leads to redistribution of iron as cementing metal, additional accumulation of iron in electrolyte, and shielding
Regardless of mechanism of iron consumption, when 1 g/L \(Fe_2^+\) of iron transfer to electrolyte, concentration of \(Cu^2+\) decreased by 1.138 g/L (1.138 – atomic mass ratio of Cu and Fe).

In practice, during electrorefining of CPRI, there can be situation when both electrodes remain in solution without current load. As such, additional experiments were conducted to evaluate rates of few chemical reactions. For dissolution of copper in BE with addition of 8 g/L \(Fe_3^+\) corrosion current \(i = 0.184 \text{ A/dm}^2\); for cementation of copper on iron in BE \(i = 5.06\) and 1.45 A/dm\(^2\) (for duration of 0.5 and 5 min respectively); dissolution of iron in H\(_2\)SO\(_4\) (200 g/L) \(i = 0.109 \text{ A/dm}^2\).

The higher reaction rate is observed for copper cementation. As such due to fast blockage of the iron surface with cement copper, the influence of reaction (8) can be ignored.

Accumulation of large amounts of \(Fe_3^+\) in BE can lead to significant losses of cathodically deposited copper. As such during electrolysis breaks, the cathode must be removed from electrolysis bath.

Experimental results on the influence of \(Fe_3^+\) concentration on CY are shown in Figure 1. The graph was plotted considering that during electrolysis (20 min at 1 A/dm\(^2\)), the \(Fe_3^+\) concentration is also reduced due to reactions (3) and (5). As such, calculated CY values are related to average \(Fe_3^+\) concentration during electrolysis.

Decrease of cathodic copper CY and increase of anodic copper CY are proportional to \(Fe_3^+\) in electrolyte, with negative effect of iron(III) on electrode process being about the same.

Influence of \(Fe_3^+\) in BE on the cathodic process was studied potentiodynamically (Fig. 2). The stationary potential of copper electrode (about +110 mV vs Ag/AgCl) turned out to be the same for solutions with \(Fe_3^+\) and without it, which can be explained by low exchange currents for reaction (3).

Polarization curves (PC) on elevation region in solution with and without \(Fe_3^+\) are almost identical. As such, this part of PC cannot be used to evaluate the contribution of reaction (3) to cathodic process. At the same time, increase in maximum on PC recorded in solution with addition of \(Fe_3^+\) in comparison to those recorded in BE, indicate concurrent occurrence of reaction (2) and (3), when \(Fe_3^+\) is present in electrolyte.

The assumption about low exchange current of reaction (3), allows expecting lower effect of

**Fig. 1.** Dependence of the current efficiency on the concentration of \(Fe_3^+\) ions

**Fig. 2.** Cathode potentiodynamic graphs, taken in BE (1) and in BE with the addition of \(Fe_3^+\) ions 8 g/L (2). Rate of potential change, mV/s: a – 5; b – 10

Fe$^{3+}$ at higher working current densities. As such, for BE with Fe$^{3+}$ 8 g/L, influence of current density on cathodic and anodic CY was studied (Fig. 3). The results confirm expected effect, as such it is rational to conduct electrolysis at higher cathodic current densities.

A future of CPRI as initial material for processing into copper is its disperse state. Because of that, experiments with CPRI were conducted inside perforated titanium alloy current collector (basket), which was placed into a microporous polypropylene jacket. Such setups are used in galvanic to make powder anode [34].

In preliminary tests involving BE and basket current collector from WT1 titanium alloy, a significant increase in voltage (up to 10–30 V) was observed, which is due to high transition voltage at dispersing MPRI – titanium oxide film.

It is known the method to activate titanium WT1 alloy with the solution of HNO$_3$ : HF (2 : 1) [35]. But because this solution is dangerous, it was decided to add NaF (30 g/L) to BE, to depassivate titanium. After this modification, the voltage in further experiments did not exceed 4 V.

In separate experiments it was found, that addition of NaF to BE containing Fe$^{3+}$ improved cathodic CY by few percents when refining CPRI. This effect can be attributed to partial complexing of trivalent iron into [FeF$_4$]$^-$, [FeF$_5$]$_2^-$ and [FeF$_6$]$^{3-}$ [36], which have difficulty for migrating towards the negatively charged cathode. It was also found that introduction of NaF, does not affect corrosion rate of copper.

A long-term (5 stages with breaks) electrorefining of CPRI experiment was conducted on a laboratory scale. Working cathode area was 0.42 dm$^2$, cathodic current density was varied from 1 to 2 A/dm$^2$. CPRI load was 188 g, 850 mL of BE with addition of NaF (30 g/L) was used. Electrode distance was 5.5 cm. Based on experimental results, cathodic CY (95.4%) and average specific power consumption (1.44 (kW · h)/kg of copper). The purity of cathodically deposited copper was measured by XRF, according to which it corresponds to M0k copper (GOST 859-2014 Copper. Grades), or Cu-ECP grade by European specification.

After each electrolysis stage electrolyte samples were taken for XRF analysis to measure Fe buildup in the electrolyte. After current consumption of 0.75; 3.85; 6.65; 9.63 and 12.1 A · h/L, the Fe/Cu ratio in electrolyte was 0.025; 0.052; 0.074; 0.11 and 0.123.

The higher rate of Fe buildup is observed on stage 1. This is because upon placing the electrode into solution significant amount of iron in copper powder partakes in cementation i.e. the major part of iron buildup occurs due to chemical reaction and not anodic dissolution. On subsequent stages (2–5), iron buildup is gradual, proportional to passed current due to anodic dissolution of iron from powder.

**Conclusion**

Possibility of processing copper powder containing 1.6–12.2% iron by means of electrorefining has been studied. This powder is formed during processing of copper-containing waste of galvanic plants by cementation and finds no use. It was found that electrorefining of dirty copper powder in sulfuric acid electrode results in high purity copper that matches Cu-ECP grade. Technological recommendations were proposed for conducting the process, namely method for depassivating titanium current collector.

It was found, that in addition to the anodic dissolution of copper and iron from powder, iron part undergoes dissolution due to cementation of copper. Influence of Fe$^{3+}$ ions in electrolyte on rate of chemical and electrochemical reaction was studied in experiments with model solution. It was found that negative effect of Fe$^{3+}$ on cathodic reduction of copper can be reduced by introduction to NaF to electrolyte and increase of cathodic current density.

**References**

ЭКОЛОГИЗАЦИЯ ПРОИЗВОДСТВА

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УВАЖАЕМЫЕ КОЛЛЕГИ!

Приглашаем Вас принять участие в работе XV Всероссийской научно-практической конференции с международным участием «Экология родного края: проблемы и пути их решения», которая будет проводиться в г. Кирове 16 апреля 2020 г.

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