Recovery of Copper from Water by Using a Reactor of Iron

Tomasz SUPONIK[1], Mirosław KURZYCA[2]

[1] Dr inż.; Institute of Mining, Faculty of Mining and Geology, Silesian University of Technology, Akademicka 2a, Gliwice 44–100, Poland; tel. 692403579, email: tomasz.suponik@polsl.pl
[2] Mgr inż.; Institute of Mining, Faculty of Mining and Geology, Silesian University of Technology, Akademicka 2a, Gliwice 44–100, Poland

Abstract

In the article the way of recovery of copper ions from water using iron reactor and magnetic separator was presented. First, the copper was precipitated on iron plates when the water flowing through a reactor, then the precipitates were scraped mechanically using sandpaper and at the end, they were separated magnetically. The magnetic and non-magnetic products were digested and the concentration of chosen metals (Fe, Cu) were measured to assess the efficiency of copper recovery. The study was conducted for two solutions with initial pH 3 and 6. For them, the efficiency of copper recovery were 85% and 45%, respectively.

Keywords: recovery of copper, iron reactor, magnetic separation

Introduction

Process water circulating in a closed cycle in a non-ferrous metal processing plant contains dissolved metals, among others. The kind of dissolved metal depends on the type of minerals in water. Due to high financial value of some metals, they might be worth to recover from water. Minerals may have also an impact on physicochemical and chemical properties of water, such as pH, redox potential and content of sulphates, chlorides and carbonates. These factors can affect the aggressiveness in relation to the machinery and equipment used in the industry, the efficiency of the enrichment process and the possibility of precipitation of stone (e.g. $CaCO_3$).

The main aim of the article was to present the way of recovery of copper ions from water using an iron reactor. The laboratory reactor was filled with iron plates placed in parallel inside [1, 2]. The reactor dimensions were $300 \times 300 \times 100$ mm, while the dimensions of iron plates were $250 \times 300 \times 0.5$ mm. 20 iron plates were installed in the reactor, with a total surface area of 3.35 m². First the copper was precipitated on iron plates when the water flowing through reactor, then the precipitates were scraped mechanically using sandpaper and at the end, they were separated magnetically. The magnetic and non-magnetic products were digested and the concentration of metals (Fe, Cu) were measured to assess the efficiency of copper recovery.

The research concerning the removal of metals using zero-valent iron has been conducted for several years [3]–[5]. Author of the article analyzed the mechanisms of removal of metals from water with the use of zero-valent iron. In case of copper ions, the formation of magnetite (in which copper replaces iron – see equation 1), and to a lesser degree Cu_2O, Cu^0 and/or CuO and/or Cu_2S, were the basic processes in the removal of copper for almost neutral pH of the aqueous solution (pH about 6), while the formation of copper in metallic form and Cu_2O, as well as probably CuO, were the basic processes for lower pHs (pH about 3) [6]. For almost neutral pH of aqueous solution, the adsorption of Cu(II) on the surface of shells were additional process causing copper removal from water. Although Suponik et al. used a small samples of square iron plates in their study (5×5mm and 0.5 mm thickness) [6], the mechanisms of removal of copper should be the same on iron plates of reactor, of course, depending on the chemical composition and physicochemical properties of the solution. While copper has been removed from solution, the metallic iron had been corroded. The corrosion products were α-FeOOH, and Fe_2O_3, mainly [6].

$$(1\text{-}x)Fe^{2+} + 2Fe^{3+} + xCu^{2+} + 2H_2O \rightarrow Cu^{2+}_{(x)}Fe^{2+}_{(1\text{-}x)}Fe^{3+}_2O_4 + 4H^+ \tag{1}$$
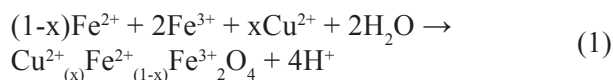
where $x \leq 1$.

Magnetic properties of substances result from magnetic properties of their chemical elements. In turn, magnetic properties of elements depend on their structure, especially of the outer electrons, and is characterized by magnetic moment of an atom [7]. Magnetic susceptibility is a feature that

Tab. 1. Specific (mass) magnetic susceptibility of chosen substances

Tab. 1. Właściwa (masowa) podatność magnetyczna wybranych substancji

| chemical formula of substance	Specific magnetic susceptibility χ_w, cm^3/g	The magnetic nature of chemical substances
Cu^0	-1.08x10^{-6} (293 K, after Hopstock [8])	Diamagnetic
Cu$_2$O	-1.76x10^{-6} (293 K, after Hopstock [8])	Diamagnetic
Cu$_2$S	-4.90x10^{-6} (293 K, calculated after Hopstock [8])	Diamagnetic
CuO	no data was found	
FeOOH	from 250 to 380x10^{-6} (293 K, after Svoboda [9])	Antiferromagnetic
Fe$_2$O$_3$	from 500 to 760x10^{-6} (293 K)	Antiferromagnetic
Fe$_3$O$_4$	from 1.4 to 1.11 - depending on intensity of the magnetic field in A/m (293 K, after Svoboda [9])	Ferrimagnetic
Fe^0		The most known representative of ferromagnetic substance
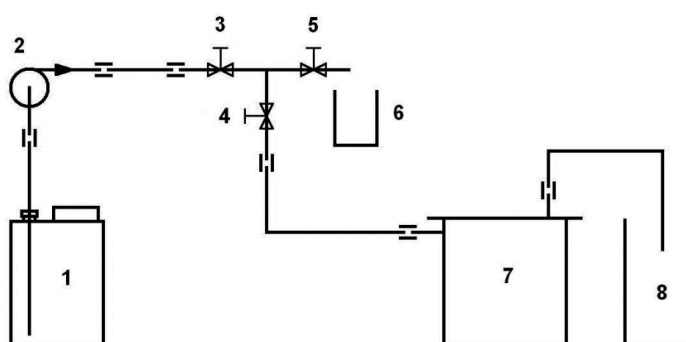
Fig. 1. Installation for removal dissolved copper from water: 1) water tank; 2) peristaltic pump ZALIMP PP1B-05A; 3, 4, 5) valves; 6) sampling point – water before precipitation; 7) iron reactor; 8) sampling point – water after precipitation [2]

Rys. 1. Instalacja do usuwania jonów miedzi z wody: 1) zbiornik z wodą; 2) pompa perystaltyczna ZALIMP PP1B-05A; 3, 4, 5) zawory; 6) punkt pobierania próbek – woda przed procesem wytrącania; 7) reaktor żelaza metalicznego; 8) punkt pobierania próbek – woda po wytrącaniu [2]

determines how the grain interact with the magnetic field. Table 1 presents specific magnetic susceptibility of substances listed above. Among them, the non-magnetic particles are Cu^0, Cu$_2$O, Cu$_2$S, while magnetic particle are FeOOH, Fe$_2$O$_3$, Fe$_3$O$_4$, Fe^0. In case of magnetite in which copper replaces iron (see equation 1) the impurities may changed the magnetic susceptibility – strictly speaking, copper may reduce the magnetic susceptibility of this compound.

Study of water
Methodology

Figure 1 presents the installation for removal dissolved copper from water. The water was pumped with the use of peristaltic pump to iron reactor. Since the iron reactor is to be located, e.g. in a non-ferrous metal processing plant, along a main line of process water (Fig. 2) the water yield in the reactor is less dependent on the yield of process water in an industrial installation. This allows to optimize a recovery of copper using an iron reactor as well as, if needed, to remove sulphates, chlorides and ferrous and ferric ions from water. Optimization of reactor is to adjust the physicochemical and chemical parameters of water, such as pH, redox potential, concentration of dissolved oxygen, etc, as well as extension of the residence time of water in a reactor and application of an electric potential in the reactor. The study was conducted in two series: for water with a pH = 3 and 6. This was because the study had a universal nature and the kind of precipitates formed on the surface of iron plates is well known for these conditions (see [6]).
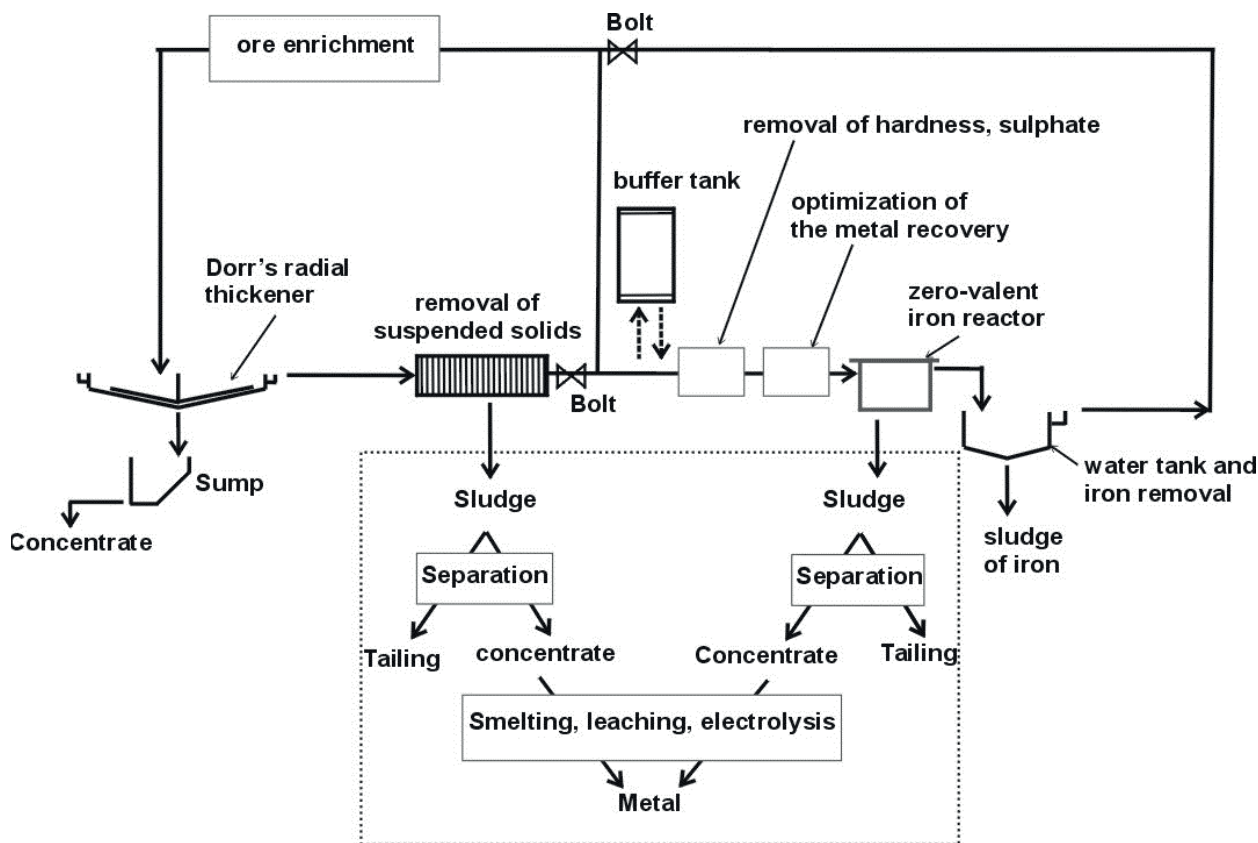
Fig. 2. A conceptual diagram of the technological system for the recovery of metals from process waters
– reactor located after the process of removing suspension

Rys. 2. Schemat koncepcyjny układu technologicznego do odzysku metali z wód procesowych
– reaktor wolnostojący umieszczony po procesie usuwania zawiesiny

In the laboratory tests the water yield was 2.0 dm³/h. The measurements of water in both series have begun after 8 hrs from the start of pumping, i.e. after the water in the reactor had been changed two times (15 dm³). After this, the solutions were passed through dense filters and assessed. The quantitative analysis of chemicals in solutions was carried out for Cutot, SO_4^{2-} with the use of UV-Vis Spectrophotometer DR5000 HachLange. The pH, oxidation-reduction potential (ORP), dissolved oxygen (DO) and conductivity were measured with the Knick PORTAMESS meters. The measurements were carried out twice. The results, shown in Table 2, were calculated applying the arithmetic mean.

The pHs of the solutions was adjusted by a slow titration with a ultra-pure sulphuric acid solution (0.1 mol/dm³) or with ultra-pure sodium hydroxide solution (0.1 mol/dm³). Copper ion solutions were prepared by adding desired amounts of metal salt ($CuSO_4 \cdot 5H_2O$) into bottles and pouring distillated water. The concentration of copper in solutions at pH 3 and 6 amounted to 64.21 mg/dm³ and 68.45 mg/dm³, respectively. The intention of

the authors was to achieve relatively high concentration of copper, which would allow to weigh the precipitates scraped from an iron plates.

Results and discussion

The iron reactor had the ability to remove copper ions from water, when the pH was low and almost neutral (Table 2). The lower the pH values, the slower the observed decrease of copper concentrations. The mass of copper in 15 litres of solutions before precipitation with an initial pH of 3 and 6 were 936.15 and 1026.75 mg, respectively, while in solutions after precipitation 236.10 and 78.15 mg. This means that retention efficiency of copper in an iron reactor were 75.5 and 92.4%, respectively. The values of ORP and DO for both of the solutions decreased as well. The lower values of pH in the tests, the faster were decreases of these parameters. Very small decreases of sulphates showed that the metals did not precipitate in the form of sulphides (or precipitated to a small degree). The concentration of SO_4^{2-} ions for initial pH of 3 was higher in comparison with stechiometry, due to the sulphuric acid was added to solution.

Tab. 2. Physicochemical parameters and concentrations of chemicals in solutions used in the iron reactor

Tab. 2. Parametry fizykochemiczne i stężenia substancji chemicznych w roztworach stosowanych w reaktorze żelaza

Parameter/chemical, unit	Values in:			
	water before precipitation		water after precipitation	
	initial pH = 3	initial pH = 6	initial pH = 3	initial pH = 6
pH	3.05	6.02	4.25	5.80
Cond., mS/cm	1.108	0.991	1.246	1.089
ORP, mV	226	186	46	28
DO, mg/dm^3	9.7	9.4	6.6	6.5
Cu_{tot}, mg/dm^3	64.21	68.45	15.74	5.21
SO_4^{2-}, mg/dm^3	154.4	101.0	138.4	91.4

Tab. 3. Particle size distribution of the precipitates

Tab. 3. Skład ziarnowy osadów

Particle size, μm	180-140	140-100	100-80	80-40	40-20
for initial pH = 3					
Mass fraction, %	14	32	24	20	10
for initial pH = 6					
Mass fraction, %	5	36	37	18	4

Tab. 4. The weight of copper and iron in the magnetic and non-magnetic products

Tab. 4. Masy miedzi i żelaza w produktach magnetycznych i niemagnetycznych

Element, unit	For initial pH = 3		For initial pH = 6	
	non-magnetic product	magnetic product	non-magnetic product	magnetic product
Cu, g	0.618	0.018	0.428	0.314
Fe, g	0.192	1.481	0.795	1.677

Study of precipitate
Methodology, results and discussion

After a peristaltic pump was turned off, all the iron plates were pulled out in each series, washed with demineralised water, wiped gently with a paper towels and dried in a drying oven. Then, the precipitates were scraped gently using sandpaper (P500 in accordance with ISO 6344). The mass of precipitates for initial pH of solutions 3 and 6 were more than 3.4 g and 4.6 g, respectively. The grain-size distribution of the precipitates was determined using laser granulometer. Table 3 presents the results. The values indicate a very small or fine particle size of precipitates.

Due to the size of the particle and the different magnetic property of precipitates (see Table 1) the separation using high gradient magnetic separator was chosen (Fig. 3). The separator worked periodically. Working channel located between the pole pieces of the electromagnet was filled with steel wool. The feeds (aqueous suspensions of precipitates having a density of 40% of solids) were prepared in a feeding tank equipped with a stirrer. The suspensions were filtered through a steel wool
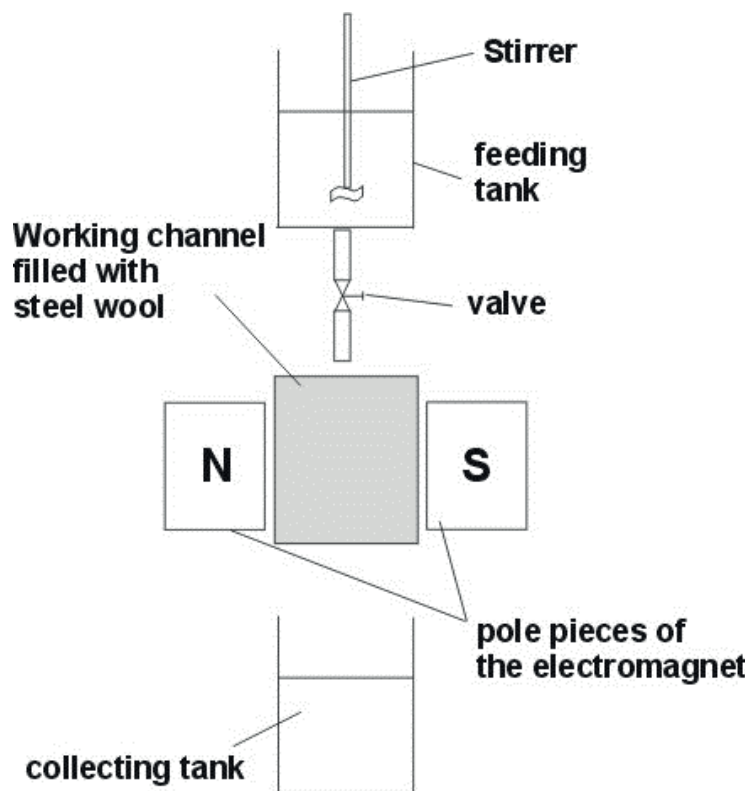
Fig. 3. Laboratory high-gradient magnetic separator

Rys. 3. Laboratoryjny separator wysokogradientowy

of the working channel. During this time the magnetic field was on. A non-magnetic product was discharged into the collecting tank, while a magnetic product remained in the working channel, which was washed to another tank after switching off the electromagnet. The solutions were filtered with the vacuum filtration, using a filter paper of 0.45 μm pore size. Then, the filters were dried in an oven at 105°C. The masses of magnetic and non-magnetic products were 0.927 and 2.388 g for initial pH of solution = 3 and 1.748 and 2.851 g for pH = 6.

In the study the low-gradient separation was omitted, due to small amount of material. This would have increased the effectiveness of separation by removing a ferromagnetic component from the feed.

In order to check the concentration of copper and iron in the precipitates, they were digested using Magnum mineralizer. A concentrated nitric acid was used as a reagent. The solution obtained was diluted with demineralized water. Then, the concentrations of copper and iron in liquid were measured with the help of UV-Vis Spectrophotometer DR5000 HachLange. The weight of copper and iron in the magnetic and non-magnetic products are presented in Table 4.

The results show that the non-magnetic product for initial pH of solution amounting 3 consists of 67% of copper and 21% of iron. The remaining 12% was probably oxygen. On this basis, it can be concluded that the main compound in the non-magnetic product was Cu^0. It need to be added at this moment, that the recovery of copper was 85%.

In the case of non-magnetic product for initial pH of solution amounting to 6 the recovery of copper was much lower and was 45%. This was, due to fact that the magnetite, in which copper replaces iron, was the main product of copper removal [6]. The specific magnetic susceptibility of this chemical compound no differ (probably) significantly from an iron compounds, which have magnetic properties. The percentage composition of copper and iron in non-magnetic product were 25% and 45%, respectively. The remaining ca. 27% was also oxygen. In this case a large amount of copper had remained in the magnetic product.

In both cases of the solutions the copper loss was noticeable (the sum of copper in non-magnetic and magnetic products was not the same as the sum of copper precipitated on iron reactor – see Table 2). It is difficult to say what is the cause. This difference probably results from the method of stripping the precipitates from an iron plates.

In order to verify a results the further measurements ought to be done, e.g. the measurements of precipitates with the use of x-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS).

Conclusions

The iron reactor had the ability to remove copper ions from water, when the initial pHs were 3 and 6. The lower the pH values, the slower the observed decrease of copper concentrations. The precipitates from the reactor was scraped mechanically, and separated magnetically. The non-magnetic products for initial pH of solution amounting 3 and 6 consisted of 67% for copper and 21% for iron and 25% for copper and 45% for iron, respectively. This means that the copper was separated magnetically much better at lower pHs. This was because the copper in metallic form was precipitated for low pH, while the magnetite in which copper replace iron ($Cu_xFe_{1-x}Fe_2O_4$) was the main product for higher pH. Cu^0 is a non-magnetic material, while $Cu_xFe_{1-x}Fe_2O_4$ magnetic probably.

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Odzyskiwanie miedzi z wody z wykorzystaniem reaktora żelaza

W artykule przedstawiono sposób odzysku jonów miedzi z wody przy użyciu reaktora żelaza i separatora magnetycznego. W pierwszej kolejności jony miedzi były wytrącane na płytach stalowych podczas przepływu wody przez reaktor. Następnie osad zdrapywano mechanicznie za pomocą papieru ściernego i poddano separacji magnetycznej. Produkty magnetyczne i niemagnetyczne były mineralizowane i w uzyskanych roztworach oznaczano stężenia metali (Fe, Cu) celem określenia sprawności odzysku miedzi z wody. Badania przeprowadzono dla dwóch roztworów o początkowej wartości pH 3 i 6. Sprawność odzysku miedzi dla tych roztworów wynosiła odpowiednio 85% i 45%.

Słowa kluczowe: odzysk miedzi, reaktor żelaza, separacja magnetyczna