

Recovery of residual copper from low-content tailings derived from waste electrical cable treatment

Georgios N. Anastassakis^{a,*}, Paolo Bevilacqua^b, Lorenzo De Lorenzi^b

^a School of Mining Engineering and Metallurgy, National Technical University of Athens (NTUA), 9 Heroon Polytechniou str., 15780 Zographou, Greece

^b Department of Engineering and Architecture, University of Trieste, Piazzale Europa 1, Trieste, Italy

ARTICLE INFO

Accepted 9 September 2015

Keywords:

Copper recovery
Electrical cable scraps
Heavy media separation
Cementation
Electrowinning

ABSTRACT

The current work aims at the recovery of residual copper from electrical cables with low content of copper (less than 5%). The sample originated from the tailings of electrical cables that had been previously subjected to copper recycling treatment. The tailings were successively treated with physical methods (sieving, heavy medium separation in ZnCl₂ bath, and counter-current separation) and electrochemical methods (cementation, electrowinning). Sieving seems to be more efficient than gravity separation methods, since, for 1.00 mm aperture and sieving time as short as 2 min, the undersize copper grade of the product was 57% in copper (from 4% in the feed), with corresponding copper recovery of 53%. Longer sieving times or larger apertures led to products with higher copper recovery but of lower grade. As regards cementation, preliminary tests were carried out to investigate the effect of pH using high purity CuSO₄ · 5H₂O instead of dissolving metallic copper. Subsequent tests using the sieving undersize product of the scrap copper wire confirmed the results of the preliminary tests; in addition to pH, this product was also used to investigate the effects of the attacking chemical (H₂SO₄, HCl, H₂O₂), sacrificial metal (aluminium, iron scrap), temperature, and surface area on cementation. The results show that cementation of the dissolved copper from scrap wire is efficient at pH = 2.5–3.2, with sufficient copper recovery within a few hours. Also, electrowinning tests on the undersize sieving product proved the feasibility to obtain pure copper by electrodeposition onto stainless steel cathode with lead anode, without contamination of the electrolytic solution. In both methods, copper purity degrades when HCl acid is used instead of H₂SO₄. Especially with the use of H₂SO₄ in electrowinning, it was observed that lead anode is passivated when the solution is entirely depleted from copper ions. The results of the current work clearly demonstrate the feasibility to obtain pure copper from low-grade electric wire scraps by successively submitting the tailings to sieving and cementation.

1. Introduction

Due to its properties (conductivity, malleability) and variety of uses (electrical and data cables, electrical and electronic equipment, cooling or heat exchangers, water pipes, etc.), copper is considered one of the most important industrial metals, with approximately 70% of the global copper being used for various electrical applications (Glösner et al., 2013).

A significant part of copper originates from recycling, since copper can be recycled and re-used countless times, without any loss of performance and difference in the quality of recycled copper in comparison to that from ore. Consequently, copper recycling significantly contributes to natural resources conservation, waste minimization, energy savings, and cost reduction (Kang and Schönung, 2005; International Copper Association Ltd., 2013). According to Glösner et al. (2013), approximately 24 Mt of copper were produced globally in 2010, 35% of which

originated from recycled copper; correspondingly for EU-27, used copper from recycling amounts to 40% (Muchova et al., 2011).

In respect to copper recycling, extensive research has been carried out on copper recovery from electronic waste with physical separation methods (Zhang and Forsberg, 1997, 1999; Lee et al., 2004, 2007; Mohabuth and Miles, 2005; Bevilacqua and De Lorenzi, 2008; de Araújo et al., 2008). Also, electrostatic separation has been applied to separate copper from plastic in artificial mixtures, with copper content higher than 50% w/w (Tilmatine et al., 2009).

Among the metallurgical methods, a lot of effort has been devoted to copper recovery from solutions by means of electrowinning (Beukes and Badenhorst, 2009; Liu et al., 2009; Al Shakarji et al., 2011; Viswanath and Sajimol, 2011; Yanping et al., 2013) or cementation.

Many authors deal with copper cementation from ores in respect to process optimisation, working either at high temperature (Karavasteva, 1996; Donmez et al., 1999; Lopez et al., 2003; El-Batouti, 2005; Fouad and Abdel Basir, 2005) or at low (Stefanowicz et al., 1997); other used fine zinc or aluminium powder as sacrificial metals (Karavasteva, 1996, 2005). Chemical additives such as surfactants can also be used

* Corresponding author.

E-mail address: ganastas@metal.ntua.gr (G.N. Anastassakis).

in the cementation process (Karavasteva, 1996; El-Batouti, 2005). Some authors (Stefanowicz et al., 1997; El-Batouti, 2005) suggest attrition to remove the cemented copper from sacrificial metal surface by collisions. Conversely, Sedzimir (2002) suggests that copper growth on less noble metal surface increases the surface of reaction, with subsequent increase of process rate, because no direct contact between copper ions and the less noble metal surface is required to allow copper cementation.

This work aims at the recovery of residual copper from low grade tailings (up to 5% copper, and high grade in polymeric material), by applying simple physical methods to counterbalance the relatively increased cost of the subsequent chemical treatment. The tailings originated from waste electrical cable treatment for copper recycling.

The physical separation methods tested were sieving, dense medium separation and counter current separation. The chemical methods examined were copper cementation onto less noble metals (iron, aluminium), and electrowinning deposition.

2. Materials and methods

2.1. Materials

The samples used during the tests originated from the tailings of a recycling plant dealing with the recovery of copper from electrical cables, after comminution to less than 4–5 mm and subsequent air-separation of copper wires from the polymeric fraction.

The test material was composed of irregular-shaped plastic grains, mainly plasticized PVC, mixed with copper wires; the sample content in copper was low, not exceeding 5% w/w.

Preliminary cementation tests were carried out using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, of 98–99% w/w purity, instead of dissolving metallic copper.

Hydrochloric acid (commercial muriatic acid for domestic use), in 10% w/w solution, and sulphuric acid, of 95–98% w/w purity, were used to dissolve the copper wires, added along with 30% w/w hydrogen peroxide.

Aluminium film for domestic use, pure aluminium drops, pure aluminium powder, shavings or filings were used for cementation tests; iron blades were also used as sacrificial metal for copper cementation.

2.2. Methods

The copper concentration by sieving was carried out on a Weston screen machine with sieve diameter of 600 mm, using 2000 g samples. The sieve apertures used were 1.00 mm and 1.35 mm, respectively.

The undersize product of sieving, which was rich in copper, was used for dense medium tests, as a rough approximation of static dense medium separation conditions. Since copper density was determined to 8.9 t/m^3 and that of insulating material to 1.42 t/m^3 , separation tests were carried out at medium density of 1.60 t/m^3 by dissolving zinc chloride in water. The undersize product of sieving was also used for counter current tests. After separation, copper was recovered, carefully washed, dried, and weighed.

X-ray analyses were performed with a Bruker AXS D5005 diffractometer with time acquisition of 0.4 s, in a 2-theta range from 25 to 100° , and a step-size of 0.01° .

Raman analyses were performed with a Renishaw inVia Raman Microscope, laser light 514 nm, Argon ions.

The undersize product from sieving was used for the chemical dissolution of copper, because its copper grade was higher compared to that of the initial scrap. The chemical dissolution of copper was performed using a mixture of hydrogen peroxide, acting as copper oxidant, along with sulphuric or hydrochloric acid. The copper solution was separated from polymeric grains by filtration. Polymeric grains were washed with water to remove the residual acid solution; subsequently, the washing water was added to the copper solution. Metallic copper was obtained from the solution by cementation or electrowinning.

Prior to tests with copper scrap from cables, preliminary tests were carried out using copper sulphate instead of metallic copper for simulation, cost and practical reasons as well as because of the anomalous behaviour observed in previous tests with aluminium and sulphuric acid solution, i.e. on some occasions cementation was fast while on others cementation did not take place (Simon Ostan, 2007).

Cementation is a spontaneous electrochemical process that occurs when ions of a more noble metal (oxidised state) come into contact with those of a less noble metal (reduced state).

Iron (as it is usually called, but actually being “steel”) and aluminium were used as sacrificial (less noble) metals for copper cementation, provided as scraps or shavings. Copper cementation is described by the following reactions (Stefanowicz et al, 1997):



or



As regards the tests with aluminium, detailed experimentation was performed to evaluate the influence of pH, temperature, and aluminium surface area on the cementation rate.

In electrowinning tests, the undersize product of sieving was used. The tests were performed by using forged lead anode of 100 mm width, 150 mm length and 10 mm thickness, and stainless steel cathode of the same dimensions but of 1 mm thickness; cathode was maintained parallel to the anode at a distance of 50 mm. A continuous DC power supply LAB EC 3020 electrical current generator was used to supply continuous electrical current in the range between 0 and 30 V or between 0 and 20 A; the tests were carried out under constant voltage (V) or current (A), by choice.

Hanna Instrument, model pH 211, was used to evaluate pH values. Microscope images were obtained using a digital camera Nikon Coolpix 4500 applied to a Nikon SMZ1000 microscope.

All tests were performed at room temperature, unless otherwise specified.

3. Results and discussion

3.1. Physical separation methods

3.1.1. Sieving

Sieving tests were carried out to evaluate the possibility of copper recovery from the tailings of the plant with quite a simple, fast and cheap method. Sieving tests were performed with sieve aperture of 1 mm and 1.35 mm, correspondingly. The results are presented in Table 1.

Table 1 reveals that, for 1.00 mm sieve aperture, the yield of the undersize product after 10 min of screening is approximately 5% of the feed weight. However, the copper grade increases to almost 51% (about 13 times higher than that of the feed), with corresponding copper recovery at 62%. When 1.35 mm screen aperture is employed, the undersize yield rises by 2.3 times, copper grade reduces to approximately the half compared to the previous case while copper recovery increases to 78.7% (increase by 27%). In both cases, there is a marked reduction in the yield of the material to be processed in the subsequent copper recovery steps, while more than 60% of the copper is recovered.

As regards the effect of time, it is observed that the greatest yield of the undersize product is obtained within the two first minutes of sieving. Sieving times between 2 and 10 min have no practical benefit, since copper recovery increases slightly while the product grade is diminished due to its dilution with polymer; on the other hand, energy consumption increases.

The use of sieves with an aperture smaller than 1 mm results in longer sieving time and higher risk of sieve obstruction, despite the

Table 1
Sieving results.

Aperture size (mm)	Product ^a	Fractional				Cumulative			
		Time (min)	Yield %	Grade %	Distr. %	Time (min)	Yield %	Grade %	Distr. %
1.00	U/S 1	2	3.71	57.2	53.1	2	3.71	57.2	53.1
	U/S 2	3	0.68	34.7	5.9	5	4.39	53.7	59.0
	U/S 3	5	0.49	25.5	3.1	10	4.88	50.9	62.1
	U/S 4	10	0.48	Negl.	0.0	20	5.36	46.4	62.1
	Oversize		94.64	1.6	37.9				
	Feed		100.0	4.0	100.0				
1.35	U/S 1	2	8.5	34.4	73.3	2	8.5	34.4	73.3
	U/S 2	3	1.6	8.9	3.8	5	10.1	30.2	77.1
	U/S 3	5	1.3	5.0	1.6	10	11.4	27.4	78.7
	U/S 4	10	1.5	Negl.	0.0	20	12.9	24.4	78.7
	Oversize		87.1	1.0	21.3				
	Feed		100.0	4.0	100.0				

^a U/S: undersize.

production of a passing product with higher copper grade. Shorter sieving times are possible with sieve aperture larger than 1 mm, but the copper is diluted into a greater amount of polymer.

By compromising copper grade and recovery of passing product, polymer concentration in the undersize, sieving time, sieve obstruction risk, and energy consumption, it is gathered that the best results are obtained with sieve aperture of 1 mm and sieving time of 2 min. Due to its efficiency, simplicity and low cost, mechanical sieving seems as a potential, much promising method for industrial application with regard to copper recovery from cable tailings.

3.1.2. Gravity separation

3.1.2.1. Dense medium separation. A representative sample of the undersize sieve fraction was treated in dense medium static bath, using concentrated zinc chloride solution of 1.6 t/m³ density. Copper wires were collected in the sink (heavy) fraction and the polymer in the float (light). The small size (<1 mm) of the polymeric grains makes the separation very slow, albeit very efficient. The products were washed to remove the residual zinc chloride from the surface, dried and weighed. The yield of the heavy product (pure copper) was 27.8% and that of the light (polymer with no copper inside) 72.8%. From the aforementioned results it is gathered that copper can be completely separated from polymer under ideal conditions, such as those prevailing in zinc chloride solution that was used as dense medium. However, the complexity and the increased cost of heavy medium separation raise questions as concern its application to larger scale operations.

3.1.2.2. Counter current separation. This method of separation was tested for its low cost. Preliminary tests, performed at water velocity between 0.12 and 0.18 m/s, revealed the severe limits of the method. Pure copper was obtained for high water velocity, but with a very small recovery, not exceeding 21% of the copper present in the sample. By lowering the water velocity, the recovery increased up to 41%, but the metal was contaminated with polymers. The reprocessing of the light fraction five times did not improve the results significantly, since the recovery increased slightly to 55.2% but its grade remained low due to its polymer contamination. In general, the overall results were inferior to those of screening.

3.2. Chemical recovery of copper

3.2.1. Copper cementation

3.2.1.1. Effect of pH on cementation with aluminium

3.2.1.1.1. Results using CuSO₄ · 5H₂O. A first mother solution was prepared by dissolving 400 g of CuSO₄ · 5H₂O in 2500 g of water; subsequently, it was split into eight aliquots of different pH each. The pH of the mother solution (sample SM1/0) was 3.33. Hydrochloric acid

(commercial muriatic acid for domestic use, 10% w/w) was used to fix the pH at the desired value, because it is of lower cost than sulphuric acid, and it was erroneously assumed that there should be no interference of the chloride ions in the cementation process. Once the solutions had been prepared, 1.000 ± 0.002 g of aluminium film was added to each solution. The results of cementation are presented in Table 2.

From Table 2, it is gathered that no cementation occurred in the mother solution (pH = 3.33) while reaction rate increases as pH lowers. The time needed for aluminium digestion was some hours for pH = 3.07 (sample SM1/1) while only 1–2 min for pH = 0.63 (sample SM1/7).

Taking into account that 1.00 g of aluminium is able to cement 3.53 g of copper (Eq. (2)), the results clearly show that there is a discrepancy between the yield of the actually cemented material using 1.000 ± 0.002 g aluminium and of the theoretically expected for pH values in a very acid region (pH < 1.86). The discrepancy increases as pH lowers. More specifically, the weight of the cemented material is by 3.1% higher than that of the theoretical for pH = 1.86 while it becomes higher by 93.2% for pH = 0.63. Microscopic examination of the products reveals that the cemented product at pH = 3.07 corresponds to metallic copper (Fig. 1a) while the material cemented at pH = 0.63 is composed of a fine, grey sand (Fig. 1b).

Microscopic examination of the other products reveals that the amount of the grey material increases while copper grade decreases, as the solution pH decreases. The cementation products were subjected to XRD analysis to further investigate their composition (Fig. 2).

It must be pointed out that, in order to avoid the superimposition of seven graph lines and to facilitate the reading of the XRD graphs, the values of each graph (except the first) have been artificially translated upwards, increasing the experimental values by a constant arbitrary value of 500 for the second graphs, 1000 for the third and soon on.

The XRD graph of the cemented product at pH = 3.07 (sample SM1/1) confirms the results of microscopic observation. The four main peaks, obtained at 2-theta angles of 43.29, 50.43, 74.12 and 89.91°, correspond to those of the metallic copper (Berry, 1967). In the graph of sample

Table 2

Effect of pH on reaction rate and copper cementation (from CuSO₄ · 5H₂O dissolution) using 1.000 ± 0.002 g of aluminium.

Sample	pH	Reaction rate	% material cemented/theoretical
SM1/0	3.33	No reaction	0
SM1/1	3.07	Very, very slow reaction (several h)	84.1
SM1/2	2.67	Slow reaction (>1 h)	85.6
SM1/3	2.25	Relatively fast reaction (<1 h)	90.1
SM1/4	1.86	Quite fast reaction (20–40 min)	103.1
SM1/5	1.37	Fast reaction (10–20 min)	148.2
SM1/6	1.02	Very fast reaction (3–10 min)	182.0
SM1/7	0.63	Extremely fast reaction (1–2 min)	193.2



Fig. 1. Cementation products on aluminium as a function of pH: a) copper cemented at pH 3.07, b) nantokite (CuCl) cemented at pH 0.63.

SM1/7 (pH = 0.63), the characteristic peaks of copper disappeared and were substituted by those of nantokite (CuCl, cuprous chloride), as gathered from the main peaks occurring at 2-theta angles of 28.59, 46.53 and 56.29° (Berry, 1967).

As Fig. 2 shows, nantokite appears for the first time at pH = 2.25 (graph of sample SM1/3), where a very small peak at 28.59° is detectable. This is the 2-theta value of the main nantokite peak, which appears although the content of nantokite in the sample is still probably very low. In sample SM1/4 (pH = 1.86) and the following, the nantokite peaks are more evident and, at the same time, the copper peaks are less clear. In sample SM1/7 (pH = 0.63), no copper peaks are detectable, except a small peak at 43.29°, which is the 2-theta value of the main copper peak.

A second mother solution was prepared by dissolving 260 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 2000 g of water; afterwards, it was split into seven aliquots with pH values ranging from 3.25 to 2.21 by adding HCl. In each solution, 3.5 g of aluminium film was added. Even though the pH range was narrower than that of the first set, it was similarly observed that the reaction rate was faster in the more acidic solutions than in those of higher pH. The results (Fig. 3) clearly show that the percentage of cemented copper remains practically constant at the level of 86–87% in the pH range tested (pH = 2.21–3.25).

These results as well as other similar, not reported here, suggest that the best conditions for cementing copper on aluminium from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution require pH values ranging from 2.5 to 3.2. In less acidic pH values, the reaction is very slow. In more acidic pH values, the reaction can be very fast, but copper could become contaminated with other minerals, like nantokite.

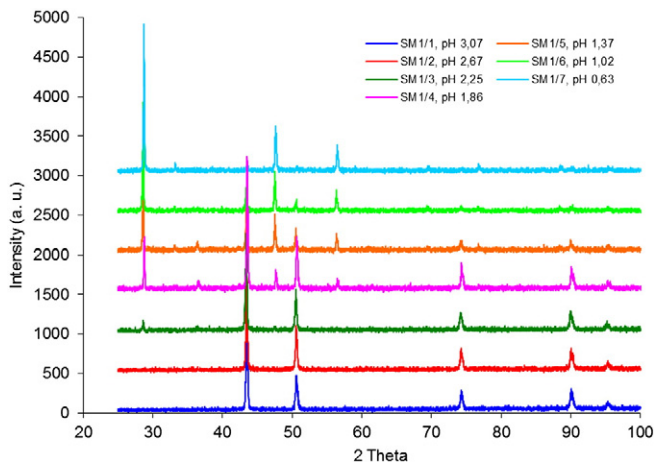


Fig. 2. XRD of cementation products of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ onto aluminium as a function of pH.

Fig. 4 shows small hemispherical drops of pure copper, no larger than 1 or 2 mm, obtained by cementation onto aluminium film at pH = 3.0.

3.2.1.1.2. Results using electrical wire scrap. After preliminary tests using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, copper solutions were prepared by using the undersize product of sieving; copper wire of the undersize was dissolved by using a mixture of sulphuric acid and hydrogen peroxide, as could possibly be the case in an industrial plant for the treatment of the copper wire scraps. The plastic component of the undersize, which is unaffected by the reagents mixture, was subsequently separated from the solution by filtration. The absence of chloride, previously introduced as HCl to lower the solution pH, is an immediate advantage, since nantokite formation is now impossible.

A mother solution (SM7) was obtained by mixing 55.24 g of undersize product, out of which 31.6 g of copper, with 85 g of hydrogen peroxide and 98 g of sulphuric acid for 3 h; after polymer separation by filtration, the copper solution was diluted with water to a final volume of 2 l. The aforementioned solution was used for cementation tests at various pH values by adding 1.3 g of aluminium film in each aliquot. At the end of the cementation process, copper was recovered on filter papers, washed, dried at 105 °C, weighed and microscopically examined.

The results (Fig. 5) show that the percentage of cemented copper remains practically constant at the level of 84–85% for pH = 0.78–1.99 while a slight drop to the level of 81–83% is observed for pH = 2.38–3.51. Microscopic observations showed that cemented copper at pH = 0.78 still contains a very small amount of aluminium, while all the other samples appeared to contain only cemented copper.

3.2.1.2. Effect of temperature on cementation with aluminium. Another mother solution of pH = 2.66 was prepared by mixing 146.75 g of undersize product, which contains 84 g of copper, with a total volume of

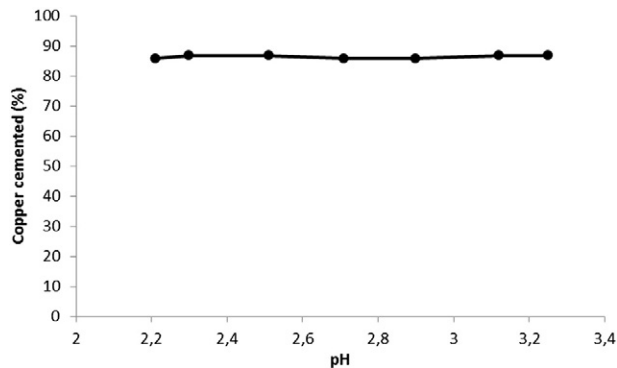


Fig. 3. Effect of pH on copper cementation (from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolution) using 3.5 g of aluminium.



Fig. 4. Small drops of pure copper obtained by cementation onto aluminium film.

6.3 l of water, sulphuric acid and hydrogen peroxide; after polymer separation by filtration, the copper solution was used for cementation tests that were carried out at temperatures of 23, 47, 60 and 84 °C, correspondingly. The results clearly show that cementation process is accelerated with temperature increase, as it is evidenced from the time required to digest 1.3 g of aluminium (Fig. 6).

3.2.1.3. Effect of aluminium surface on cementation rate. The mother solution used to investigate the effect of temperature was also used to evaluate the effect of aluminium surface (i.e. the total aluminium surface) on the cementation rate, at pH = 2.66. The aluminium film used in the previous tests was substituted by aluminium drops of diameter 6–7 mm, aluminium powders with maximum sizes 45 and 100 µm respectively, and aluminium filings of various size fractions: fine (– 50 µm), medium (– 500 + 250 µm) and coarse (– 1000 + 500 µm). For comparison reasons, a test was carried out using aluminium film, as previously done. In each case, the mass of aluminium added was 1.3 g, regardless of shape and size.

The aluminium film reacted slowly until complete consumption. The aluminium drops also reacted slowly and, due to the very small reaction surface of the three aluminium drops used in the test, a small amount of copper was cemented in 24 h.

Quite surprisingly, aluminium powder and filings, having a much larger total surface with respect to the film or drops, reacted in a very slow rate or did not react at all. This could be possibly attributed to the passivation of the aluminium surface that spontaneously takes place, because of the formation of aluminium oxide (alumina) on the surface that protects the aluminium from further oxidation. In the same way, the surface passivation could hinder ion exchange, thus reducing or preventing the cementation process.

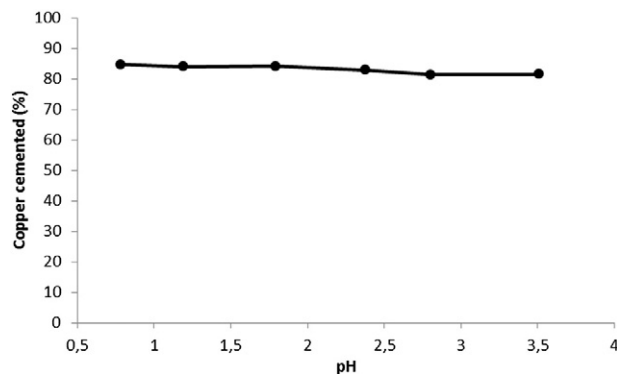


Fig. 5. Effect of pH on cementation of electric scrap copper using 1.3 g of aluminium.

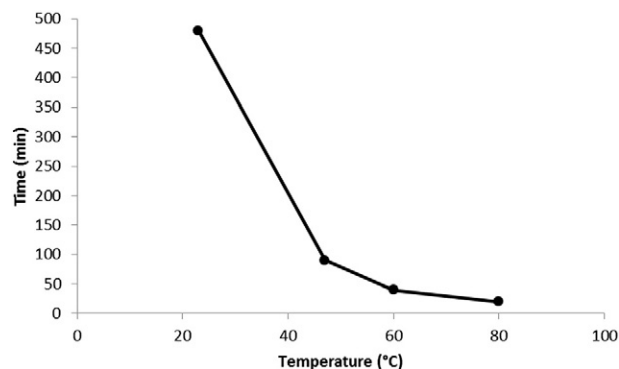


Fig. 6. Effect of temperature on time required to digest 1.3 g aluminium (or cement 4.6 g copper).

In order to verify this hypothesis, a mixture of the former fine aluminium filings and aluminium shavings (the last produced by turning an aluminium bar just before the experiment) was used in another test. After cementation, all the shavings were consumed (non-passivated surface) while the aluminium filings did not react (passivated surface). According to these results, the hypothesis of passivation seems to be confirmed.

3.2.1.4. Cementation tests with iron scrap. A series of tests was also carried out replacing aluminium with iron as sacrificial metal. Iron blades of 40 mm width, 2 mm thickness and 200 mm length were used, with a total reacting surface varying from about 460 to 550 mm², depending on the immersion depth of blades into the solution. Blades were always hung vertically to allow the cemented copper to detach by gravity, through manual scraping or shaking, and to be deposited at the bottom of the vessel. Copper solution was prepared with hydrochloric or sulphuric acid.

The solution prepared with hydrochloric acid contained 26.76 g of dissolved copper (from a total weight of 46.75 g of sieve undersize product), with solution pH at the beginning of the test being 0.30 at temperature 22.8 °C. Correspondingly, the solution with sulphuric acid contained 38.70 g of dissolved copper (from a total weight of 67.61 g of sieve undersize product), with solution pH being 1.03 at 24.4 °C.

From the kinetics of copper cementation (Fig. 7), it is gathered that the process of using iron is quite fast, with cementation rate being slightly faster using HCl than H₂SO₄. Within 4 h, 85% of copper has been cemented using HCl, and 76% using H₂SO₄. For a reaction time of 6 h, cemented copper reaches 90% for HCl and 85% for H₂SO₄, while

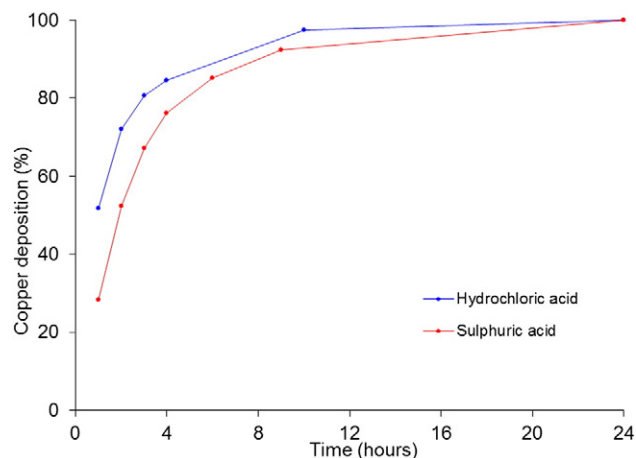


Fig. 7. Kinetics of copper cementation on iron from solution with hydrochloric or sulphuric acid.

for 8 h it is higher than 90% for both cases; copper is almost completely cemented within 24 h.

The process could be accelerated by increasing the deposition area, solution stirring to facilitate ion diffusion or by solution heating, although an additional process cost is imposed.

The results denote that copper cementation on iron scraps is a technique that allows an efficient recovery of dissolved copper from solutions, acidified with H_2SO_4 or HCl.

3.2.2. Electrowinning

Preliminary tests showed that the process can be performed using solutions obtained with sulphuric or hydrochloric acid, whereas nitric acid causes problems due to its chemical aggressiveness with respect to lead anode. Throughout electrowinning tests, copper solutions were prepared by dissolving copper wires from the undersize product of sieving with the corresponding acid.

The efficiency of electrowinning was examined using an acidified solution with sulphuric acid, of initial pH = 0.58 at 28.6 °C. The application of 2 V voltage for 10 h generated a current intensity of 0.5 A, but copper deposition on the cathode surface was very small. The rise of voltage to 4 V for the next 6 h resulted in current intensity of 3.5 A, and more rapid copper deposition. Afterwards, the voltage was reduced to 3 V for 18 h, generating a current intensity of about 2 A. At the end of the process, all copper ions of the solution were reduced and deposited on the stainless steel cathode, and a loose, spongy, dendrite copper deposit was obtained. The anode surface exposed to the cathode was progressively covered by a black cake of passivation of 0.5 mm thickness; the cake is a mixture of PbO and fine-powdered metal Pb, sinking to the bottom of the vessel, upon removal from the anode surface. The solution was clear and colourless at the end of the process, with pH lower than zero.

A second electrowinning test was carried out using the acid solution of the previous test by adding hydrogen peroxide only. The pH of the prepared solution was 0.69 at 27.0 °C. The reuse of acid solution from electrowinning process minimises the consumption of sulphuric acid and provides the process with economic benefits.

A potential difference of 3 V was applied for 10 h, generating a current intensity of 1.6 A that spontaneously increased to 2.5 A during the test. A quite regular film of copper of about 17 g was obtained, which was easily removable from the stainless steel cathode surface. After 10 h, the pH was 0.25, at 26.7 °C. In the next 10 h an electric current of 3.3 V was applied, generating a current intensity of 2.5 A that increased to 4.1 A during the test. The copper deposit obtained was irregular, with dendrite growths and powdery appearance. At the end of the process the pH of the solution was less than zero again.

A series of tests was carried out under constant current intensity using the acid solution of the previous test plus hydrogen peroxide. The results showed that the best conditions of copper deposition are obtained for current intensity 2–3 A. For lower current intensity, copper tends to deposit in the form of a regular film, but the process efficiency is very low; in contrast, at higher current intensity dendrite structures are formed, which are able to concentrate the electric field locally and further promote the growth of dendrites that may be 20 mm long or even longer. All the tests showed that a regular copper deposit (i.e. film) is obtained in the beginning of the process, while the formation of a great number of small columnar structures takes place subsequently; the structures protrude outwards and are perpendicular to the cathode surface, with each one being made up of many acicular copper crystals (Figs. 8 and 9).

In order to estimate the process kinetics, two final tests were carried out by using solutions acidified with sulphuric acid. From the first solution, there were obtained 48.8 g of copper in 25 h and 50.9 g in 24 h from the second one, which denote that the average copper recovery is 2 g per hour.

In case hydrochloric acid is used to dissolve the copper wires, tests reveal that copper deposition through electrowinning occurs in two stages. During the first, pure copper was deposited on the cathode;



Fig. 8. Stainless steel cathode covered by copper through electrowinning deposition.

this stage was followed by generation and growth of cotunnite crystals ($PbCl_2$) on the cathode, as revealed by XRD and Raman analysis, mixed with the copper that continued its deposition (Fig. 10).

This contamination of copper can be a serious limitation to its electrowinning, when lead anodes are used and the solution contains chlorides.

To further investigate the process, a solution was prepared using HCl, with pH 1.64 at 27.9 °C. During the initial stage of the electrowinning process, a constant voltage of 3 V was applied, which was able to generate a current intensity of 0.9–1.0 A that decreased progressively to 0.6 A. In contrast to the former tests, lead anode was progressively covered by cotunnite crystals; these crystals can adhere to the surface or detach and sink to the bottom of the vessel. At the same time, a regular film of copper was deposited on the cathode, 14 g in total.

Seven hours later the potential difference rose to 4 V and the current intensity to 1 A again, while the process continued for the following 15 h overnight. After this period, all the copper ions in the solution were reduced and deposited on the cathode, covering the former copper film with an irregular dendrite deposit. For longer reaction time, copper deposit is covered by a black patina, probably lead, due to the initiation of undesirable electrochemical reactions.

4. Conclusions

This work has demonstrated the feasibility to recover copper from low grade tailings (less than 5% copper, high grade in polymeric material) by applying a combination of mechanical separation methods and chemical ones.

Sieving seems to be more efficient than gravity methods, since, for a 1.00 mm aperture and sieving time as short as 2 min, the copper grade of the undersize product increased to approximately 57% (from 4% in the feed), with corresponding copper recovery 53%; in addition to the

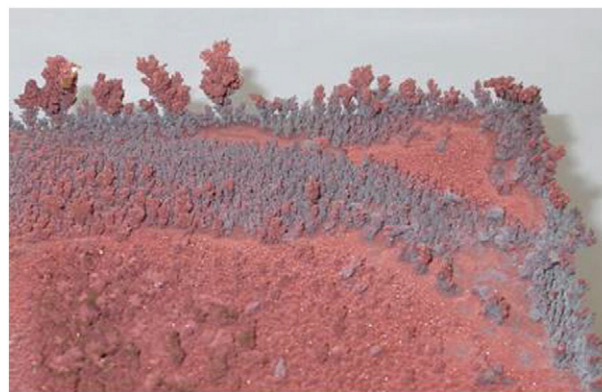


Fig. 9. Growth of dendrite structures on the cathode.



Fig. 10. Simultaneous deposition of metallic copper and cotunnite (PbCl_2) on the stainless steel cathode.

results, the high capacity, low cost, and easy scaling-up of sieving render it favourable for industrial application. Longer sieving times or larger sieve apertures lead to products of increased copper recovery, but of lower grade.

Subsequently, pure copper may be recovered from the undersize product of sieving by applying electrochemical methods, such as cementation or electrowinning under well controlled operating conditions. With regard to copper cementation onto aluminium or iron scraps, used as sacrificial metals, the best results are obtained for $\text{pH} = 2.5\text{--}3.2$, with copper recovery reaching the level of 60–70% at room temperature and within a few hours, while recovery reaches 100% within 24 h. The quality of cemented copper deteriorates, when HCl acid is used instead of sulphuric, since the cementation product is nantokite (CuCl) instead of pure copper.

Electrowinning allows the recovery of the dissolved copper from the sieving undersize product, which was acidified with sulphuric acid and hydrogen peroxide, by using a lead anode and stainless steel cathode. The process must be interrupted before total copper deposition in order to avoid the initiation of undesirable electrochemical reactions (passivation) on the lead anode.

In conclusion, the application of sieving followed by cementation, being of lower cost than electrowinning, results in efficient recovery of pure copper from low-grade tailings derived from the recycling treatment of waste electric cables.

References

- Al Shakarji, R., Yinghe He, Y., Gregory, S., 2011. The sizing of oxygen bubbles in copper electrowinning. *Hydrometallurgy* 109, 168–174.
- Berry, L.G., 1967. Powder Diffraction File, Inorganic Volume. Joint Committee on Powder Diffraction Standards, Philadelphia.

- Beukes, N.T., Badenhorst, J., 2009. Copper electrowinning: theoretical and practical design. *J. South. Afr. Ins. Min. Metall.* 109, 343–356.
- Bevilacqua, P., De Lorenzi, L., 2008. Copper and PVC recovery from electrical cables. *Proceedings of the XXIV International Mineral Processing Congress, Beijing, China, September 24–28*, pp. 3947–3951.
- De Araújo, M.C.P.B., Chaves, A.P., Espinosa, D.C.R., Tenório, J.A.S., 2008. Electronic scraps – recovering of valuable materials from parallel wire cables. *Waste Manag.* 28, 2177–2182.
- Donmez, B., Sevim, F., Sarac, H., 1999. A kinetic study of the cementation of copper from sulphate solution onto a rotating aluminium disc. *Hydrometallurgy* 53, 145–154.
- El-Batouti, M., 2005. Removal of copper metal by cementation using a rotating iron cylinder. *J. Colloid Interface Sci.* 283, 123–129.
- Fouad, O.A., Abdel Basir, S.M., 2005. Cementation-induced recovery of self-assembled ultrafine copper powders from spent etching solution of printed circuit boards. *Powder Technol.* 159, 127–134.
- Glösser, S., Soulier, M., Tetero Espinoza, L.A., 2013. Dynamic analysis of global copper flows. Global stocks, postconsumer materials flows, recycling indicators, and uncertainty evaluation. *Environ. Sci. Technol.* 47 (12), 6564–6572.
- International Copper Association Ltd., 2013. Copper recycling. <http://copperalliance.org/wordpress/wp-content/uploads/2013/06/ica-copper-recycling-1305-A4-Ir.pdf> (accessed from web 24-9-2014).
- Kang, H.Y., Schönung, J.M., 2005. Electronic waste recycling: a review of U.S. infrastructure and technology options. *Resour. Conserv. Recycl.* 45, 368–400.
- Karavasteva, M., 1996. The effect of certain surfactants on the cementation of copper by suspended zinc particles. *Hydrometallurgy* 43, 379–385.
- Karavasteva, M., 2005. Kinetics and deposit morphology of copper cementation onto zinc, iron and aluminium. *Hydrometallurgy* 76, 149–152.
- Lee, C., Chang, C., Fan, K., Chang, T., 2004. An overview of recycling and treatment of scrap computers. *J. Hazard. Mater.* B114, 93–100.
- Lee, J., Song, H.T., Too, J., 2007. Present status of the recycling of waste electrical and electronic equipment in Korea. *Resour. Conserv. Recycl.* 50, 380–397.
- Liu, R., Shieh, R.S., Yeh, R.Y.L., Lin, C.H., 2009. The general utilization of scrapped PC board. *Waste Manag.* 29, 2842–2845.
- Lopez, F.A., Martin, M.I., Perez, C., Lopez-Delgado, A., Alguacil, F.J., 2003. Removal of copper ions from aqueous solutions by a steel-making by-product. *Water Res.* 37, 3883–3890.
- Mohabuth, N., Miles, N., 2005. The recovery of recyclable materials from waste electrical and electronic equipment (WEEE) by using vertical vibration separation. *Resour. Conserv. Recycl.* 45, 60–69.
- Muchova, L., Eder, P., Villanueva, A., 2011. End-of-waste Criteria for Copper and Copper Alloy Scrap: Technical Proposals. Publications Office of the European Union, Luxembourg.
- Sedzimir, J.A., 2002. Precipitation of metals by metals (cementation) – kinetics, equilibria. *Hydrometallurgy* 64, 161–167.
- Simon Ostan, P., 2007. Un processo per il recupero del rame residuo da scarti di cavi elettrici provenienti dal recupero primario. University of Trieste (Italy). Unpublished Diploma Thesis. (in Italian).
- Stefanowicz, T., Osinska, M., Napieralska-Zagodzka, S., 1997. Copper recovery by the cementation method. *Hydrometallurgy* 47, 69–90.
- Tilmatine, A., Medles, K., Bendimerad, S.-E., Boukholda, F., Dascalescu, L., 2009. Electrostatic separators of particles: application to plastic/metal, metal/metal and plastic/plastic mixtures. *Waste Manag.* 29, 228–232.
- Viswanath, S.G., Sajimol, G., 2011. Electrowinning of copper powder from copper sulphate solution in presence of glycerol and sulphuric acid. *Indian J. Chem. Technol.* 18, 37–44.
- Yanping, X., Yongxiang, Y., van den Berg, J., Sietsma, J., Agterhuis, H., Visser, G., Bol, D., 2013. Hydrometallurgical recovery of copper from complex mixtures of end-of-life shredded ICT products. *Hydrometallurgy* 140, 128–134.
- Zhang, S., Forssberg, E., 1997. Mechanical separation-orientated characterization of electronic scrap. *Resour. Conserv. Recycl.* 21 (4), 247–269.
- Zhang, S., Forssberg, E., 1999. Intelligent liberation and classification of electronic scrap. *Powder Technol.* 105, 295–301.