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Chameleon behaviour of iodine in recovering Noble-Metals from WEEE: towards sustainability and "zero" waste

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An effective and sustainable method for the selective leaching of metals from the non-ferrous metal fraction of Waste Electric and Electronic Equipments (WEEE), is described here. This method consists in a sequence of steps which involve the selective leaching of the different metals from the shredded sample by using environmental friendly lixiviants in water. In particular: 1) refluxing citric acid (3M) solution which dissolves Sn, Zn, Pb, Ni, and other base metals; 2) NH_3 in combination with I^-/IO_3^- mixture which allows to oxidize Cu and Ag, and to separate them by selective AgI precipitation; 3) I^-/I_2 mixture (5.3:1 molar ratio) which is capable to leach quantitatively Au metal from the solid residue. Each step is followed by a further treatment for: i) high-rate metal and reagent recovery, in the case of NMs; ii) inertization, in the case of heavy metals. The "chameleon" behaviour of iodine, which shows versatile red-ox/complexing/precipitating capabilities, allows to achieve, on the one hand, a selective noble-metals (NMs) leaching and, on the other hand, a simple and effective reagent and metal recovering. The comparison of the above described method with a similarly effective one previously patented by some of the same authors, allows to point out that a significant improvement in sustainability is achieved in terms of lixiviants employment, which are of lower cost, easier available and recyclable, and able to work in water solutions, while maintaining or improving their environmental friendly character.

1. Introduction

Waste of Electric and Electronic Equipments (WEEE) represents the most promising secondary source of raw materials, in particular metals, in our contemporary world. Due to the large amount, growing accumulation rates and peculiar composition of WEEE, world-wide governments have promulgated specific directives in order to promote a sustainable waste management and to face the increasing demand on the planet's limited resources.[1,2] Accordingly, the new world-wide waste management strategy is addressed to convert "*trash*" in "*resource*" by creating value from waste, through reuse, recycling, waste-to-energy and recovery, where meanwhile only safe and sustainable processes or methods are allowed. Noble metals (NMs) have a wide application in the manufacture of electronic equipments, working as contact materials due to their high chemical stability and their good conducting properties.[3] As a consequence, WEEE may contain noble and in addition other critical metals[4] in amount comparable or even higher than in their ores. It happens in Printed Circuits Boards (PCB) or other Hi-Tech scraps, on account of this called "urban mines". Although pyrometallurgical processes have been typically employed to recovery NMs from WEEE,[5] in the last decades several studies have been addressed to investigate known or new hydrometallurgical processes, with the view to limit economical and environmental costs. Regarding the hydrometallurgical processes for gold reclamation from ores and for refining NMs slags and ashes, it must however be reminded that the well-known "*Cyanidation*"† and "*aqua-regia*"‡ processes are still the most widely employed despite they are based on the use of highly toxic and/or aggressive chemicals.[5,6] The effectiveness of these processes is relatable to the joint presence of complexing and oxidizing agents. In the above-mentioned cases CN^- and Cl^- act as complexing agents capable to lower the high NMs reduction potential through the formation of stable metal-complexes, and O_2 and NO_3^- act as oxidants. On these bases, alternative leaching mixtures, such as thiourea or thiosulfate solutions in the presence of oxidizing reagents, have been proposed for gold etching but they have not found large-scale application mainly due to the large consumption of not recyclable reagents.[5,6] More recently mixtures of thionyl chloride and organic solvents/reagents such as pyridine, N,N-dimethylformamide and imidazole, named "*organic aqua-regia*", have raised great interest for their capability to dissolve gold and other NMs with high dissolution rates under mild conditions.[7] This method was applied for etching Au metallization on a circuit board. The enhanced reactivity of "*organic aqua-regia*" was ascribed to the formation of donor-acceptor adducts between reagents and taken as unique when compared to the so-far available etching reagents. However the harmful nature of employed reagents/solvents, makes it not appealing for a safe and friendly use.[8] Moreover, we note that similar etching properties towards NMs have been recognized since the late 90s[11] in donor/acceptor (dihalogens, mainly I_2) mixtures, which may form adduct, stable[9] or undergoing further transformation in organic solvents.[10] In particular in our laboratory the etching properties of dihalogen mixtures with donors bearing two vicinal thionic groups, such as cyclic-dithioxamides [e.g. N,N'-dimethylperhydrodiazepine-2,3-dithione (Me_2dazdt) and N,N'-dimethylpiperazine-2,3-dithione (Me_2pipdt)] have been extensively investigated.[11a,12] It is found that Me_2dazdt/I_2 mixtures, in particular the Me_2dazdt$\cdot 2I_2$ adduct, in organic solvents dissolve Au[13] and Pd[14] selectively in mild conditions, while are inactive towards Pt, which, in turn, can be dissolved by Me_2pipdt/I_2 mixtures in the above cited solvents.[15] Remarkably, organic solutions of Me_2dazdt$\cdot 2I_2$ have been used successfully on a laboratory scale both for gold recovery from WEEE (ink-jet cartridges, smart cards, PCBs and selected shredded R4 WEEE)[16] and from microelectronic devices in deprocessing procedures for the failure analysis.[17] Moreover the use of organic solvents allows to avoid a detrimental wetting of electric contacts. Thus effectiveness and homogeneity of etching, combined with a safe and friendly use, make these reagents a very challenging alternative to the less selective and inhomogeneous ones commonly employed for this kind of applications. On the other side, their relative high cost, market unavailability and use of an organic solvent for the leaching, may limit their appeal for a large scale applicability to WEEE recovery processes. With the view to overcome these limits for a better match with industrial requirements of technical, economical and environmental sustainability and based on our knowledge of donor-acceptor systems and of iodine chemistry,[18] we have exploited the versatility of this "chameleonic" element to design a process for NMs recovery from WEEE, where only water is used as solvent and elemental sustainability is pursued as much as possible. The versatility of iodine is relatable to its red-ox properties which allow that several species in different oxidation states, exhibiting a variety of properties, can be reversibly formed. For example, I_2 can behave as an oxidizing agent towards reducing species, such as elemental metals, forming I^-. This capability, shown in organic solvents,[19] can be preserved in water, where I_2 is almost insoluble, employing I_3^- ion (formed through I^--I_2 donor-acceptor interactions) which shows similar oxidation properties.[20] The iodide ion may be employed as donor towards suitable metal ions to form stable metal complexes or also as a precipitating agent to form salts of low solubility. These properties are largely applied to lower the reduction potential of metals favouring metals oxidation, as occurs in the case of gold,[21] or for the selective ion separation. On the other hand, I^- can be quite easily oxidized back to I_2, and this capability can be useful to recover the reagent at the end of the leaching process.[22] Finally, I_2 produces IO_3^-/I^- mixtures through a disproportion reaction. Thus a further tuning of the oxidating/complexing/precipitating properties of the reagents is achieved on simple pH variation.[21] The versatility of the "chameleonic" iodine, combined with its low environmental impact and elemental sustainability, make I_2-based lixiviants very appealing to be employed in "green" metals recovering processes, as described in this paper.[23] We report here an effective and sustainable hydrometallurgical method for NMs recovering from WEEE. The obtained results are thoroughly discussed in comparison with those obtained for our previous patented method to point out the advantages/disadvantages of the two methods. The full characterization of the used real sample, is also presented here to point out the test specimen.

2. Experimental

2.1 Materials and Methods

Reagents and solvents were purchased from Sigma-Aldrich (except citric acid anhydrous FU-E 330 from ACEF, Italy) and used without further purification.

The real sample is used as provided by a Company which treats WEEE by applying a conventional mechanical process[24] and consists in a milled mixture of metals (average particles size: 0.4mm) which represents the non-ferrous metallic fraction output of the de-processing plant. In this plant the incoming material consists in PCBs and selected small electronic equipments e.g. mobile phones, notebooks, etc., and this is submitted to crushing, separation from residual hazardous components, shredding and mechanical separation (Magnetic and Eddy Current separation) of ferrous and non-ferrous metals, and of plastics.

2.2 Characterization of the test specimen

The test specimen has been fully characterized by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) and by X-ray-based techniques such as Scanning Electron Microscopy interfaced with X-ray microanalysis (SEM-EDS), X-ray Photoelectron Spectroscopy (XPS), Wide-angle X-ray Diffraction (WA-XRD), and X-ray Fluorescence (XRF).

ICP-AES characterization. 0.5g aliquots were sub-sampled from the original solid mixture, then introduced in TFM vessels containing a mixture of HNO_3 (65%, 2mL), HCl (37%, 6mL) H_2O_2 (30%, 0.5mL) and treated in a Milestone Ethos 1 Microwave digestor, equipped with a HPR1000/10S high pressure segmented rotor, ATC-400CE automatic temperature control and Terminal 640 with easyCONTROL software. The treatment was performed applying a microwave program consisting in two steps lasting 10 and 20 minutes, respectively, at the temperature of 200 °C and microwave power up to 1000W. The samples were prepared for the analysis by diluting the digested solutions with 1% HCl/HNO_3 blank and then the metals determined using a ICP-AES Varian Lyberty 200 Spectrometer, with respect to 5-points calibration plots in the 1-50 ppm range for copper and in the 1-10 ppm range for the other metals. Three independent experiments were used to determined the averaged values which are reported in Table 1.

Morphological, dimensional and compositional analysis. Morphological characterization of the sample has been obtained by metallographic and electronic microscopy, by means of the Zeiss Axioskop 40 Metallographic Microscope equipped with a 100× objective and a Canon PowerShot G5 to collect images, and of SEM (ESEM Quanta FEI 200, equipped with EDS detector), respectively. Dimensional characterization has been obtained by using particles sieves and SEM images. Finally, compositional information have been collected, on representative aliquots of the sample, by means EDS microanalysis, XPS analysis (Theta Probe spectrometer, Thermo Electron Corporation, using monochromatic Al Kα source and sample deposited on discs of double adhesive graphite fitted on the sample holder), WA-XRD (Panalytical Empyrean diffractometer equipped with a graphite monochromator on the diffracted beam and a X'Celerator linear detector. The scans were collected within the range of 10°-90° (2θ) using CuKα radiation), and XRF (ASSING S.p.A., mod. ASX-DUST) measurements.

2.3 Characterization of recovered metals

Recovered metals have been weighed and then characterized by ICP-AES after acid dissolution (concentrated HNO_3 for Cu and Ag; *aqua-regia* for Au), as described above. Copper recovered by *cementation*, has been also characterized by SEM-EDS.

2.4 Electrowinning experiments

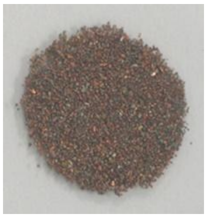
Metal copper, silver and gold have been recovered from the leaching solutions by electrodeposition. The electrowinning apparatus was formed by two metallic electrodes (Pt-wire for the anode and Cu-layer for the cathode) connected, to their perspective ends, with an external electron supply (Thurlby Thandar Instruments, mod. PL 310) which drives the process.

3. Results and discussion

3.1 Description of test specimen of WEEE

The sample which has been submitted to the leaching consists in the non-ferrous metallic fraction obtained as output of a mechanical de-processing plant, where a selection of PCBs and small electronic equipments are shredded and submitted to pre-treatments in order to separate the incoming mixture into homogeneous particle flows with high concentration of target materials: aluminium, ferrous metals, vitreous-plastic materials and non-ferrous metals. Table 1 summarizes the metals content of the non-ferrous metal fraction determined by ICP-AES spectrometry, as described in the Experimental section.

Table 1 Average metal content of the specimen sample.

Test specimen	Metal	Composition ($\%_{w/w}$)
	Cu	79
	Sn	10
	Pb	7
	Zn	2
	Ni	0.5
	Ag	0.06
	Au	0.01
	Others (Al, Cr, Mn, Fe, Co)	1

Figs. 1a and 1b show the morphology of the sample by metallographic and scanning electron microscopy, respectively.

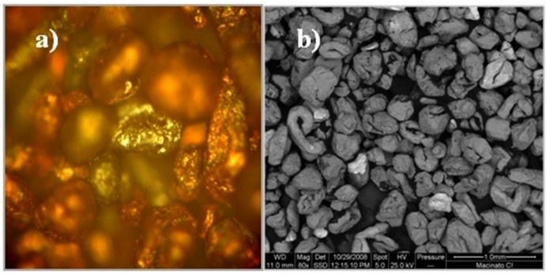


Fig. 1 Top-view micrographs of the test specimen by: a) metallographic (magnification 100x); and b) scanning electron (magnification 80x) microscopy.

An average particles size of approximately 0.4mm has been determined by using particles sieves and SEM images. The average metal composition obtained by SEM-EDS on three different aliquots of the test specimen, as well as the qualitative XRD and XRF characterization, agree with the chemical composition reported in Table 1. Punctual SEM-EDS and XPS determinations on the surface of selected grains of the sample show the presence of oxidized metals. Details on the chemical-physical characterization are reported in Supporting Information.

3.2 Selective leaching and recovery of metals from WEEE specimen sample

The employed method (named Method A) was applied on a laboratory scale, starting from 10g of the sample and is based on a sequence of three main steps which allow to remove selectively base metals and copper and silver, leaving as residue the WEEE fraction enriched in gold, as summarized in Fig. 2.

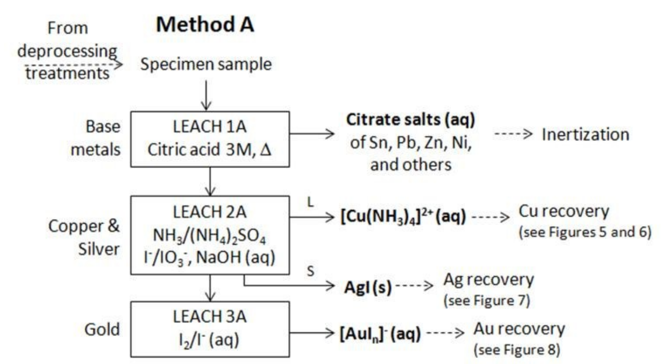


Fig. 2 Schematic diagram of the leaching steps of Method A. L, S = Liquid and Solid fractions.

3.2.1 LEACH 1A: Base metals dissolution and inertization

Citric acid, a weak natural acid solid at room temperature, has been employed for the dissolution of base metals (Leach 1A, Fig. 2) in spite of more harmful acids such as HNO_3 or H_2SO_4, typically employed in WEEE treatments.[25] In Fig. 3 the weight loss with the time of 10g of test specimen for reaction with citric acid 3M under different leaching conditions (room temperature; under reflux; room temperature and addition of 27.3mL H_2O_2 35%), is reported.

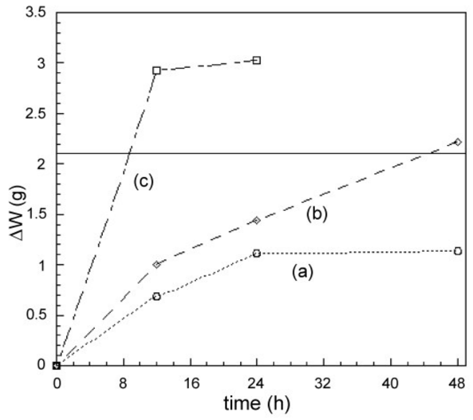


Fig. 3 Weight loss of 10g of test specimen in the time (hours) by treatment with citric acid 3M at: a) room temperature (···○···); b) refluxing (--◊--); c) by H_2O_2 35% addition (– ·□– ·). The solid line represent the expected amount of base metals in the sample (2.1g).

As shown, a quantitative base metals dissolution is achieved in the conditions described in b) and c) in the observation time. Approximately 48 hours are required to complete treatment b). The colour of the solution changes from colourless to greenish and no precipitation is formed. As expected, a faster leaching, approximately 8 h, accompanied with a loss in selectivity, is obtained in the presence of H_2O_2 (c). In fact a partial copper dissolution (about 12% in 24h) is observed as suggested qualitatively by the dark green-blue colour of the solution and quantitatively by the weight loss of the sample which exceeds, in the time, the expected base metals amount. Moreover on standing, the leaching solution forms a $Cu(C_2O_4){\cdot}H_2O$ precipitate, which was identified by the WA-XRD spectrum, shown in Fig. 4.

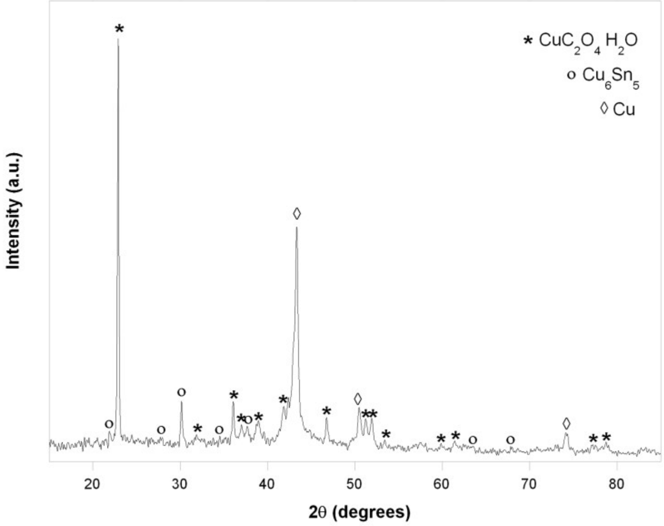


Fig. 4 WA-XRD spectrum and peaks assignment for $Cu(C_2O_4){\cdot}H_2O$ precipitate obtained in (c) leaching conditions.

This behaviour could be explain invoking Fenton chemistry.[26] In fact, the metals dissolution generates the required $M^{(n-1)+}$/ M^{n+}/H_2O_2 mixture able to activate the radical reactions which start from the formation of the OH· radical.[♦] In the described conditions, a reproducible partial degradation of citric acid to oxalic acid through C-C bond breaking occurs. Further studies are in progress to clarify the mechanism of the reaction. After leaching, metals can be recovered from the aqueous solutions in form of citrate salts or through conventional treatments with suitable precipitating reagents. The excess of citric acid is recovered directly from the resulting solution by solvent evaporation and/or by solvent extraction. In the described conditions, Cu, Ag and Au, remain unreacted.

On the basis of the results above described for the Leach 1A, we can conclude that the treatment b) is most suitable to maximize selectivity and to avoid by-products, while treatment c) may be preferred if faster but less selective processes are privileged.

3.2.2 LEACH 2A: Copper and silver separation and recovery

The solid residue from Leach 1A is treated with a mixture of ammonia (33%, 29mL) and ammonium sulfate (25.6g). To this mixture, a solution containing IO_3^- and I^-, prepared through I_2 (50g) disproportion in 300mL of NaOH 1.5M, is slowly added dropwise. The solution becomes coloured for the formation of the blue $[Cu(NH_3)_4]^{2+}$ complex. The reaction is stopped when no change in the colour of the solution is observed. To ascertain that a complete copper dissolution is achieved, the procedure is repeated on the solid residue until a colourless solution appears. A quantitative copper dissolution is achieved in approximately 48h. Meanwhile the precipitation of AgI occurs. Thus, as predictable, the oxidation of the metals by iodate $[E°(IO_3^-/I^-$

)=+0.26V]♣ is favoured by the presence of complexing (NH_3) and precipitating (I^-) reagents which affect the reduction potential through the formation and solubility constants (K_f and K_{sp})♣ of related equilibria. In the employed ammonia excess, on the one hand, the copper oxidation and the quantitative formation of the very stable $[Cu(NH_3)_4]^{2+}$ complex, are achieved according to Eqs. 1 and 2:

Eq. 1) $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$ $K_f = 1.1x10^{13}$

Eq. 2) $[Cu(NH_3)_4]^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) + 4NH_3(aq)$ E° = -0.05V

On the other hand, in the presence of I^-/IO_3^-, the cited ammonia excess is not sufficient to favour silver complexation, and the quantitative AgI(s) precipitation occurs in agreement with the following equilibria (Eqs. 3-6):

Eq. 3) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ $K_{sp} = 1.2x10^{-16}$

Eq. 4) $AgI(s) + 1\ e^- \rightleftharpoons Ag(s) + I^-(aq)$ E° = -0.152V

Eq. 5) $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ $K_f = 1.6x10^7$

Eq. 6) $[Ag(NH_3)_2]^{2+}(aq) + 1e^- \rightleftharpoons Ag(s) + 2NH_3(aq)$ E° = +0.373V

Finally, the comparison between the standard reduction potentials related to gold oxidation/complexation [E°($[AuI_2]^-$/Au) = +0.58V, E°($[AuI_4]^-$/Au) = +0.56V, at 298K] and that reported for IO_3^-/I^- red-ox couple, suggests that gold dissolution should not occur, as found.

Accordingly, a selective copper and silver separation, leaving gold unreacted, is achieved.

Cu^0 recovery from Leach 2A solution: Both chemical and electrochemical reduction, well-known as "*cementation*" and "*electrowinning*", have been applied for copper recovery from the solution containing $[Cu(NH_3)_4]^{2+}(aq)$. Accordingly, a Zn(s) excess, in form of powder, is added to the Leach 2A blue solution, which undergoes decolouration as a consequence of copper reduction. The unreacted Zn(s) excess has been removed by washing the solid residue with diluted HCl. A quantitative copper recovery (8.1±0.3g on 10 g of test specimen), with purity >90% and in form of uniform particles of approximately 500nm, has been obtained through *cementation*, as shown in the SEM micrograph reported in Fig. 5.

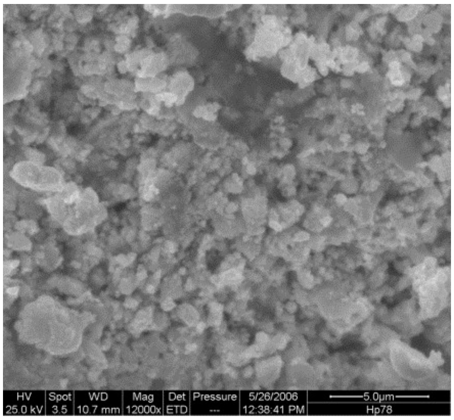


Fig. 5 SEM micrograph of copper recovered by *cementation* with Zn. Average particles size = ~500nm.

NH_3 and I_2 can be selectively recovered from the resulting solution. NH_3(aq) is recovered bubbling the vapours produced by distillation into water, meanwhile an abundant precipitation of $Zn(OH)_2$ occurs when NH_3(g) leaves the solution. This hydroxide can be recovered as it is or dissolved with HCl dil., and zinc recovered from the chloridric solution by precipitation. After that, H_2O_2/H^+ is added to the solution under warming, to oxidize iodide ions to I_2. In that conditions, purple vapours of I_2 are formed and collected as solid on cooling. Copper *cementation* process, with the complete recovering of reagents and products for elemental sustainability, is summarized in Fig. 6.

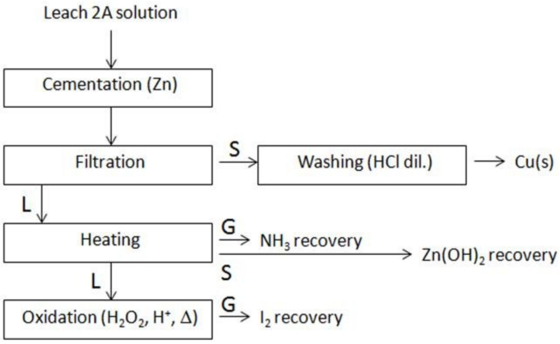


Fig. 6 Schematic diagram of Cu(s) recovery by *cementation* on Leach 2A solution. Reagents recovery/valorisation. S, L, G = Solid, Liquid and Gaseous fractions.

With the view to obtain the complete recovery of reagents and products, minimize reagents consumption and avoid by-products, the alternative copper *electrowinning* has been performed as summarized in Fig. 7. In that case, preliminary NH_3 and I_2 removals from the Leach 2A solution, in the same way described for *cementation*, are performed. The resulting solution undergoes a conventional electrochemical metal deposition, obtaining a quantitative copper deposition (8.9±1.5g on 10 g of test specimen) on a copper electrode.

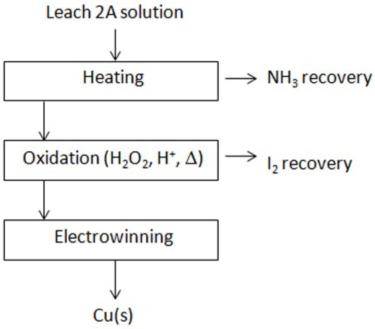


Fig. 7 Schematic diagram of Cu(s) electrochemical recovery from Leach 2A solution. Reagents recovery/valorisation.

Ag^0 recovery: As summarized in Fig. 8, the solid residue of the Leach 2A treatment, is filtered on a glass Buchner funnel and then washed repeatedly on the frit with an aqueous solution of $Na_2S_2O_3$ (0.5g in 50 mL of H_2O dist.), in order to dissolve AgI(s) and separate aqueous $[Ag(S_2O_3)_2]^{3-}$ ($K_f = 4.7x10^{13}$) from the metallic residue. Silver metal recovery in almost quantitative yields (6±2mg on 10g of test specimen) is obtained by submitting the latter solution to the *electrowinning* process, where Ag(s) and $S_4O_6^{2-}$(aq) are produced at cathode and anode, respectively. Ag^0 can be also obtained by *cementation* with Zn (or other reducing metals such as Fe, Mg,...).[27]

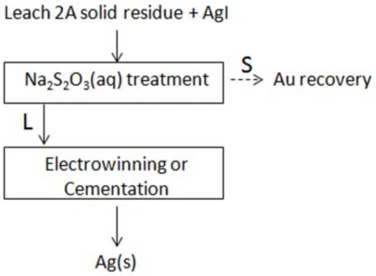


Fig. 8 Schematic diagram of Ag(s) electrochemical/chemical recovery from Leach 2A solid residue.

3.2.3 LEACH 3A: GOLD DISSOLUTION AND RECOVERY

The solid residue lasting from Leach 1A and 2A, containing mainly gold and inert plastic/vitreous materials, is treated for few minutes with a 10 mL water solution containing 0.46g of KI (2.7mmol) and 0.13g of I_2 (0.51mmol) in the 5.3:1 molar ratio. Gold is dissolved and forms $[AuI_n]^-$ complexes,[22] according to reactions 7 - 10, due to the presence of the I_3^- reagent [$E°(I_3^-/I^-)$ = +0.54V] whose oxidation capability is

$$\text{Eq. 7)}\quad Au^+(aq) + 2I^-(aq) \rightleftharpoons [AuI_2]^-(aq) \qquad K_f = 7.9\times10^{18}$$

$$\text{Eq. 8)}\quad [AuI_2]^-(aq) + 1e^- \rightleftharpoons Au(s) + 2I^-(aq) \qquad E° = +0.58V$$

$$\text{Eq. 9)}\quad Au^+(aq) + 4I^-(aq) \rightleftharpoons [AuI_4]^-(aq) \qquad K_f = 5.0\times10^{47}$$

$$\text{Eq. 10)}\quad [AuI_4]^-(aq) + 3e^- \rightleftharpoons Au(s) + 4I^-(aq) \qquad E° = +0.56V$$

enhanced by formation of complexes shown in Eqs. 7 and 9.

After leaching, H_2O_2/HCl are added to the solution in order to oxidize iodide and recover I_2 as described above. Metal gold, in 94-100% yields (0.97±0.03mg on 10g of test specimen), is recovered from the chloridric solution by *electrowinning* (see Fig. 9).

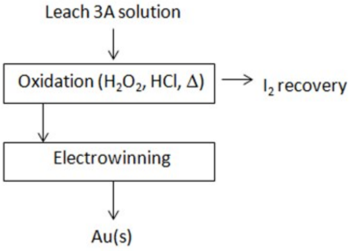


Fig. 9 Schematic diagram of Au(s) electrochemical recovery from Leach 3A solution. Reagents recovery/valorisation.

The gold recovery yields have been confirmed also by adding spikes of 2 and 5mg (0.02 and 0.05%$_{w/w}$, respectively) of gold powder at the incoming test specimen.

3.3 Two effective methods for WEEE recovery at comparison

As said in the Introduction, Method A has been designed with the view to improve the matching of a previously patented method, very effective in NMs recovery from WEEE,[16] with industrial requirements of technical, economical and environmental sustainability. This method, here named Method B, is summarized in Fig. 10.

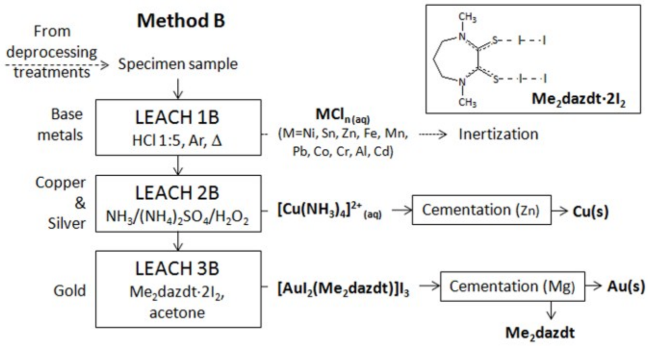


Fig. 10 Schematic diagram of the previous patented method (Method B).

The comparison of the two methods is discussed below.

3.3.1 LEACH 1

In Leach 1B, HCl is employed as lixiviant. This acid was preferred with respect to other commonly employed strong acids such as HNO_3 or H_2SO_4 being more selective towards base metals (it does not contain species more oxidizing than H^+) and less harmful in terms of toxic fumes and by-products production. Moreover, most of the base metal chloride salts show a high water solubility, which is an important factor to separate these metals from the milled mixture sample under treatment. The base metals dissolution in refluxing HCl (1:5, ~2M) is quite effective (24h to dissolve base metals) but not fully selective due to a partial NMs dissolution in the presence of O_2, likely relatable to the complexing capability of Cl^- towards these metals.[21b] By working in an inert atmosphere (e.g. by Ar) conditions, a selective and quantitative base metals dissolution has been achieved. Base metals may be recovered from the chloridric solution with conventional treatments with suitable precipitating reagents.

As described, in Leach 1A the weaker citric acid is used to substitute hydrochloric acid. The quite low acidity of citric acid (pK_{a1} = 3.13; pK_{a2} = 4.76; pK_{a3} = 6.40), limits its effectiveness in metals dissolution, but the lower efficiency with respect to HCl can be overtaken by increasing the acid concentration and the temperature. Accordingly a quantitative base metals dissolution is achieved refluxing citric acid 3M for about 48h. Nevertheless, differently from HCl, the leaching does not require inert atmosphere thanks to its full selectivity towards base metals. The described behaviour coupled with the natural availability and low cost of citric acid, a solid and non-harmful reagent, makes Leach 1A preferable with respect to Leach 1B.

3.3.2 LEACH 2

An ammonia solution has been employed in Leach 2B to favour copper and silver dissolution, using as oxidizing reagent H_2O_2 (28-35%) which is slowly added to the $NH_3/(NH_4)_2SO_4$ mixture. A fast and quantitative copper and silver dissolution occurs at room temperature. Meanwhile an effervescence due to the exothermic H_2O_2 degradation to O_2 catalyzed by metals, is produced.

In Leach 2A, instead, copper and silver are oxidized through a milder one-step oxidating/complexing/precipitating reaction, with an alkaline I^-/IO_3^- mixture, added to the ammonia solution. Fig. 11 shows the comparison of the weight loss in the time of a calibrated copper wire (500mg, ∅ = 0.3mm) for reaction with three different formulations of Leach 2 solution, at room temperature and at the same $NH_3/(NH_4)_2SO_4$ concentration (4.4×10^{-3}M and 6.0×10^{-4}M, respectively).

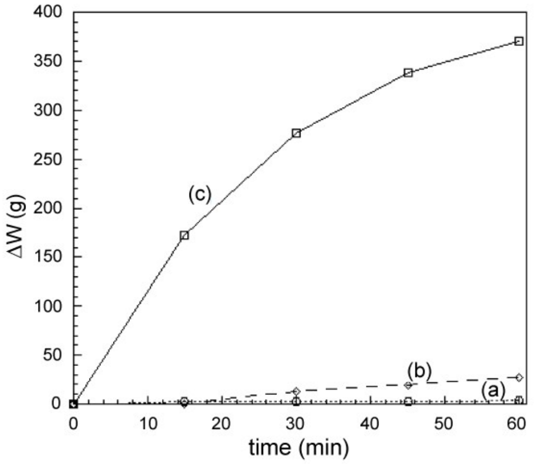


Fig. 11 Weight loss of calibrated copper wires (500mg, ∅ = 0.3mm) in the time (minutes) by treatment with $NH_3/(NH_4)_2SO_4$ (4.4×10^{-3}M and 6.0×10^{-4}M, respectively): a) without additions (···○···); b) with 30mL NaOH 1.5M/I_2 (5g) solution (--◊--);, and c) 2.7mL H_2O_2 35% (– ·□– ·), additions.

Although the leaching with the I^-/IO_3^- alkaline solution is less effective than those with H_2O_2, it shows the following advantages: i) it allows a one-step dissolution/separation of copper and silver from the test specimen; ii) it ensure a high atom economy, due to the recyclability of the employed reagents; iii) metal-oxidations undergo smoothly than in Leach 2B. These features make Leach 2A the treatment that better faces the requirements of safety and sustainability which are the most privileged aspects in designing Method A.

3.3.3 LEACH 3

[$Me_2dazdt{\cdot}2I_2$], described in the Introduction, has been employed as leaching agent towards elemental gold in Leach 3B. This reagent is easy to handle, shows low toxicity and effectiveness in very mild conditions (room temperature and pressure, any protection from air and moisture). Its effectiveness in organic solvent, in terms of reaction rate, homogeneity, and selectivity of gold dissolution, has been compared with I^-/I_2 aqueous solution of the same concentration (5.0×10^{-3} mol dm^{-3}) previously. As reported in refs. 11a and 17a, and summarized in Supporting Information, the comparison on calibrated gold wires and $Si/SiO_2/Ti/Au$ thin layers (thickness 300μm/0.5μm/15nm/200nm) showed that in both cases the diiodine adduct works better than the I^-/I_2 aqueous solution, making the former reactive the most suitable, in particular for the gold removal from microelectronic devices (e.g. GaAs-based laser diodes, GaN-based LEDs and Al-silicon ICs) where effectiveness, selectivity and homogeneity of leaching are required to perform *end-of-life* failure analysis.[17b]

Regarding the [$Me_2dazdt{\cdot}2I_2$] application in WEEE treatment, a quantitative gold recovery is achieved from the test specimen under discussion, obtaining also a 60%-100% ligand recovery depending on the employed solvent (acetone or CH_3CN respectively), by *cementation* with Mg(s).

On the other hand, I^-/I_2 water solution, used in Leach 3A to oxidize gold, can improves its effectiveness by tuning concentration and molar ratio of iodide-diiodine mixtures. In fact, a fast and quantitative gold leaching is obtained at room temperature by using a 0.05M and 0.27M solutions for I_2 and I^-, respectively.

In conclusion, whether aqueous solvents can be preferable and high selectivity and homogeneity of etching are not strictly required, such as in the case of WEEE recovery, I^-/I_2 mixtures in water seem more suitable for a practical application with respect to the more effective [$Me_2dazdt{\cdot}2I_2$] reagent in organic solvent, since these reagents are more easy available, fully recyclable and have lower cost.

Concluding remarks

In this paper an effective and sustainable method for recovery of valuable metals recovery from secondary sources has been described. In particular, the non-ferrous metallic fraction of a real sample of shredded WEEE has been investigated, fully characterized and submitted to a friendly closed-loop process for metals separation and valorisation with the view to evaluate all aspects related to technical, economical and environmental sustainability. A crucial role in the described method is played by iodine, whose versatile behavior has been successfully exploited for the selective dissolution-recovery of NMs. Moreover its non harmful nature and easyness of recovery increase its appeal as “green” reagent.

Method A as whole, which allows to recover NMs almost quantitatively by using “green” reagents in very mild conditions, represents, in our opinion, a very challenging and greener alternative to the methods currently in use for the large scale NMs recovery from real WEEE samples. It is remarkable that the investigated sample is representative of a complex mixture of WEEE consisting of a very heterogeneous material with a low content of NMs when compared, for example, with the corresponding milled sample obtainable from the “richer” PCBs. The satisfactory separation of a complex material like this and the quantitative recovery of the small amount of gold and silver contained in the test specimen, demonstrates the effectiveness of the method and suggests its wider applicability both in terms of process scale and of selectable WEEE, with particular reference to PCBs, ink-jet printer cartridges and smart cards, widespread and typically richer in gold. Nevertheless, we note that, if other NMs removal applications are considered, the selection of the leaching solutions and the sequence of the steps should be tailored on a case-by-case basis depending on which aspect is privileged (i.e., efficiency, homogeneity, rate, cost, recyclability and nature of reagents, product value, metal recovery, etc.), as demonstrated by the best results obtained by using [$Me_2dazdt \cdot 2I_2$] organic solutions with respect to the aqueous I_2/I^- mixture in gold etching for *end-of-life* failure analysis of microelectronic devices.

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Notes and references

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† Cyanidation is based on the use of cyanide salts into basic media with subsequent adsorption on activated carbon and reduction of the complex by electro-winning.

‡ Aqua-regia, the well known 3:1 mixture of concentrated hydrochloric and nitric acids, is highly aggressive and produces toxic fumes e.g. NO_x.

♦ The nature of the oxidizing species obtained in the Fenton reaction is still a subject of discussion. In fact, this reaction, which was observed by H. J. H. Fenton over 110 years ago, is still very difficult to describe and understand.[26b]

♣ All standard reduction potentials (E°) and equilibrium constants (K_f and K_{SP}) are given at 298K.

Electronic Supplementary Information (ESI) available: [Chemical-physics characterization of the test specimen; Comparison between the reactivity of the $Me_2dazdt \cdot 2I_2$ acetone solution and the I_2/I^- water solution towards gold]. See DOI: 10.1039/b000000x/

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Table of content entry

Chameleon behaviour of iodine in recovering Noble-Metals from WEEE: towards sustainability and “zero” waste

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The peculiar properties of iodine and safe lixiviants for a sustainable and effective noble-metals recovery from shredded WEEE.