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RECOVERY OF LEAD AND NOBLE METALS AFTER PROCESSING PRINTED CIRCUIT BOARDS FROM CELL PHONES BY LEACHING WITH MIXTURES CONTAINING HYDROGEN FLUORIDE

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This work examines the leaching of printed circuit boards (PCBs) from cell phones in aqueous solutions containing HF + H_2O_2 or HF + NaClO under mild experimental conditions. The PCBs were not ground but were previously treated with 6 mol L^{-1} NaOH at 50 °C for 1 h to remove their soldering mask. The HF + H_2O_2 mixtures leached copper and base metals (except lead) at 35-40 °C, leaving a solid residue containing lead and noble metals. Leaching was fastest (1 h) when HF and H_2O_2 concentrations were at least 5 mol L^{-1} and 3 mol L^{-1}, respectively. The processing of the solid residue is also described in detail. It was leached with water at ~90 °C followed by $HNO_{3aq.}$ at 25 °C. Lead, palladium and silver were recovered in this order, leaving gold as final solid. After 1 h at 35-40 °C, 5 mol L^{-1} HF + 0.3 mol L^{-1} NaClO mixtures leached the base metals, copper, gold and palladium. Gold was recovered by liquid-liquid extraction with methyl isobutyl ketone. Silver precipitated as chloride. This salt was isolated by leaching with NH_{3aq}. Loss of fluoride ions (as HF) was below 0.5 wt.% after leaching and handling the solid residue.

Keywords: PCB; metals recovery; acidic leaching; gold; silver; hydrofluoric acid.

INTRODUCTION

With advancements in the electronic world almost occurring on a day-to-day basis and increased availability of products to the public, the production of electrical and electronic equipments (EEE) has been one of the fastest-growing sectors both in industrialized and industrializing countries. At the same time, the average lifetime of electronic products has also been drastically reduced due to rapid increase in demand of advanced products. Consequently, it is not surprising to see a staggering increase of Waste Electrical and Electronic Equipments (WEEE or ''e-waste'') over the past decades.[1-4] The current global production of WEEE is expected to increase rapidly at an alarming rate of 20–25 million tons per year,[4,5] with an estimated growth rate going from 3% up to 5% per year.[6-8]

This fast obsolescence makes the linear 'extraction-production-usage-disposal' chain even more resource-intensive, increasing, therefore, their impacts on environment, human health and economy. This scenario is aggravated by the peculiarities of WEEE: they contain more than a thousand different substances, many of which are high-valued or highly toxic.[9] As this waste is a potential source of valuable materials, it has been called an 'urban ore'[5,8,10] and recycling of the printed circuit boards (PCBs) represents the most economically attractive portion of WEEE.[2,11] Handling and treatment of WEEE is a topic of worldwide concern.[3] However, only about 15% of the scrap PCBs are subject to any kind of recycling.[12]

The mobile phone is widely utilized as an integrated telecommunication and information equipment.[13] The life of the mobile phone is getting reduced drastically (2-3 years). Hence, a copious mobile phone waste of more than 8.2 billion objects is expected to be accumulated worldwide in the coming years.[7] The composition of a PCB from a cell phone varies from model to model of each brand. Its basic structure is the copper-clad laminate consisting of glass-reinforced epoxy resin and a number of metallic materials.[7,11,12]

The elements in mobile phones may be categorized as precious metals (Au, Ag), platinum group metals (Pd, Pt, Rh, Ir and Ru), base metals (Cu, Al, Ni, Sn, Zn and Fe), hazardous metals (Hg, Be, Pb, Cd, As and Sb), scarce or trace elements (In, Te, Ga, Se, Ta and Ge).[7] PCBs from cell phones contain copper, silver, gold and palladium in higher concentrations than their respective ores.[2,4,5,12] From an economic perspective, recycling mobile phones is very attractive.[7,8,14,15]

About 30% of gold, 20% of palladium and 12% of silver come from secondary sources.[7,16,17] Yet, the fact that such a highly complex concoction of various valuable and sometimes hazardous materials are intermingled in such a small volume poses serious engineering challenges for the recovery and recycling of the constituent materials. The heterogeneous mix of organics, metals, fiber glass and plastics makes the PCB processing a challenging task,[3] and is the main barrier in the recovery of metals from scraps.[8,14]

In a typical recycling line of waste PCBs, physical processing operations such as grinding, sieving, magnetic, electrostatic, gravity separations and density-based separation are applied as pretreatments to liberate and concentrate the metallic fractions (MFs) and non-metallic fractions (NMFs).[1] A great deal of dust and poisonous gas are produced during crushing, sieving, dissolved air flotation etc. In general, a well-designed recycling line must be equipped with dusting system and waste gases disposal system.[5]

Increasing attention on precious metals recovery such as gold, silver and platinum from waste PCBs (WPCBs) has boosted the development of new processes including physical[18-20] and thermochemical techniques.[12,18,19,21] Hydrometallurgical methods are one of the key technologies in metal recycling because they enable a fine separation between chemically-similar metals in small-scale operation.[1,22-26] The base metals recovery has a substantial impact on the economics of the process due to larger available amount in WPCBs.[27] Moreover, previous leaching of base metals ensures the enrichment of precious metals in the solid residue, making it easier to leach out subsequently.[11] Acidic leaching has been investigated with inorganic acids (HCl, H_2SO_4, HNO_3, $HClO_4$). As metals in

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WPCBs are present in native and/or alloy form, the development of oxidative leaching processes using an oxidant such as H_2O_2, O_2 and Fe^{3+} is required.[1,14,25,26] In order to avoid the possible interference of copper, it is strongly necessary to dissolve this metal before gold leaching.[13] Some leaching processes have been developed to recover copper from WPCBs for their high leaching selectivity to date, the leaching system including nitric acid, ammoniacal sulfate and chloride solution.[18,28]

Cyanide, thiourea, halide, and thiosulfate have been the most common leaching agents for the recovery of precious metals of PCBs from mobile phones. Although cyanide is very efficient, it is very toxic.[29,30] Many studies have been performed to replace it.[14,24,31,32]

In spite of dynamic research on this field, many of the processes have not reached commercial-scale operation due to various drawbacks, such as great energy consumption and large amount of waste acid liquid produced during the processes. The flow of recycling metals in waste PCBs may be long and complicated due to poor selectivity of inorganic acids as leaching agents, leading to a high recovery cost.[2,11,33]

This work describes a novel hydrometallurgical process to recover valuable metals of PCBs from cell phones under mild experimental conditions on lab-scale using an oxidant in acidic medium. The PCBs were not ground. Hydrofluoric acid was used as leachant taking advantage of its complexing properties. This acid reacts with many base metals because fluoride is a very hard base and forms very stable complexes with cations with noble gas-like configuration (the so-called hard acids). This is generally found in cations with a high charge and a small ionic radius, like Al^{3+}, Sn^{4+} and Fe^{3+}. Furthermore, it rapidly dissolves silicon dioxide and silicates as very stable $[SiF_6]^{2-}$ ions are produced.[34,35] Therefore, this acid reacts with the PCB laminate (ceramic/fiberglass components), thus increasing exposition of metals to the leachant. The leachates and the insoluble matter were chemically characterized to determine the effect of some experimental parameters on leaching and to develop a suitable scheme for recovery of noble metals from the insoluble matter.

EXPERIMENTAL

PCB samples

Thirty PCBs from the same model and brand were collected from the inventory of obsolete components at a dismantling WEEE unit. These PCBs were kept in their original form (i.e. they were not ground).

Processing of the PCBs

First step: removal of the soldering mask

The first step was the removal of the transparent thin polymeric film (typically, 25-250 µm thickness) which protects the board's components against moisture, dust, chemicals, and extreme temperatures.[36] This coating does not allow leaching of metals present in PCBs.[37,38] Taking into account that epoxy resins are frequently used as coatings,[37,39] the PCBs were immersed in 6 mol L^{-1} NaOH (10 mL g^{-1} PCB) in a Teflon beaker at 50 °C for 1-4 h under stirring (100 rotations per minute). After this treatment the PCB was removed with plastic tweezers and washed with water (5 mL g^{-1}), dried at 25 °C and weighed. A fine greenish-milky solid deposited at the bottom of the beaker. It was filtered, washed with water (3 mL g^{-1}), dried at 25 °C and weighed. This solid was placed in a ceramic crucible and calcined in a furnace (600 °C, 3 h). The roasted mass was cooled down in the furnace and weighed.

Second step: chemical leaching (HF + H_2O_2 or HF + NaClO)

All leaching experiments were carried out in a fume hood (face velocity 0.5 m s^{-1}) in 250 mL closed Teflon vessels. HF (40 wt.%, ~20 mol L^{-1}), H_2O_2 (30 wt.%, ~10 mol L^{-1}) and NaClO (6 wt.%, ~0.8 mol L^{-1}) were of analytical grade and were used as received without further purification. Handling of these reactants was performed using appropriate personal protective equipment (chemical splash goggles together with a face shield, neoprene rubber gloves that cover the hands, wrists, and forearms and a laboratory coat). The initial experiments were performed combining equal volumes of HF and oxidant (therefore, the leachants contain ~10 mol L^{-1} HF and ~5 mol L^{-1} H_2O_2 or ~0.4 mol L^{-1} NaClO). Time varied from 1 to 4 h. The solid/liquid ratio was fixed at 10 mL leachant g^{-1} PCB. Initial temperature was 25 °C. Stirring was fixed at 200 rotations per minute. In a second set of experiments the effect of HF and oxidant concentrations was studied. Distilled water was added to adjust concentration of one or both reactants prior to mixing them. The remaining experimental conditions were kept as such.

After adding the treated PCB to the leachant, temperature increased by 15 °C after ~1 h in the presence of H_2O_2. Temperature decreased to ~30 °C at the end of the experiment. No thermal effect was observed when NaClO was the oxidant. Therefore, its experiments were slowly heated during 1 h to ~40 °C, after which temperature was slowly decreased to ~30 °C at the end of the experiment. The vessel was opened at 25 °C. The PCB was removed using plastic tweezers, washed with water (3 mL g^{-1}) and dried at 25 °C. Then, it was ground in a knife mill to a size fraction below 0.2 mm.[40] The insoluble matter consisted of the components released from the PCBs (resistors, relays, connectors, chips etc.) and a fine solid. The leachate was passed through a plastic sieve (0.5 mm) in order to retain the PCB components, which were washed with water (6 mL g^{-1} processed PCB). The washings and the filtrate were combined and filtered (under vacuum) through an ordinary quantitative filter paper. The fine solid was washed with water (4 mL g^{-1} processed PCB), dried at 110 °C for 2 h and weighed. The following equations describe the possible reactions between copper, lead, tin, noble metals, aluminum, iron and silicon dioxide with HF and the oxidative leachants with values of ΔG^0 at 30 °C.[41,42]

$$Cu + H_2O_2 + 2\,HF \rightarrow CuF_2 + 2\,H_2O \qquad \Delta G^0 = -71.3\ kJ \tag{1}$$

$$Pb + H_2O_2 + 2\,HF \rightarrow PbF_2\downarrow + 2\,H_2O \qquad \Delta G^0 = -90.1\ kJ \tag{2}$$

$$Sn + 2\,H_2O_2 + 6\,HF \rightarrow [SnF_6]^{2-} + 4\,H_2O + 2\,H^+ \qquad \Delta G^0 = -168.4\ kJ \tag{3}$$

$$SiO_2 + 6\,HF \rightarrow [SiF_6]^{2-} + 2\,H^+ + 2\,H_2O \qquad \Delta G^0 = -43.2\ kJ \tag{4}$$

$$2\,X + 3\,H_2O_2 + 12\,HF \rightarrow 2\,[XF_6]^{3-} + 6\,H_2O + 6\,H^+\ (X = Al, Fe) \qquad \Delta G^0 \sim -283.1\ kJ \tag{5}$$

$$Cu + ClO^- + 3\,Cl^- + 2\,HF \rightarrow [CuCl_4]^{2-} + H_2O + 2\,F^- \qquad \Delta G^0 = -61.3\ kJ \tag{6}$$

$$Pb + ClO^- + 3\,Cl^- + 2\,HF \rightarrow [PbCl_4]^{2-} + H_2O + 2\,F^- \qquad \Delta G^0 = -85.2\ kJ \tag{7}$$

$$Sn + 2\,ClO^- + 6\,HF \rightarrow [SnF_6]^{2-} + 2\,H_2O + 2\,H^+ + 2\,Cl^- \qquad \Delta G^0 = -158.1\ kJ \tag{8}$$

$$2\,Au + 3\,ClO^- + 5\,Cl^- + 6\,HF \rightarrow 2[AuCl_4]^- + 3\,H_2O + 6\,F^- \qquad \Delta G^0 = -201.5\ kJ \tag{9}$$

$$Pd + ClO^- + 3\,Cl^- + 2\,HF \rightarrow [PdCl_4]^{2-} + H_2O + 2\,F^- \qquad \Delta G^0 = -73.7\ kJ \tag{10}$$

$$2\,Ag + ClO^- + Cl^- + 2\,HF \rightarrow 2\,AgCl\downarrow + H_2O + 2\,F^- \qquad \Delta G^0 = -73.4\ kJ \tag{11}$$

All experiments were performed to verify the reproducibility of them. It was found that the error percentage was on the order of ± 4%.

Recovery of lead and noble metals

The strategy adopted to process the solid after leaching PCBs with HF + H_2O_2 mixtures is based on the solubility of lead(II) fluoride in water and the reactivity of noble metals and alkali-earth fluorides in the presence of nitric acid (HNO_3):

- Water: based on the solubility data for lead(II) fluoride ($K_{sp} = 2.7 \times 10^{-8}$) it is expected to dissolve it in hot water.[43] Alkali-earth fluorides do not dissolve significantly in this solvent whatever the temperature. Distilled water was added to the gray solid (25 mL g^{-1}) under heating at ~90 °C (200 rotations per minute). After 15 min the hot aqueous solution was filtered as quickly as possible through a filter paper under vacuum into a plastic vessel. The solid was washed with 0.1 mol L^{-1} HF (2 mL g^{-1}). The washings were added to the filtrate and the system was cooled down to ~0 °C. This procedure accelerated crystallization of a white solid (PbF_2) due to the common ion effect and the lower solubility of this salt in cold water.[43] Lead(II) fluoride was isolated by filtration.

- 2 mol L^{-1} HNO_3: it dissolves the base metals via oxidation and the lead and alkali-earth fluorides[44] by conversion of fluoride to non-ionized HF ($K_a = 7.2 \times 10^{-4}$). The noble metals are not affected but copper may be dissolved:[45,46]

$$XF_2 + 2\,H_3O^+ \rightarrow X^{2+} + 2\,HF + 2\,H_2O \qquad (X = Pb, Mg, Ca, Sr, Ba) \qquad (12)$$

$K_{eq} = K_{sp}\,XF_2/(K_a\,HF)^2$ ranges from 8×10^{-5} (CaF_2) to 0.4 (BaF_2)

$$3\,Cu + 8\,HNO_3 \rightarrow 3\,Cu^{2+} + 2\,NO + 4\,H_2O + 6\,NO_3^- \qquad \Delta E^0 = +0.620\ V \qquad (13)$$

- 8 mol L^{-1} HNO_3: it dissolves silver metal:[35,45,46]

$$3\,Ag + 4\,HNO_3 \rightarrow 3\,Ag^+ + NO + 2\,H_2O + 3\,NO_3^- \qquad \Delta E^0 = +0.157\ V \qquad (14)$$

- 16 mol L^{-1} HNO_3: it dissolves palladium metal. The solution acquires a brownish color.[35,45,46] Gold is the final insoluble matter.

$$3\,Pd + 8\,HNO_3 \rightarrow 3\,Pd^{2+} + 2\,NO + 4\,H_2O + 6\,NO_3^- \qquad \Delta E^0 = +0.042\ V \qquad (15)$$

The solid/liquid ratio was fixed at 5 mL HNO_{3aq} g^{-1} solid. Experiments were run for 1 h at ~50-60 °C under stirring (200 rotations per minute). After each step the remaining insoluble matter was isolated by centrifugation, washed with water (2 mL g^{-1}) and again centrifuged.

The solid obtained after leaching PCBs with HF + NaClO mixtures was treated with 6 mol L^{-1} $NH_{3\,aq.}$ (2 mL g^{-1}) at ~25 °C under stirring (200 rotations per minute) for 15 min. Silver chloride can be easily separated from the other compounds via a complexation reaction:[35]

$$AgCl + 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^- \qquad K_{form} = 1.7 \times 10^7 \qquad (16)$$

The insoluble matter was isolated by centrifugation, washed with 0.01 mol L^{-1} $NH_{3aq.}$ (2 mL g^{-1}), and again centrifuged. Silver chloride was recovered by slow evaporation of the aqueous ammoniacal solution.

A classical method was used to extract soluble gold from the leachate after leaching with HF + NaClO. Pure methyl isobutyl ketone (methyl-4-pentan-2-one, MIBK) was used.[47-49] It is suitable to separate small amounts of gold from other elements in complex matrices. The experiments were performed at 25 ºC. The aqueous/organic (A/O) phase ratio was 1 vol/vol. pH of the leachate was not changed. The system was shaken for 10 min. Phase separation was achieved in ~10 min. The experiments were carried out in triplicate. The error percentage was in the order of ±5%.

Analytical methods

The greenish-milky solid recovered after treating PCB with 6 mol L^{-1} NaOH was analyzed by FTIR (Nicolet 6700 FTIR, 2 wt.% in KBr pellets). Metal ion concentrations in the solutions were determined by atomic absorption spectrometry (Perkin Elmer AAS 3300). pH measurements of aqueous solutions were conducted using a combination of a glass electrode and a Ag/AgCl reference electrode (Orion 2AI3-JG). Free fluoride was determined by potentiometry using an ion selective electrode (Orion 9409) attached to a pH/ion meter (Orion 720A). A total ionic strength adjustment buffer (TISAB) consisting of an acetic acid - sodium acetate buffer and NaCl was used. Total fluoride was also determined by potentiometry after addition of TISAB III (Thermo Scientific) containing CDTA (*trans*-1,2-cyclohexylenedinitrilotetraacetic acid), which releases fluoride ions from metal-F complexes.[50]

The solids obtained during processing of PCBs were weighed in an analytical balance (Scientech SA 120) and analyzed by energy dispersive x-ray fluorescence (XRF, Shimadzu model XRF 800HS). Calibration curves (0.1–1000 mg kg^{-1}) of the metals found were employed for quantitative analyses. Crystalline phases in the solid samples were identified by X-ray powder diffraction (XRD, Shimadzu model XRD 6000) by continuous scanning method at 20 mA and 40 kV, using Cu Kα as the radiation source.

RESULTS AND DISCUSSION

Treatment of PCBs with 6 mol L^{-1} NaOH

The effect of time on removal of the soldering mask is shown in Figure 1. After 1 h the mass loss was constant (~2.5 wt.%). The treated PCB lost its original bright (Figure 2). No component attached to the PCBs was released during this treatment. Apart from sodium ions, XRF data did not detect any other metal present in the alkaline solution.

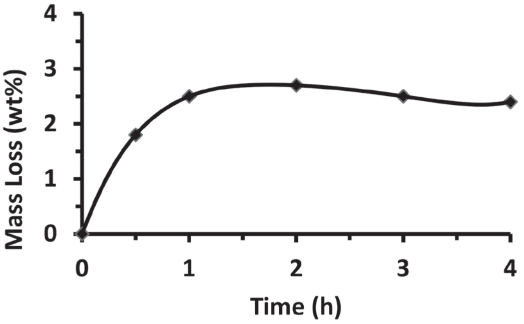

Figure 1. Mass loss of PCBs after treatment with 6 mol L^{-1} NaOH at 50 °C

The inorganic elements present in the greenish solid (Table 1) come mainly from the laminate.[51,52] Of particular interest is the presence of bromine. It comes from the flame retardants added to the PCBs.[52,53] The FTIR spectrum of this solid (Figure 3) is rather complex but presents typical bands of organics functional groups: O−H, N−H, aliphatic chains, carbonyl compounds, C=C and C−O bonds and probably C−Br (597-719 cm^{-1}).[54]

After burning the greenish solid, the ash corresponds to only ~4 wt.% of the initial mass (~0.1 wt.% of the original PCB). Except

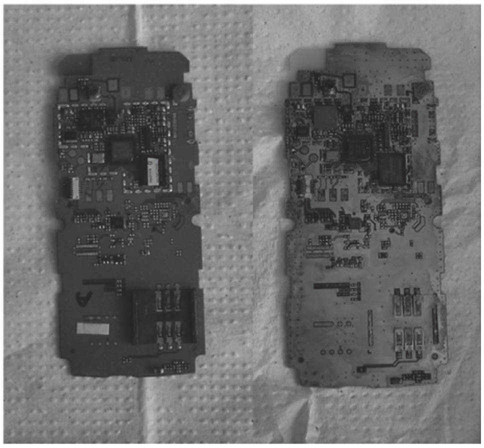

Figure 2. *Aspect of the PCB before (left) and after (right) treatment with 6 mol L^{-1} NaOH at 50 °C for 1 h*

Table 1. XRF data of the greenish solid before calcining

Element	wt.%	Element	wt.%
Si	56.1	Fe	1.5
Ba	22.5	Mg	1.0
Br	15.8	Ca	0.9
Al	2.2	Sr, Pb, Sn, Ni, Zn	< 0.1

for bromine, all elements listed in Table 1 were found in this residue. The greenish solid is essentially organic matter.

Leaching of pretreated PCBs

General aspects

The raise of temperature during leaching with HF + H_2O_2 mixtures is explained by the decomposition of the oxidant, which is catalyzed by various transition metals (such as silver, gold and platinum), their oxides and aqueous ions (such as Cu^{2+}, Ni^{2+}, Co^{2+} etc.).[41,55,56]

$$2\,H_2O_2 \rightleftarrows 2\,H_2O + O_2 \qquad \Delta G^0 = -119.6\text{ kJ} \qquad (17)$$

The leachate presented a blue color, typical of $[Cu(H_2O)_6]^{2+}$ ions. The components attached to the PCBs were released as long as the solder was dissolved by the leachant. The leachates from HF + NaClO mixtures are green in color due to a mixture of $[Cu(H_2O)_6]^{2+}$ and $[CuCl_4]^{2-}$ ions.[35,55]

Effect of time

From data on Table 2, the masses of the epoxy resin (laminate), the components attached to the PCB and the fine solid (Figure 4) are constant after leaching for ~1 h irrespective of the leachant. The laminate is light brown in color and the most important solid waste generated (~40 wt.% of the mass of the processed PCB), followed by the attached components (~12 wt.%) and the fine solid (1.5-3.0 wt.%).

Table 2. Average masses of the solids recovered after leaching treated PCBs with 10 mol L^{-1} HF + 5 mol L^{-1} H_2O_2 or 10 mol L^{-1} HF + 0.4 mol L^{-1} NaClO

Time (h)	Leachant	Mass (mg g^{-1} PCB)		
		PCB laminate	PCB components*	Fine solid**
0.5	HF + H_2O_2	520	76	37.5
1	HF + H_2O_2	406	122	27.9
2	HF + H_2O_2	399	122	27.9
3	HF + H_2O_2	404	119	29.6
0.5	HF + NaClO	495	74	23.8
1	HF + NaClO	399	116	14.3
2	HF + NaClO	395	125	14.2

* Leds, capacitors, chips, quartz crystals etc.

Metal ion concentrations in the leachates did not change significantly after 1 h (Table 3). The leachates are very complex in nature, but copper is largely the main element present, followed by silicon. Sodium hypochlorite was a less selective oxidant than

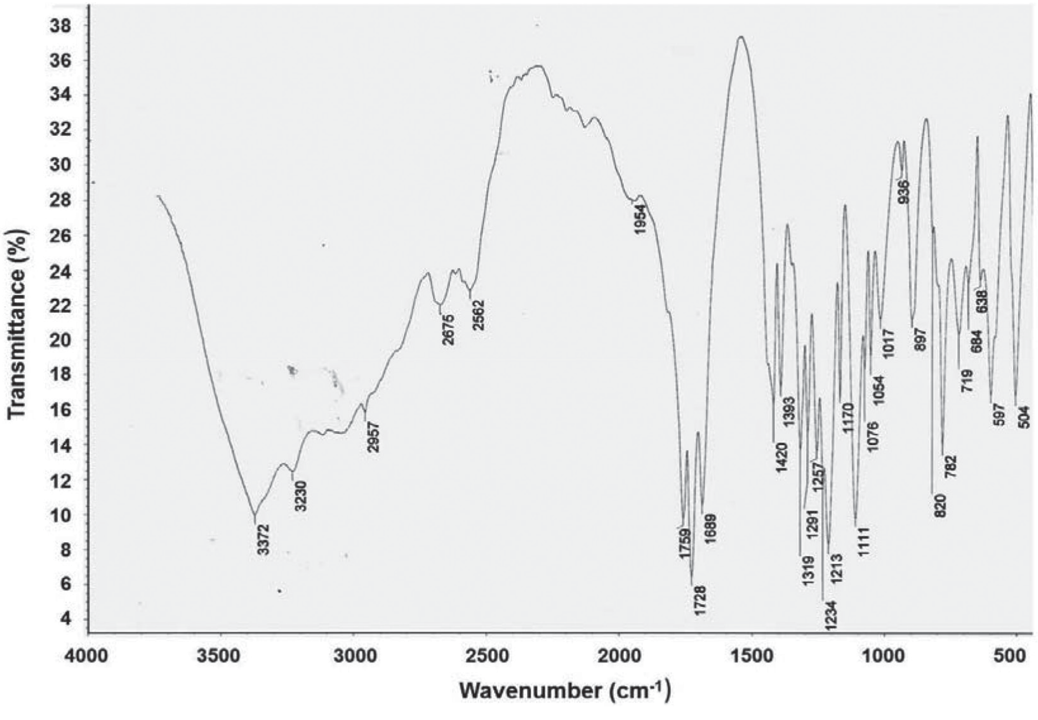

Figure 3. *IR spectrum of the greenish solid recovered after treatment of PCB with 6 mol L^{-1} NaOH at 50 °C for 1 h*

hydrogen peroxide. Besides the leached elements with HF + H$_2$O$_2$ mixtures, lead and the noble metals were also oxidized and leached (Table 3), except silver, which precipitated as AgCl.

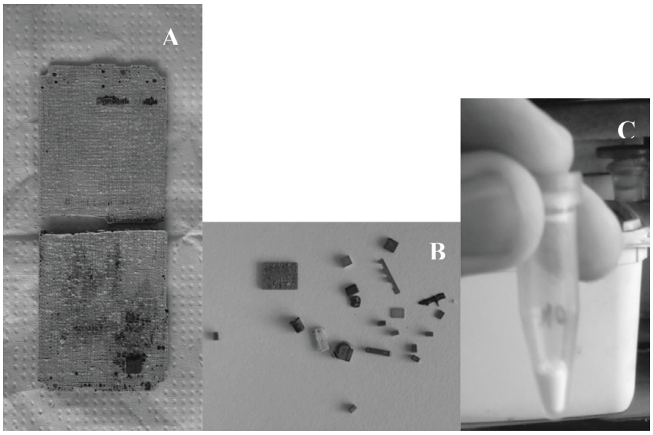

Figure 4. The final solids obtained from PCBs after pretreatment with 6 mol L^{-1} NaOH followed by leaching with HF + H$_2$O$_2$ mixtures: (A) the epoxy resin laminate; (B) the components released from the PCBs; (C) the precipitate containing lead, alkali-earth and noble metals

pH of all leachates was in the range 1.1-1.3 after leaching for 1 h (or more). It is slightly higher than the pH of the original leachate (1.0-1.1). Reactions (1) to (11) consume some acidity from the leachate. The remaining acidity is mainly due to excess of HF used for leaching. However, anions such as SiF$_6^{2-}$, SnF$_6^{2-}$, AlF$_6^{3-}$ and FeF$_6^{3-}$ come from strong acids (reactions 3, 4, 5 and 8),[35,57] thus also contributing to the acidity of the leachate.

The aspect and composition of the fine solid (Table 4) depend on the leachant employed. The gray solid (HF + H$_2$O$_2$) is mainly composed by lead, noble metals and alkali-earth elements (> 80 wt.%). Some Al, Fe, Si, Sn and Cu were also found. The white solid (HF + NaClO) is mainly composed by silver chloride, alkali-earth elements and lead (> 80 wt%). In both cases the alkali-earth elements were probably precipitated as fluorides (XF$_2$, X = Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}), which are insoluble in water and HF$_{aq}$.[44] Both leachants oxidized lead (reactions 2 and 7) but its solubility was strongly dependant on the halide ion present. Lead(II) fluoride readily precipitated because of the high F$^-$ concentration in the leachates (common ion effect). It does not form soluble fluorocomplexes. On the other hand, PbCl$_2$ ($K_{sp} = 1.6 \times 10^{-5}$) is more soluble in water and Pb(II) is easily complexed by Cl$^-$ ions ($K_{form}\,[PbCl_4]^{2-} = 2.5 \times 10^{15}$).[34,35] Tin was highly leached (> 95 wt.%) by both leachants as very stable [SnF$_6$]$^{2-}$ anions are formed (K_{form} ~10^{25}),[35] see reaction 3). The amount of fine solid is lower after experiments with HF + NaClO (Table 2), due basically to the solubility of lead in this leachant (Table 3).

Elements distribution

According to data of Tables 3 and 4, the elements can be divided into three groups: those which ever remained in the insoluble matter (Ag, Mg, Ca, Sr, Ba); those which were mainly (Cu, Sn, Si, Al, Fe: > 80 wt.%) or even fully (Zn, Cr, Ni) leached due to oxidation/complexation reactions; those whose behavior depended on the oxidant present in the leachant (Pb, Au, Pd). Of particular interest is that copper was highly leached (> 99.5 wt.%) after a very short time (~1 h) and under very mild experimental conditions ($T_{max.}$ 40 ºC). High copper leaching yields normally require longer times (> 2 h) and higher temperatures (> 60 ºC) using ground PCBs in sulfuric, nitric or hydrochloric acid medium.[7,31,58-60] The recovery of copper and other leached elements as well as the fluoride ions employed for leaching has already been performed.[61]

HF + H$_2$O$_2$ mixtures presented a particular feature: all noble metals were concentrated into a very small and less complex mass fraction (~3.0 wt.%) of the original PCB, thus meaning a mass concentration factor of 30-35. This makes their separation

Table 3. Average metal ion concentrations in the leachates

Time (h)	Leachant**	Concentration (mg L^{-1})										
		Cu	Ni	Zn	Cr	Al	Fe	Pb	Sn	Si	Au	Pd
0.5	HF + H$_2$O$_2$	11600	970	1200	30	210	290	< 0.1	720	1715	nd*	nd
1	HF + H$_2$O$_2$	12570	1320	1770	45	340	330	< 0.1	780	1790	nd	nd
2	HF + H$_2$O$_2$	12600	1320	1800	48	340	340	< 0.1	790	1780	nd	nd
0.5	HF + NaClO	11480	1000	1280	37	270	325	490	730	1660	35	10
1	HF + NaClO	12820	1330	1730	44	395	355	525	780	1810	55	17
2	HF + NaClO	12870	1320	1700	46	375	350	515	785	1810	55	16

*nd - not detected;**10 mol L^{-1} HF + 5 mol L^{-1} H$_2$O$_2$ or 10 mol L^{-1} HF + 0.4 mol L^{-1} NaClO.

Table 4. Mass percentage of elements in the gray or white fine solid

Time (h)	Leachant**	Amount (wt.%)										
		Cu	Ag	Au	Pd	Al	Fe	Pb	Sn	Si	Mg/Ca/ Sr/Ba	Cl
0.5	HF + H$_2$O$_2$	18.6	8.8	3.4	1.0	8.0	3.8	37.0	5.1	2.7	11.6	nd*
1	HF + H$_2$O$_2$	5.4	11.9	4.5	1.4	2.9	4.4	48.7	5.0	0.3	15.5	nd
2	HF + H$_2$O$_2$	5.1	11.7	4.7	1.5	2.7	4.7	48.8	4.9	0.3	15.6	nd
0.5	HF + NaClO	23.0	13.8	nd	nd	10.5	5.4	11.8	6.0	7.1	18.0	4.4
1	HF + NaClO	6.2	23.1	nd	nd	5.6	5.8	18.4	2.8	0.7	29.8	7.6
2	HF + NaClO	5.7	23.2	nd	nd	5.6	5.9	18.5	2.6	0.7	30.2	7.6

*nd - not detected;**10 mol L^{-1} HF + 5 mol L^{-1} H$_2$O$_2$ or 10 mol L^{-1} HF + 0.4 mol L^{-1} NaClO.

by conventional methods easier. An efficient recovery of precious metals of PCBs from WEEE is essential to offset demand for primary resources.[17] HF + NaClO mixtures were less performant in this aspect because gold and palladium were brought into a complex leachate as minor components, making their recovery more difficult.

After leaching for 1 h the laminate did not present any visible vestige of copper. Other metals, silicon and bromine were not detected by XRF. Thus, based on data of Tables 3 and 4 and the masses of the processed PCBs (15.11 ± 0.35 g), the average copper and precious metals content in these samples are: copper, 299 g kg^{-1}; silver, 3.25 g kg^{-1}; gold, 1.28 g kg^{-1}; palladium, 380 mg kg^{-1}. These results are in the range reported in the literature for PCBs from cell phones.[6,7,17,32,58-60]

Influence of reactants concentration

Copper was chosen to monitor the leaching processes. The presence of an oxidant is essential to perform leaching as HF alone is practically not reactive towards treated PCBs (Figure 5). Concentrations above 3 mol L^{-1} H_2O_2 did not change leaching yield. An excess of H_2O_2 leads to HF losses from the leachant.[62,63] Taking into account the metals content in the leachates (Table 3), this concentration is in large excess as expected from the oxidative leaching reactions (1 to 3 and 5). This oxidant plays a double role during leaching. It oxidizes Cu, Pb, Sn etc. at the same time it is partially decomposed, thus heating the reaction mixture. Concentrations above 0.3 mol L^{-1} NaClO served no advantage. Taking into account copper concentration in the leachates (Table 3) and its oxidation reaction (reaction 6), this concentration is about 30% higher than the stoichiometric amount required for such.

Figure 6 shows that, under our experimental conditions, HF concentration may be reduced to ~3.5 mol L^{-1} without changing significantly the time and leaching yield. A lower HF concentration allows a safer handling of the leachants and leachates. Below 3.5 mol L^{-1} HF, traces of copper and blue-green spots on the surface of the laminate were still observable after leaching for 1 h.

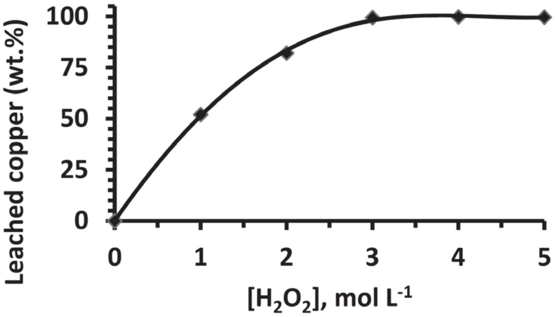

Figure 5. *Effect of H_2O_2 concentration on leaching. [HF] = 10 mol L^{-1}, t = 1 h*

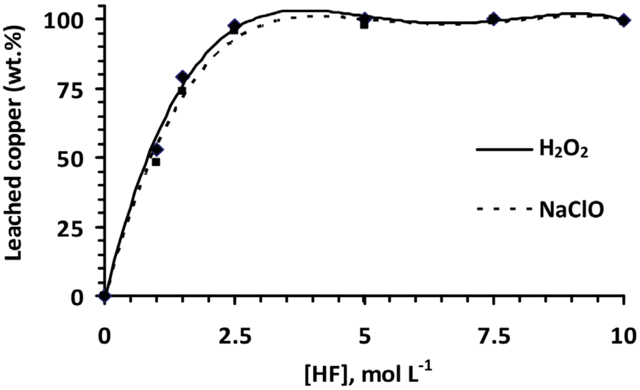

Figure 6. *Effect of HF concentration on leaching. [H_2O_2] = 5 mol L^{-1}; [NaClO] = 0.4 mol L^{-1}; t = 1 h*

Recovery of lead

The diffractogram (Figure 7) of the white solid corresponds to α-PbF_2.[64] It contains 99.6 wt.% of lead present in the processed PCBs. Barium (0.1 wt.%) and calcium (0.1 wt.%) are the only foreign elements found according to XRF data.

Recovery of noble metals

Gray solid (HF + H_2O_2 mixtures)

The sequential treatment of the fine gray solid with nitric acid proved to be successful (Table 5). The first step "cleaned" the solid, removing copper, alkali-earth elements and almost all base metals. The Ag(I) acidic solution can be evaporated (in darkness) to recover silver nitrate.[55] Pd(II) can be isolated by solvent-extraction techniques.[65,66] Gold was recovered as very thin yellow blades. XRF data show these blades contain minor amounts of silicon (< 0.1 wt.%).

White solid and leachate (HF + NaClO mixtures)

As expected, the purity of silver chloride recovered after evaporation of its ammoniacal solution surpasses 99.9 wt.%, with minor amounts of copper (< 0.1 wt.%). This solid is white.

The effectiveness of liquid-liquid extraction of gold using pure MIBK is shown in Table 6. More than 99.9 wt.% of Au(III) was extracted in one stage. Traces of Fe(III) and Sn(IV) were also extracted. They are normally interferents in gold extraction using MIBK,[48,67,68] but their low extraction may be explained by the formation of very stable fluorocomplexes (FeF_6^{3-}, SnF_6^{2-} - reactions (3) and (5))[35,55] which masks solvent-extraction of these elements by MIBK.

Mass balance for fluoride

Any WEEE recycling process must intent the pollution reduction of soil and groundwater caused by leached percolation and compliance with the existing laws. Hydrofluoric acid is recognized as a hazardous

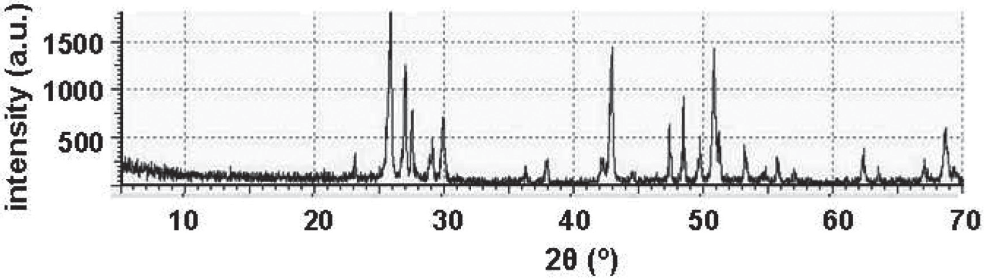

Figure 7. *Diffractogram of the white solid isolated after adding H_2O (~90 °C) to the gray solid followed by filtration, washing of the insoluble matter with 0.1 mol L^{-1} HF and cooling the filtrate + washings to ~0 °C. The peaks represent α-PbF_2*

Table 5. Mass percentage of elements (wt.%) in the fine solid (HF + H_2O_2 experiments) after sequential treatment with aqueous HNO_3

HNO_3 (mol L^{-1})	Color of the solid	Cu	Ag	Au	Pd	Al	Fe	Pb	Sn	Si	Mg + Ca + Sr + Ba
0	Gray	5.4	11.9	4.5	1.4	2.9	4.4	48.7	5.0	0.3	15.5
2	Silvery	-	66.8	25.1	7.8	-	-	0.1	0.1	< 0.1	0.1
8	Yellowish	-	< 0.1	76.2	23.7	-	-	-	-	0.1	-
16	Yellow	-	< 0.1	99.9	-	-	-	-	-	< 0.1	-

Table 6. Elements extracted by pure MIBK from HF + NaClO leachates (25 ºC, A/O phase ratio 1 vol./vol., one stage)

Element	Cu	Au	Pd	Al	Fe	Pb	Sn	Si
wt.% extracted	< 0.1	> 99.9	n.d.	n.d.	0.4	n.d.	0.2	n.d.

n.d. - not detected.

chemical. Any process in which it is used requires monitoring of fluoride losses (final effluents, release to the gaseous phase).

The starting point is the HF + H_2O_2 mixture, which contains all fluoride of the leachant. Fluoride ion is present (i) in the insoluble matter after leaching PCBs (alkali-earth fluorides and PbF_2); (ii) in the leachate either as free fluoride or fluorocomplexes (Al, Sn, Fe, Si). Two potential sources of loss of fluoride ions were identified: (i) as HF in the gas phase due to heat and O_2 released during leaching of PCBs; (ii) during leachate handling.

The fluoride mass balance was performed using 5 mol L^{-1} HF + 5 mol L^{-1} H_2O_2 leachant. Data are presented in Table 7. Over 99 wt.% of fluoride ions are present in the leachate, mainly (~90 wt.%) as free fluoride. It comes from the excess of HF of the leachant. The remaining fluoride is present in the form of fluorocomplexes (Al, Fe, Sn, Si). The insoluble matter contains less than 0.2 wt.%. On the other hand losses of HF were very low (~0.4 wt.%). This result can be attributed to: (i) the low leaching temperature (40 °C maximum); (ii) the smooth H_2O_2 decomposition; (iii) the opening of the vessel after cooling down to 25 °C.

Table 7. Fluoride distribution in the leachates and insoluble matter (base: 1 L leachate)

Leachant/Fraction	Mass of F^- L^{-1} leachate (g)	Relative amount (wt.%)
HF 5 mol L^{-1} + H_2O_2 5 mol L^{-1}	95.0	100%
Insoluble matter		
XF_2 ($X = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}$)*	~0.08	0.08
PbF_2*	~0.07	0.07
Leachate		
Free fluoride	84.68	89.14
Complexed fluoride	9.78	10.29
Total fluoride	94.46	99.43
Losses	0.39	0.41

*Precipitated together with noble metals as insoluble matter in the leachate.

CONCLUSIONS

Processing of non-ground PCBs from cell phones was fast (~1 h) under mild conditions ($T_{max.}$ 40 °C) using HF + oxidant mixtures provided the soldering mask is previously removed by treatment with $NaOH_{aq}$. This step did not attack significantly the metals present (even those of the solder), removed bromine from the PCB, and plays the same role of crushing or grinding the PCB reported in the literature to expose metals to the action of leachants and hence to facilitate their efficient leaching.

Three solids were recovered after leaching: i) the epoxy resin, the attached components released during leaching and a fine gray or white solid. Copper, silicon and other base metals (Cr, Ni, Zn, Fe, Al, Sn) were almost completely leached by both leachants, whereas the alkali-earth elements remained in the fine solid. The main difference between the two leachants was the behavior of lead and noble metals. Lead was oxidized and precipitated using HF + H_2O_2 mixtures, but the noble metals were not oxidized. Lead, palladium and gold were oxidized and leached by HF + NaClO mixtures, whereas silver precipitated as chloride. Leached gold was extracted using methyl isobutyl ketone. Silver chloride was separated from the white solid using aqueous ammonia. Processing of the gray solid by hot water followed by oxidative leaching using nitric acid (2 to 16 mol L^{-1}) allowed recovery of lead, silver, palladium and gold in this order.

HF + H_2O_2 mixtures were able to separate the elements present in PCBs from cell phones into four groups: those that are precipitated by fluoride ions (Mg, Ca, Sr, Ba, Pb); those which form soluble fluorocomplexes (Sn, Al, Fe, Si, Cr); those that are not oxidized (Au, Ag, Pd); those whose fluorides are soluble in the leachate but do not form fluorocomplexes (Cu, Ni, Zn). The replacement of H_2O_2 by NaClO moved Pb, Au and Pd to the group of elements which are soluble in the leachate due to the formation of chlorocomplexes. In this aspect, the HF + H_2O_2 mixture was a better leachant than HF + NaClO one because all noble metals were concentrated into a very small mass fraction of the original PCB.

This route was developed for PCB from small EEE (cell phones). It is unlikely that this route is applicable to large size PCBs (like motherboards) due to their greater mass, complexity and heterogeneity, thus increasing the cost of a multistage leaching and separation process.

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