METAL RECOVERY FROM SCRAP OF PRINTED CIRCUIT BOARD MANUFACTURE BY SELF-REACTIVE SYSTEMS[1]

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Abstract

The manufacture of Printed Circuit Boards (PCB) generates wastewater and solid waste containing copper and tin solder alloy as scrap metal. In this work the possibility of recovery of these metals through a hydrometallurgical self-reacting process was studied, which is made of the solubilization of metals through dissolution reactions with hydrochloric acid in an oxidizing environment at 90ºC, followed by cementation of copper without contamination of the solution. Process products are: metallic copper, lead salts, demetallized PCI waste and waste containing only copper. Tin remains in solution. Basing the experimental study, simulations were conducted using relevant thermodynamic systems with the aid of the FactSage tool.

Keywords: Printed circuit boards; Copper; Tin; Lead.

RECUPERAÇÃO DE METAIS DE RESÍDUOS DA FABRICAÇÃO DE PLACAS DE CIRCUITO IMPRESSO ATRAVÉS DE SISTEMAS AUTORREAGENTES

Resumo

A fabricação de Placas de Circuito Impresso (PCI) gera efluentes e resíduos sólidos, dentre os quais aparas contendo os metais cobre e liga de solda estanho/chumbo. No presente trabalho estudou-se a possibilidade de recuperação destes metais através de um processo hidrometalúrgico autorreagente, no qual é feita a solubilização dos metais através de reações de dissolução ácida controlada em meio clorídrico oxidante a 90ºC, seguido de cementação do cobre sem contaminação da solução. No processo se obtém: cobre metálico, sais de chumbo, resíduos de PCI desmetalizados e resíduos contendo somente cobre. O estanho permanece em solução. Fundamentando o estudo experimental, efetuaram-se simulações termodinâmicas dos sistemas relevantes com o auxílio da ferramenta computacional FactSage.

Palavras-chave: Placas de circuito impresso; Cobre; Estanho; Chumbo.

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1 INTRODUCTION

The technological development of the electronics industry releases new products in such a rate that makes the older obsolete sooner than imagined before.(1) This factor, coupled with a rising rate of electronics products consumed by the population, has motivated a significant growth of this industry in recent years.

The Printed Circuit Boards (PCB) are an integral part of most electronics products consumed and are composed of polymer films, nylon or composite fiberglass and thermoset resins.(2) These plates are coated on the surface or on both sides with a thin film of metal (good conductor of electricity), usually copper, in which conducting paths are delimited that form interconnections with the electronic components fixed later. The PCB can, thus, be understood as a base platform that serves to mount and link together the various components forming the electronic circuit itself.

Basically, the fabrication of the PCB is initiated with the preparation of the circuit layout. Through photographic methods or serigraphy the tracks that will compose the circuit are demarcated and excess copper is removed by chemical corrosion. Currently, in some manufacturing processes, a layer of tin / lead (67/33) alloy is made on the copper surface by electrolytic deposition, especially in the remaining points of welding which contact components with conducting paths. This procedure facilitates the subsequent coupling of electronic components in automated welding.

The manufacturing process generates wastes like the exhausted PCB stripping baths for copper and tin/lead alloys. These baths are already the subject of study for the recovery of dissolved metals, which are there in high concentrations.(3-5) It generates also solid wastes in the form of chips, originated both from suitability to the size and from the removal of parts where the necessary electrical contact for the Sn / Pb coating bath of the finished plates was established. Next to these, there are also the plates discarded for being out of compliance standards.

These solid wastes, although, have significant amounts of copper and Sn / Pb alloy, and have been mostly sent to landfills for industrial wastes. The recovery and separation of metals in these residues presents problems related to the presence of organic material from the substrate and the bond of the solder alloys with copper, which hinders the separation of metals by physical procedures, such as comminution.

For clarity, a differentiation should be made between the base plates (PCB) and the fully assembled cards; cards with the electronic set can be called Electronic Circuit Board (ECB). Due to the accelerated scrapping of electronics products, the environmental impact assessment and recovery of metals contained in ECB, after disposal, has also been studied by various authors, worldwide.(6-8)

Aim of this work is to study the possibility of removal, separation and recovery of nonferrous metals (Cu, Sn and Pb) present in the solid waste from the manufacture of PCBs through a hydrometallurgical self-reactive system. By this treatment, the copper will be recovered in metallic form and the solder alloy (Sn/Pb) will be separated from the substrate composed of the polymer plates coated with copper by stripping.

2 THEORETICAL CONSIDERATIONS

2.1 Extraction Fundamentals

Fundamentally, the process for the recovery of metals in this study makes use, as much as possible, of the properties of the materials contained on the cards, in a system called here ‘self-reactive’.

Observing the half-cell potentials of the metals Cu, Pb and Sn in a simplified diagram (Figure 1), it is easy to understand that metallic Pb and Sn can *cement* in a very effective way the cupric ions of an aqueous solution. This is due to a fortuitous, but very helpful, combination of the noblest metal among the base metals – copper – with two very active metals: lead and tin. Pb and Sn are, in fact, not pure, but alloyed in the solder metal. Nevertheless, the simplified analysis is justified when one realizes that the alloy consists of a mixture of grains of two almost ‘pure’ phases: FCC (97.9 wt.% Pb) and BCT (99.6 wt.% Sn).

But even the cementation of ions of a relatively noble metal such as copper may be hampered by high levels of dissolved oxygen and low pH value, because the standard half-cell potential production of gaseous oxygen is very noble, with 1.23V. However, the overpotential associated with production of gas bubbles of a species is able to mitigate to some extent gaseous reductions of this type.

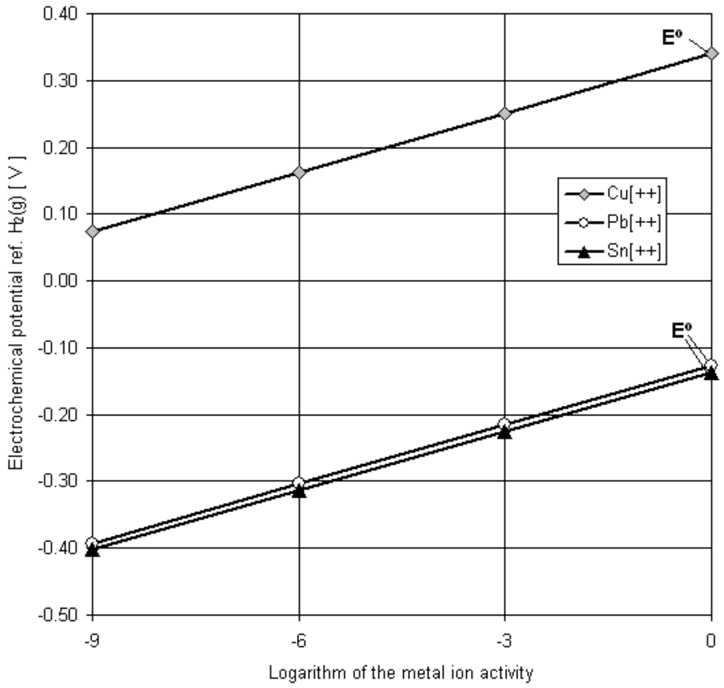

Figure 1: Electrochemical potential (with respect to standard hydrogen electrode) as a function of the logarithm of aqueous ion activity for the reduction half-cells of Cu^{2+}, Pb^{2+} and Sn^{2+}

The chloride ions present in the aqueous solution can promote the formation of a loose layer of hardened deposit composed of particles with a dendritic structure.(9) Its achievement is also encouraged by a high voltage of the galvanic cementation cell – such as between copper and the solder alloy. A loose layer is important because it greatly facilitates the removal of metallic copper.

Given the above, if the metal of some part of the PCB chips are completely dissolved, cupric ions could be cemented out from solution by the addition of the remainder of the chips. On the other hand, lead could be precipitated in the form of a salt, leaving space for the extraction of Sn alone.

2.2 Dissolution of the Metal on Plate Chips

The simulation of the dissolution of metals from the circuit board chips was made with the use of hydrochloric acid. For determining the masses of HCl and water contained in 1 liter of solution, the following equation obtained from linear regression of experimental data from literature was used, Figure 2:

$$y = 0.0049\,x + 1$$

where y is the specific gravity of the solution g/mL and x is the concentration of HCl wt.%.

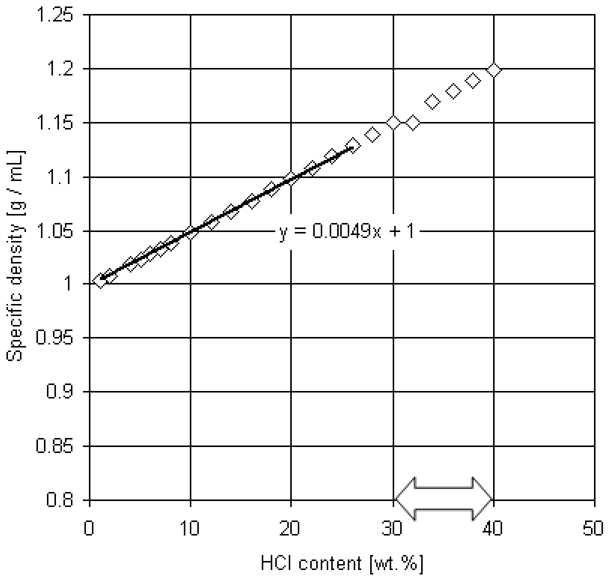

Figure 2: Specific density of hydrochloric acid solutions as a function of HCl content (large double arrow points out the range of HCl *concentrated* solutions).(10)

According to Havlik e Pomosov,(11) copper is leached significantly only in an oxidizing environment. As HCl is not an oxidizing acid, a significant reaction between HCl and copper should not be expect unless some compensatory measures are taken.

This can be confirmed by the Pourbaix diagram for copper: a high ion concentration establishes only in very acidic and oxidizing conditions – the Cu^{2+} cation is there predominant.

The results of an analysis of the dissolution of Cu in an aqueous solution of HCl due to the oxidizing potential of an atmosphere composed of a mixture of Ar-O_2 at a temperature of 25ºC can be seen in Figure 3. For this analysis 1 L of a solution with 3 wt.% HCl used. The Ar-O_2 atmosphere had a total mass of 10 mol and the initial mass of copper was 1 mol or 63.5g. *FactSage* software was employed.

It may be noted that 'without oxygen' – in fact, with a small amount of O_2 supplied to the system – copper remains in the acid solution. As oxygen is supplied to the system, its partial pressure in the atmosphere is increasing (pO_2 values $<1\text{x}10^{-75}$ atm were ignored), and copper metal will dissolve while some condensed phases may precipitate. The precipitation of chloride hydroxide yields to the direction of increasing oxygen in the system.

A similar result occurs under a temperature of 80ºC.

Any difficulties in precipitation were simulated by blocking all condensed phases than metallic copper. In this case, the copper metal just needs a little more oxygen to dissolve.

As the PCB also contains Sn and Pb, a new simulation was carried out using the three metals simultaneously. The total mass of solder tin used was variable from 10 to 30g. Other conditions are those from the previous simulation, with 0.35 mol O_2 in the initial atmosphere.

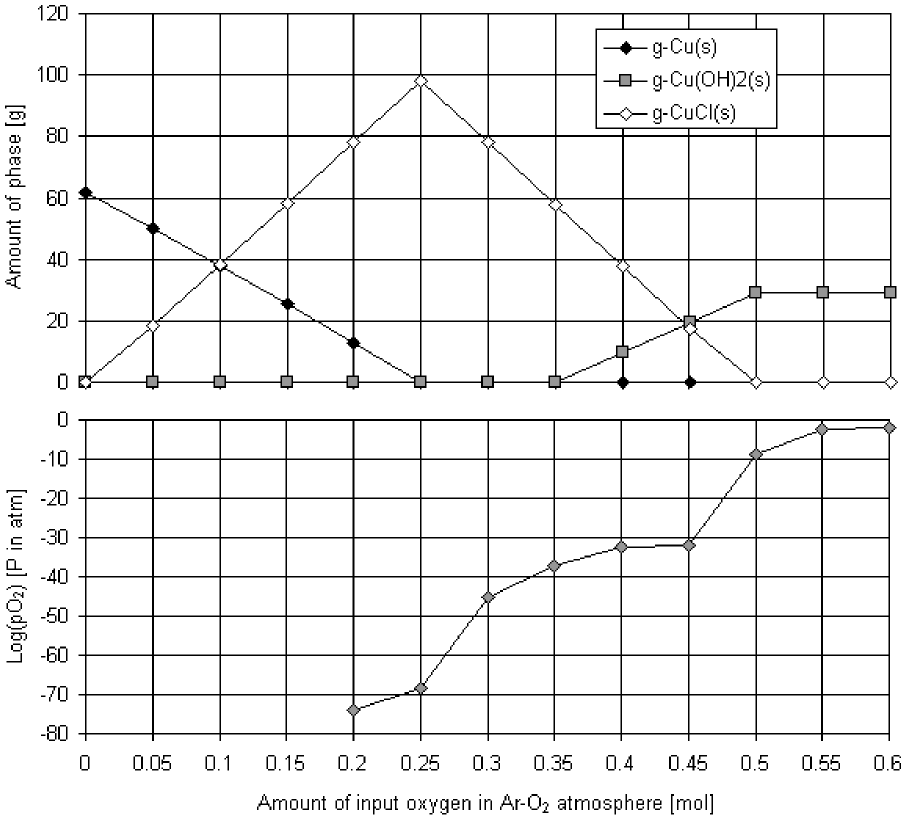

Figure 3: Amount of condensed phases and O_2 partial pressure in the equilibrium state as a function of the amount of input oxygen in Ar-O_2 atmosphere over 1 L,3 wt.% HCl solution and 1 mol copper at 25ºC.

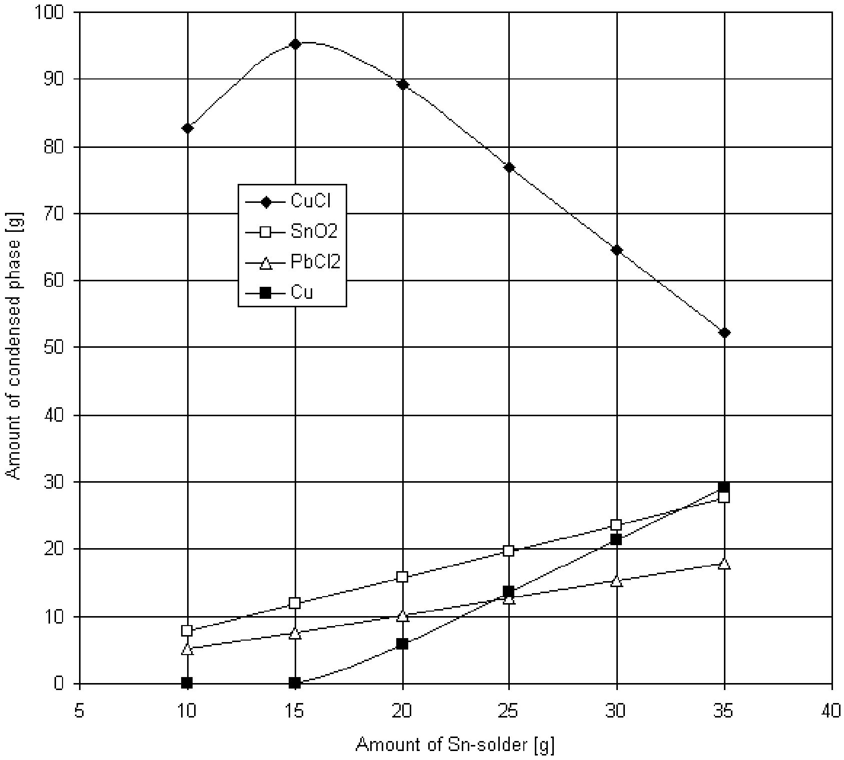

Figure 4: Amount of condensed phases in the equilibrium state as a function of the amount of input Sn-solder in 1 L, 3 wt.% HCl solution and 1 mol copper at 25 ºC; atm: 0.35 mol O_2

Observing the simulation results, it is clear that under oxygenated conditions there is an amount of tin solder that dissolves completely in hydrochloric acid solution (Figure 4). This region can be understood as the conditions where *both* the solder and the copper metal are completely dissolved. The mass of CuCl stands out in precipitate. Larger amounts of solder, however, cause the 'transfer' of copper chloride to the metallic phase.

Again, a similar result occurs for the temperature of 80 ºC. Only the amount of copper chloride increases, in detriment of the metallic copper amount.

From observing the results we can say there are conditions under which the solution can dissolve all metals and, if the resistance related to the kinetics of non-metal condensed phases precipitation of is significance, then the aqueous solution is the only condensed phase in the metastable equilibrium state.

2.3 Separation of Copper, Lead and Tin

It can also be said that it is possible to produce the cementation of the dissolved copper – process goal – making the amount of tin solder to exceed a certain value in the system. This can be understood, in practice, as taking some action such as the addiction of a new batch of plate chips to a pregnant solution (containing only *dissolved* metals). The cooper of these cards will probably not dissolve, but it will be subsequently treated with a *new* acidic solution. It is interesting to note the relatively advantageous position of the tin solder for the cementation process – since it covers the sheet of copper plate, is thus directly exposed to acidic solution.

After removal of copper, the solution can be left resting until it cools. In this situation (long times and low temperature), the necessary conditions for the precipitation of condensed phases – especially the lead chloride – would be given, leaving the tin in solution. Its extraction should be done by means of another process, for example, by electrolysis.

3 MATERIALS AND METHOD

3.1 Metal Content Characterization

In this study, solid waste from the manufacture of PCBs from a plant of this sector in south of Brazil was employed. The waste, in the form of chips with about 30 to 40 cm long, consisting of a substrate polymer composite reinforced with fiberglass and coated on both sides with a copper strip, can be seen in Figure 5. On the copper strip is an electrolytic deposition of Sn / Pb solder alloy, at an approximate ratio of 63% tin and 37% lead, which corresponds to a low melting point eutectic (183ºC). The residues are from the size adjustment and the removal of electrical contacts.

Despite the relative homogeneity of the material, there are lots with different amounts of varnish for protection, which implies also in the variation of the Sn / Pb content in the waste. In order to establish the approximate average share of metals present in waste a simple dissolution process was carried out. Before this procedure, each sample was submitted to a decrease in size by cutting the trimmings into fractions of three to five centimeters long, with the aid of a guillotine. Following, three batches of pre-prepared waste with a mass of 50 grams each were subjected to an aqueous solution with an excess nitric acid (reagent-grade, p.a.) for the *total* dissolution of metals. The residue demetallized, washed and dried at room temperature, was weighed and, by difference with the initial weighting, the mass of copper plus Sn / Pb was obtained.

Figure 5. Solid waste (chips) from the manufacture of PCBs.

Further, having at hand waste only covered with plates of copper, belonging to the same manufacturing batch, similar procedure was made up, obtaining now, the average mass of copper residue, which is standardized, given that lots of plates are coated with a copper layer of same thickness for each application. On the difference between the total content of metals and copper, then, the approximate content of Sn / Pb solder alloy in the material was obtained.

3.2 Dissolution Methodology and Metal Separation

For the tests, a batch of 4kg of waste was subjected to prior preparation that consisted of cutting the trimmings into pieces three to five centimeters long, that would fit comfortably in beakers of 500mL capacity each. Subsequently, the batch was homogenized and quartered, separating the quantities needed for each test, both for the dissolution as for the later stage of cementation.

The process of separating the metals in the PCB waste occurs through a hydrometallurgical process in two stages: in the first phase the total removal of metals from a lot of waste in an oxidant hydrochloric acid medium in the temperature range between 70 and 90ºC is done. At this stage the metals copper, tin and lead enter the solution as chlorides. In the second stage, after the withdrawal of demetallized polymer plates a new batch of waste is introduced into the solution to dissolve. Keeping the same temperature range and volume of solution constant by the addition of deionized water, there is a cementation process of the copper dissolved in the first stage, resulting in metallic copper.

During the deposition of copper, metals from the Sn / Pb layer dissolve into the solution as chlorides, leaving the pre-existing copper layer on boards. After separation of cemented copper and cooling the solution, solid lead chloride – which is slightly soluble in the hot solution – is deposited by the common ion effect. Tin chloride remais in solution. The products of the process, then, are: metal-free PCB waste, metallic copper, solid lead chloride, solution of tin chloride and PCB covered only with a layer of metallic copper. In Figure 6 the flowchart of the overall process can be seen.

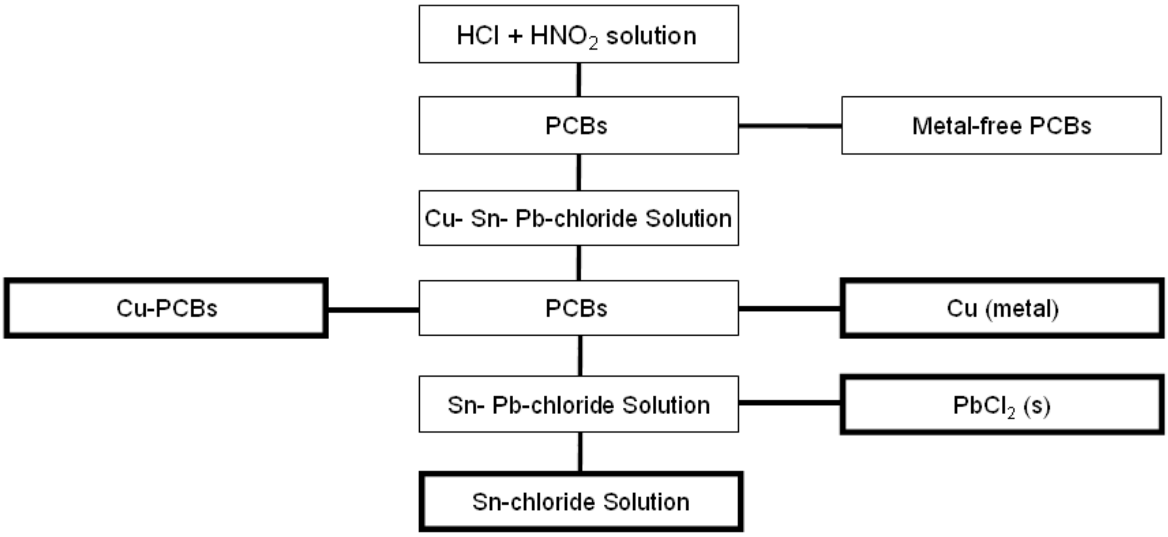

Figure 6. Flowchart of the process for metals recovering from PCB waste; the (four) process products are highlighted

The process steps and reagents used in each experiment are detailed below:

a) *Stage of total dissolution of metals*: this step was the total removal of the metal layers on chips by using diluted HCl (p.a.) in an oxidizing environment (created by a small addition of HNO_3). The dissolution occurs at temperatures between 70 and 90ºC by heating in a sand bath. Qualitative assays were performed with 200mL of HCl solution to 30, 40 and 50 vol.% (Approximate concentrations of 3.6, 4.8 and 6.0M, respectively), with 30g of waste each. These tests were designed to verify the kinetics and the most favorable range of concentrations for both the dissolution as well as the cementation steps. To experimentally evaluate the ability of cementation and removal of the layer of Sn / Pb, a single test with 2000mL solution of HCl 4.8M, plus 0.2mL of HNO_3 p.a. by g of the residue, 400g of waste at a temperature between 80-90°C was done. The resulting solution was subjected to a progressive cementation process, as described below. In all experiments the solution volume was kept constant by adding deionized water.

b) *Stage of copper cementation and dissolution of Sn / Pb alloy*: this procedure was applied to all tests. After the attack with the acid bath in an oxidizing environment, the demetallized trimmings were taken out of the solution and replaced by a new load of crude residue. Keeping the temperature in the range of 70 to 90°C, and the volume of the solution with the addition of deionized water, the conditions of cementation of copper in each test were observed. In this step, exploratory tests with residues masses of 40, 60 and 80g in stage of dissolution, using solutions of HCl 3.6M, volume of 200mL and addition of 0.2mL HNO_3 per gram of waste were conducted, in order to verify the effect of concentrations of metal salts present in the later stage of cementation. For progressive cementation testing, after the dissolution of the initial amount of chips, the solution is diluted to 3000mL and added to the initial quantity of 600g of crude residue. Later, residue additions were made, of 100g each, until the total mass of 1200g was achieved. In several experiments qualitative assessments of the results obtained in relation to the conditions and kinetics of dissolution and cementation, as well as quantitative, are made both for the dissolution as well as for the progressive cementation tests

4 RESULTS AND DISCUSSION

4.1 PCB Waste Composition

Results concerning the residue constitution can be found in Table 1. It can be observed that (average) mass of metals represents a significant fraction of the material – which makes recovery attractive.

Table 1. PCB waste composition

Item	**Wt.%**
Fiberglass substrate	81.5
Copper	10.5
Sn/Pb solder alloy	8.0

4.2 Metalic Layer Dissolution

The qualitative analysis of dissolution of the metal layer on PCB waste made with 200mL of HCl, at concentrations of 3.6, 4.8 and 6.0M, showed that the attack made only with the hydrochloric acid in these concentrations has a slow kinetics (Figure 7).

When 6mL of HNO_3 is added in increasing amounts of 2mL each, the reaction starts and proceeds vigorously and in a few minutes, the total dissolution of the metal layers occurs (Figure 8).

Figure 7. Residues after pure HCl attack.

Figure 8. Residues after HCl + HNO_3 attack.

These tests confirm that a hydrochloric oxidant environment at a suitable temperature is necessary so that the dissolution of metals can take place efficiently and quickly. The attack occurred in all concentrations, causing a progressive darkening of the solution. The kinetics, however, is faster at higher concentrations of HCl.

The solutions of dissolved metals were subsequently utilized for the qualitative analysis of the cementation.

After etching, the complete removal of the metal layer present in the waste at the beginning of the tests can be verified (Figure 9).

Figure 9. PCB chips before and after stripping process.

4.3 Cementation of Copper, Tin Solder Dissolution And Pb Precipitation

Exploratory tests were performed with the shady solutions containing metals from the dissolution tests performed previously (Figure 10). There has been a gradual lightening of the solutions in so far as PCB chips were added, signaling that the cementation reaction occurred (Figure 11). With the clear solution, it became possible to observe PCB trimmings without the layer of tin solder, but containing the underlying copper foil, which remained with the residue. A cemented copper deposited at the bottom of the beakers was a sure indication of a successful cementation reaction – as predicted by thermodynamics. Copper had cemented itself in the form of loose dendrites, which favored the separation (Figure 12).

Cementation of copper in solution and the dissolution of part of the metal layer were confirmed in all tested concentrations.

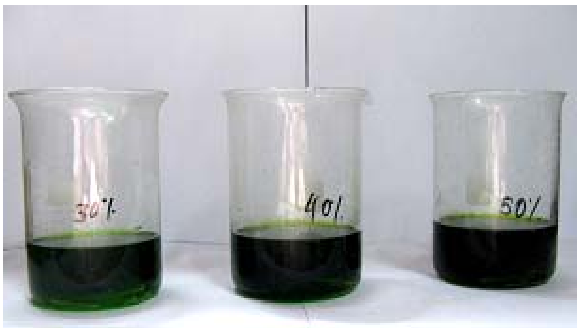

Figure 10. Solutions before Cu^{2+} cementation

Figure 11. Solutions after Cu^{2+} cementation

Figure 12. Appearence of cemented copper .

While the cementation reaction occurs, there is a change in the reagent system, which moves from oxidizing – which favored the dissolution of copper and solder alloy – to reducing. This change relates to the depletion of the oxidizing agent – nitric acid – and the introduction of a new quantity of waste in solution.

In Figure 13 we observe the lead chloride precipitate; precipitation occurs after cooling of the solution. To facilitate the separation, it becomes necessary to remove pre-hardened copper and PCB scrap while the solution is still hot.

Under those conditions, the tin remained in the aqueous solution in the form of chloride.

Figure 13. Lead chloride precipitate

The qualitative analysis of dissolution of increasing amounts of waste and the subsequent cementation test showed that, for the batch of 40g dissolved waste, the cementation stage worked fine. For lots of 60 and 80g there was a relative process inhibition, which was again working with the dilution of the solution. This fact indicates that there is a range of concentrations of constituents in the system where the process is optimized.

The data relating to the dissolution/cementation of the single test are presented in Table 2.

Tabela 2. Single test results for dissolution / cementation

Product	**Amount [g]**
Demetallized PCB chips waste	400
PCB chips devoid of Sn/Pb solder alloy	1000
Cemented cooper	23.4
Dissolved tin solder	77.3

By analyzing the information obtained in the test, it can be verified that, under the experimental conditions, it is possible to strip tin solder from a mass of about 2.5 times greater than the initial mass of PCBs chips which, when dissolved, give origin to the copper-rich solution. The efficiency of removal of the solder alloy in this mass is approximately 97 wt.% and recovery of copper by cementation (which was dissolved only in the *first* stage) is 52 wt.%, the rest remains in solution.

Comparing the mass of copper recovered with the amount of dissolved alloy, it is clear that there is possibility of parallel mechanisms in the stripping of tin solder, such as the formation of Sn^{+4} during the dissolution stage.

5 CONCLUSIONS

The results demonstrated that it is possible to carry out the dissolution and separation of copper, tin and lead present in residues from the manufacture of PCBs by a self-reactive hydrometallurgical process, which uses mainly the properties of the elements themselves.

The solution of metal ions obtained in first stage acts as a convenient stripper of the solder alloy layer of the treated waste in the second step, which ends up depositing copper metal by cementation.

The process becomes attractive for its selectivity and economy of reagents. It is evident, however, both in practical tests and theoretical analysis, the existence of limiting factors to the process, one being the range of concentrations of the system constituents at each step.

It becomes necessary, then, an additional study in order to elucidate the possible phenomena and interfering factors, as well as for process optimization.

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