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A simple process for the recovery of palladium from wastes of printed circuit boards

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ABSTRACT: An efficient process for the recovery of palladium from waste printed circuits boards (PCBs) is detailed. Palladium is employed as an electrode material in multi-layer ceramic capacitors (MLCCs). These components can be easily removed from PCBs by de-soldering. As palladium is alloyed with silver, its dissolution is readily achieved using dilute nitric acid. As a result, a solution containing palladium along with base metals, mostly copper and iron, is obtained. This solution is then processed through solvent extraction (SX) with a solvent based on $N,N'$-dimethyl,$N,N'$-dibutyltetradecylmalonamide (BDMA), a robust extracting molecule previously developed in the frame of the reprocessing of waste nuclear fuel. The volume of effluents generated during the SX sequence is limited: iron scrubbing is operated with a very low aqueous to organic phase volume ratio, no specific metal chelator is required for palladium stripping, and no shift from acidic to basic media is required. Finally, a ca 1 g/L Pd(II) aqueous solution with 99.4% purity is obtained, from which palladium is directly isolated as dichlorodiammine palladium(II) salt ($\text{Pd}(\text{NH}_3)_2\text{Cl}_2$) after precipitation with ammonia. Overall, palladium is quantitatively recovered from the leaching solution, and no palladium was detected in the remaining solid residue. Purity is high, as no contaminating metal could be detected in the final palladium salt. The proposed approach is simple and complementary to existing hydrometallurgical processes dedicated to gold and copper recovery.

Keywords:

Palladium; e-waste; Solvent extraction; Malonamide
1. Introduction

Palladium is a precious metal which is principally employed in autocatalysts. The increasing demand in palladium for this application combined with stable production has recently led to a sharp rise in palladium price as the market remains tight (Cowley, 2019). Palladium price more than doubled over the last three years, and even, in January 2019, reached that of gold. Since then, palladium price regularly reaches ca. 45 k€/kg (1600 $/oz). Palladium market is expected to go further in deficit and production from other secondary resources becomes a key to fulfil palladium needs (Sverdrup and Ragnarsdottir, 2016). Supply from the so-called urban mine appears as a very attractive alternative to traditional mining, especially for Western countries, poorly endowed with natural mineral ores (Sun et al., 2016). Collected waste volume is increasing, and largely unexploited resources are regularly disclosed, such as printed circuits boards (PCBs) contained in end of life vehicles (Xu et al., 2019). Gold represents the principal value fraction of metals contained in waste of electric and electronic equipment (WEEE) (Diaz et al., 2016). Copper and silver represent respectively the highest base-metal and semi-precious metal contents and are present in important quantity. Processes dedicated to the recovery of metals from WEEE have been widely investigated, and mostly optimized for gold and copper recovery (Hsu et al., 2019; Işıldar et al., 2018; Kaya, 2018). Precious metals apart from gold have been generally much less detailed in these studies (Lu and Xu, 2016). Existing copper smelters have been successfully adapted for the reprocessing of WEEE, and several industrial companies claim to recover palladium along with gold and copper from WEEE (Cui and Zhang, 2008). This technical solution is well-adapted to the reprocessing of used autocatalysts, as precious metals are supported on an inert alumino-silicate (cordierite) (Ding et al., 2019). But reprocessing of used PCBs in copper smelters
necessitates complicated off-gas treatments (Cui and Zhang, 2008; Li et al., 2018). In complement, hydrometallurgical processes have been developed to recover valuable metals from waste PCBs: These are generally soaked in acidic baths to remove unwanted base metals (copper, iron, nickel…), which leaves a solid residue, enriched in gold, further processed through dissolution/isolation sequences (Birloaga and Vegliò, 2018). Very often, the outcome of palladium in these processes is not detailed. Efficient techniques targeting palladium recovery from secondary resources are scarce to our knowledge. Detailed analysis of the proposed approaches reveals the difficulty to design a simple process which enables isolation of pure palladium (Table 1). All approaches rely on poorly selective halide based precious metals leaching agents (chloride or iodide media), and (when operated) the purification of palladium can be tedious. Proposed processes often end up with a mixture, of low or unspecified palladium concentration, and isolation of pure palladium is seldom performed. Finally, some proposed processes clearly raise safety issues (Table 1). As 8 to 9% of the total palladium demand is employed in electronic goods manufacturing, it is clearly understandable that palladium recycling from waste PCBs deserves a much deeper consideration.

Available data suggest that palladium concentration in waste PCBs ranges between 10 and 100 mg/kg (Yazici and Deveci, 2013; Zhang and Zhang, 2014). Higher concentrations have been found in specific cases, though on quite old samples (Cui and Zhang, 2008). In PCBs, palladium is principally employed in multi-layer ceramic capacitors (MLCCs) because of its electrical conductivity and its durability (Işıldar et al., 2018; Prabaharan et al., 2016). Palladium is found in the conductive electrode material sandwiched between insulating ceramic layers. Apart from very old MLCCs (more than 20 years old), where 100% Pd electrode material was employed, palladium is found in an alloy with silver (Lee, 2010; Wang et al., 1994). A cheaper alternative to the use of silver-palladium alloys is the
use of nickel electrodes, which leads to heavier and less durable MLCCs. As nickel is a ferromagnetic metal, different MLCC classes can be easily discriminated with a simple magnet: Base metal electrodes (BME) MLCCs are magnetic, whereas precious metal electrodes (PME) MLCCs are not. Most of precious metals recovery processes from waste PCBs start with a shredding or grinding step (Table 1). The purpose of this step is to ensure access to the metallic parts for the leaching/dissolving agent, and is directly inspired from the comminution step of natural ores processing. In the case of waste PCBs, a different approach is also sometimes considered as i. metallic parts are often easily accessible (surface layers, continuous contact...) and ii. reducing PCBs into powder also leads to total mixing of the metals. Several studies focusing on gold and copper suggest removing electronic components from boards prior to leaching in order to lower the amount of leaching agent required (Choudhary et al., 2017; Fontana et al., 2018). Components are connected to the boards through solders, mostly made of Sn-Pb based alloys in waste PCBs, which can easily be removed either via thermal or chemical treatment (Kaya, 2018). This simple step enables obtaining electronic components separated from naked boards. The location of palladium in MLCCs pushes towards such an approach, which enables simple separation of palladium and gold/copper flows.

In this work, we describe a complete detailed study which enables the recovery of palladium from used PCBs, through a hydrometallurgical process based on chemical de-soldering of components, including MLCCs, followed by selective leaching with nitric acid, selective palladium extraction with a malonamide (N,N'-dimethyl,N,N'-dibutyltetradecylmalonamide, BDMA, Figure 1) based solvent, and precipitation of a pure palladium salt using standard techniques. The choice of the extracting molecule was motivated by our previous results which demonstrated its excellent performance in the processing of complex aqueous nitrate solutions containing palladium (Mastretta et al.,
2019; Poirot et al., 2016), along with the consequent technical knowledge gathered during process development studies dedicated to spent nuclear fuel reprocessing with same molecule (Modolo et al., 2007). The adaptation of an existing technology for a new application thus only deserves proof of concept at the laboratory scale, as most process issues have already been tackled out. Overall, the proposed process generates a solid residue which contains most initial gold and copper content, and a controlled volume of aqueous effluents, which can be in part reemployed in the leaching step.

2. Experimental

2.1 Materials and reagents

Used electronic devices were picked up randomly from WEEE collection points and manually dismantled to recover the PCBs contained inside. Concentrated nitric acid, concentrated hydrochloric acid, sodium chloride, toluene and aqueous 28% ammonia solution were purchased from Carlo Erba reagents. N,N'-dimethyl,N,N'-dibutyltetradecylmalonamide (BDMA, Figure 1) was kindly provided by the Commissariat à l’Energie Atomique et aux Energies Alternatives (CEA, France).

2.2 Dissolution of solders

A 3 M aqueous nitric acid solution (200 mL) was placed in a beaker and heated at 50°C. Entire PCBs were placed in the solution and regularly gently swirled into the solution until components fall to the bottom of the beaker (maximum 15 min). The boards were removed, and the components recovered after filtration. The solution became turbid, and a white solid settled in the bottom, and it was isolated after centrifugation.
2.3 Complete digestion of components

With aqua regia: Components were weighed and placed in a glass vessel. A mixture of 32% HCl and 69% HNO₃ (v/v) at a 25 g/L solid/liquid ratio (S/L = 1/40) was then added, and the vessel was covered with a glass slip. The resulting mixture was stirred at 80°C for 24 h using an IKA-Mag magnetic stirrer and a teflon coated bar. The resulting suspension was filtered with a 0.20µm filter and the resulting solution analyzed by ICP/AES. The residual solid was analyzed by SEM.

With aqueous nitric acid solution: The same procedure was applied, using a 3 M aqueous HNO₃ solution.

2.4 Palladium leaching from MLCCs

Components were weighed and placed in a glass beaker. A 3 M aqueous HNO₃ solution at a 100 g/L solid/liquid ratio (S/L = 1/10) was then added, and the beaker was covered with a glass slip. The resulting mixture was stirred at 80°C for 4 h using an IKA-Mag magnetic stirrer and a teflon coated bar. The resulting suspension was centrifuged to remove fine particles (ceramics, remaining tin(IV) oxide).

2.5 Solvent Extraction

Extractions were carried out in 50 mL glass vials by putting in contact the aqueous solution resulting from leaching of components with an organic phase containing BDMA in toluene. The two phases were vigorously shaken at 1000 vibrations per min with an IKA-Vibrax VXR basic shaker in a 20-22°C environment during 1 h. The vials were removed and let to stand for 5 min and the phases were separated. Scrubbing and stripping stages were
performed in 50 mL glass vials by putting in contact the organic phase resulting from previous stage, with an adequate aqueous solution (diluted nitric acid solution, pure water of sodium chloride solution, see text). The volume of the aqueous phase was chosen according to the A/O ratio detailed in the text. The two phases were vigorously shaken at 1000 vibrations per min with an IKA-Vibrax VXR basic shaker in a 20-22°C environment for 1 h. The vials were removed and let to stand for 5 min and the phases were separated. When necessary, 500 µL of each phase were taken for analysis.

2.6 Palladium precipitation

To the aqueous sodium chloride solution containing Pd(II) was added dropwise an aqueous 28% ammonia solution until the solution became clear and colorless and the medium became basic (ca. 5% of the initial volume needed). To the resulting solution, a 6 M aqueous hydrochloric solution was added dropwise under constant stirring until precipitation of a yellow solid. The resulting suspension was stirred until it cooled to room temperature, and filtered. The resulting solid was washed with water and dried in an oven at 40°C overnight.

2.7 Determination of metal concentration in solutions

Aliquots of aqueous phases were directly diluted into a 2% HNO₃ aqueous solution. Metals contained in the aliquots of the organic phases were back-extracted with 800 µL of an aqueous 0.1 M thiourea solution at 20-22°C for 1 h. Both phases were separated, and 500 µL of the resulting aqueous solution were taken and diluted into a 2% HNO₃ aqueous solution. Concentrations of each metal in both aqueous phases (extraction and stripping phases) were determined by inductively coupled plasma atomic emission spectroscopy (ICP/AES, SPECTRO ARCOS ICP Spectrometer, AMETEK Materials Analysis). Given
concentrations are calculated as the means of three replicates on three different wavelengths for each metal; relative standard deviations were determined and lie between 1 and 4%. Quantification limits (LoQ) in each analyzed phase were determined for each metal from the dilution factor applied and from the background equivalent concentration (BEC), calculated by the spectrometer for each optical line.

2.8 Powder X-ray diffraction (PXRD)

The PXRD pattern of the obtained solid was recorded at ambient temperature on a Bruker D8 ADVANCE powder diffractometer using Ni filtered CuKα1 (λ=1.5406 Å) radiation. Data was collected in the range 5-60° (2θ), with a step of 0.01°, and a scanning rate of 0.1°/min.

2.9 Scanning Electronic Microscopy (SEM) and elemental analysis

SEM characterization was obtained with a FEI QUANTA FEG 200 environmental scanning electron microscope (ESEM) equipped with a gaseous secondary electron detector (GSED). Experiments were performed at 100 Pa and an accelerating voltage of 15 kV. Elemental analysis was performed with X-ray Energy dispersive spectrometry (X-EDS) analyses using a Bruker AXS X-flash 5010 detector coupled to the ESEM.

3. Results and discussion

3.1 Chemical de-soldering and isolation of MLCCs

Thermal de-soldering of components from PCBs has been implemented at the industrial scale. Its application requires specific equipment and temperature control to enable complete melting without emission of toxic lead fumes. On smaller scale, it may be
interesting to turn to chemical de-soldering (Zhang et al., 2015). Several media have been
employed, and the most efficient technique appears to be immersion into an aqueous nitric
acid bath (Yang et al., 2011; Yoo et al., 2012). We evaluated at laboratory scale the
removal of electronic components from boards after immersion into 3 M aqueous nitric
acid solution. Small pieces (ca. 2 x 2 cm²) of different PCBs were cut off and immersed
into 3 M nitric acid. According to the board studied, complete dissolution was either
observed after a few minutes at room temperature, or after 10 to 15 min of gentle heating.
This behavior may be related to the composition of solders employed and/or the presence
of varnish. Altogether, a 3 M aqueous nitric acid bath was prepared and heated at 50°C in
order to achieve removal of components from all PCBs studied. Most small components
fall to the bottom of the bath, while some pinned components remain on the board.
Interestingly, MLCCs are not pinned on the boards (Figure 2), and pinned components are
generally memory bars or processors, which often contain gold. De-soldered components
are then recovered after simple filtration.

Chemical de-soldering has several advantages. First of all, it is a safe operation. Only
dilute aqueous nitric acid is employed, no brown NOₓ fume could be observed. It is a rapid
process, as tin, lead and Sn-Pb alloys dissolution are very easy in nitric acid. Secondly,
no gold is leached into nitric acid in the absence of chloride ions, and copper is almost not
attacked during this process. The de-soldering solution was analyzed (Table 2) and
contains Cu at a g/L level, but this does not represent an important quantity considering
the large amount of Cu contained in PCBs. A rough estimate based on an average weight
Cu content of 15% in PCBs suggests that more than 95% of Cu remains on the board.
Thirdly, tin can be easily recovered in the process. A white precipitate was observed in the
filtrate after few minutes, and its isolation followed by X-EDS analysis revealed that it is
exclusively composed of Sn. Actually, oxidation of metallic tin by nitric acid has been
described to lead to complete oxidation into Sn(IV) species, which are soluble only in the presence of chloride ions. Otherwise, hydrolysis of the metallic cation occurs, and leads eventually to precipitation of Sn(IV) oxide (as SnO₂ or H₂SnO₃), as long as concentrated nitric acid is not employed (Yoo et al., 2012). Finally, no Ag nor Pd were detected in the solution, so that it is relatively uncomplicated, and contains only Cu, Pb, Ni and Fe as major metallic salts (Table 2). Re-use and reprocessing of such solutions have been already successfully investigated by several authors (Lee et al., 2003; Yang et al., 2017).

As a consequence, we have not fully optimized this step.

Components recovered after filtration are of various natures. It is possible to operate following leaching step on the whole mixture (Figure 2), or to remove magnetic components and/or processors (black components) and plastic parts. It is also possible to isolate large non-magnetic MLCCs to check their integrity and evaluate their Pd content. At laboratory scale, all these steps were performed manually. But physical techniques to operate sorting of WEEEs pieces have been well developed and can easily be envisioned.

3.2 Location of Pd in waste PCBs and consequences for leaching

Several non-magnetic MLCCs were selected and collected after de-soldering, and analyzed with optical and scanning electronic microscopy (SEM). The multilayer structure is well visible at low magnification with optical microscopy, but the electrode can only be seen thanks to SEM as its thickness is only in order of 1 µm (Figure 2). Chemical analysis by X-ray Energy dispersive spectrometry (X-EDS) revealed the presence of both Ag and Pd, in a ratio varying between 4/1 and 2/1 according to the considered sample. Pd was always found along with silver, confirming the use of Ag-Pd alloys. Barium and titanium were the main elements found in the thick layer, in full agreement with the well-described use of a BaTiO₃ ceramic as the dielectric material. Ag was also detected in the connecting
terminations of the MLCCs, pure in most cases, containing a small amount of Pd in some cases (up to 5% respective to Ag). Similar analysis performed on magnetic MLCCs revealed the use of Ni or Ni-Sn based electrodes, with Ni or Cu based connecting terminations.

In order to evaluate the amount of palladium present in MLCCs, we tried to perform complete digestion with aqua regia of one MLCC reduced to coarse powder after manual grinding in a mortar. Almost no Pd was detected in the leaching solution (4 mg/L). A white solid residue was left, and its analysis by X-EDS revealed the presence of both Ag and Pd in the solid, along with Ti from the ceramic. This result is quite surprising since aqua regia is often proposed for complete dissolution of precious metals present in waste PCBs.

Previous studies give however contradictory information about the leaching of Pd and Ag by aqua regia: Metallic palladium leads to soluble chloro complexes in aqua regia even in the presence of Ag (Jung et al., 2009; Prabaharan et al., 2016). The reduction of nitric acid into NH$_4^+$ could lead to the precipitation of stable red Pd(NH$_4$)$_2$Cl$_6$ without the need for stronger oxidizing agent to stabilize the Pd(IV) in the system. This has been observed in the presence of Zn(II) or Ni(II) ions (Park and Fray, 2009). Ni(II) has been quantified in our study (550-1100 mg/L), but no red precipitate was observed. Silver is not soluble in dilute chloride media, but can be solubilized by concentrated aqua regia as AgCl$_2^-$, and this has been observed also using a low 2/1 (v/v) ratio of hydrochloric to nitric concentrated acids (Wang et al., 2016). Surface passivation by AgCl has also been described during attack of metallic Ag alone in aqua regia even at low concentration, using a 1/40 S/L ratio (Park and Fray, 2009). It is thus reasonable to assume that no dissolution of the Ag-Pd alloy occurred, and that Pd dissolution was prevented by the presence of Ag. Two hypotheses can be put forward: the temperature may be too low, as sometimes complete digestion is performed at higher temperature in pressure vessels, or the S/L ratio may be still too high.
We therefore turned to the use of nitric acid alone. Ag is readily soluble in nitric acid and 3 to 6 M aqueous nitric acid solutions have been successfully employed for efficient Ag leaching from metals mixtures (Petter et al., 2014). Dissolution of Pd in the absence of chloride ions may be sluggish, but its oxidation is accelerated through alloying with Ag (Cole, 1985). Although available literature regarding selective leaching of palladium alloys, especially Ag-Pd alloys, is scarce, we were pleased to find that dissolution using 3 M aqueous nitric acid instead of aqua regia led to efficient Pd dissolution, even after only 4 h. Although it is not possible to state whether Pd leaching is complete, no Pd was detected in the remaining solid, and Pd content in the MLCCs studied was determined to be between 0.5 and 3% wt (5 to 30 g/kg). Latter value demonstrates that Pd content in MLCCs can be very high, and that focusing a recovery process on MLCCs should enable to recover substantial Pd contained in waste PCBs. Finally, these results demonstrate that the use of aqua regia for the dissolution of complex matrices containing precious metals is not so simple. It would be possible, using a higher temperature or a lower S/L ratio (i.e. a higher volume of liquid), but this approach does not appear as a good process solution.

It is conceivable to use the same nitric acid solution to perform first chemical dissolution of solders then leaching of Pd from components. But such a strategy leads to a solution rather diluted in Pd (3 to 5 mg/L). It appears thus judicious to employ a first bath for de-soldering, regenerate it according to existing techniques, and then to perform leaching of Pd from components with another aqueous solution, of limited volume. It is also possible to select from the mixture of components obtained after de-soldering only non-magnetic MLCCs. Preliminary leaching experiments (not optimized) led to Pd containing solutions of relatively simple composition (Table 2). On the other hand, dissolution of magnetic components led to mixtures containing no Pd, but relatively important concentration of Cu, Fe and Ni instead (Table 2). As in both case contaminating metals are the same, and only
their concentrations differ, the selection of specific MLCCs from the components mixture is not necessary. Indeed, leaching of metals from a mixture of components not selected (Figure 2) led to a solution containing ca. 100 mg/L Pd along with Ag, Cu, Fe, Ni and Pb at higher concentration, and low amount of Sn and Zn (Table 2).

3.3 Separation and purification of Pd from a nitric acid solution

Palladium recovery from nitrate media resulting from the dissolution of used nuclear fuel in nitric acid has been largely documented (Kolarik and Renard, 2003). However, we recently highlighted that the proposed solutions are not adequate for a mixture containing common base metals such as Fe, Cu, Pb, Zn, Ni, etc…, and turned to the use of malonamide based solvents (Mastretta et al., 2019). Malonamides make up a family of extracting molecules developed in the frame of the reprocessing of spent nuclear fuel (Musikas, 1988). Although dedicated to the actinide(III)/lanthanide(III) separation in advanced purification process, e.g. DIAMEX (Facchini et al., 2000; Sypula et al., 2012), their affinity for Pd(II) was also evidenced (Poirot et al., 2014). The optimal process in the nuclear fuel cycle is based on \(N,N\)-dimethyl\(N,N\)-dioctylhexylethoxymalonamide (OEMA, Figure 1), but the previous candidate, BDMA, showed a higher affinity for Pd(II) (Mastretta et al., 2019; Serrano-Purroy et al., 2005). Latter molecule is also simpler to prepare, as the tetradecyl chain is commercially available. Both molecules are very robust, stable after prolonged contact with concentrated nitric acid, and even resistant to radiolysis (Le Caër et al., 2012).

Process studies performed with continuous feeds in mixer-settlers revealed nice phase splitting (Modolo et al., 2007), probably thanks to low viscosity of the solvent (less than 10 cP). Benchmarking with commercially available extractants recently demonstrated that malonamides are very well positioned and should be considered for the recovery of palladium from complex mixtures such as those arising from the dissolution of electronic waste (Mastretta et al., 2019).
Regarding the present study, two key points need to be addressed in order to validate the malonamide technology in Pd recovery processes: i. the possibility to generate low amount of effluents during solvent extraction step, and ii. the effective isolation of Pd from waste PCBs at laboratory scale. Considering the composition of the leaching solution obtained beforehand, we evaluated the impact of each metal separately on the extraction step (Table 3). It is clear that Fe is the impurity of concern, and that Cu should be also controlled. All other metals have a lower distribution coefficient and/or a lower concentration in aqueous phase, so that their concentration in organic phase is lower, and that scrubbing of both Fe and Cu will guarantee their elimination from organic phase.

Suitable Pd distribution coefficients and Pd/Fe selectivity have been achieved using BDMA in toluene (Poirot et al., 2016). Modelling a counter current process based on Pd extraction step, Fe scrubbing step and Pd stripping step, each of one with 6 stages, leads to quantitative Pd recovery (Mastretta et al., 2019). As it is much simpler to operate cross-current processes at laboratory and pilot scale, we evaluated a cross-current process at the laboratory scale. The key step in the Pd isolation sequence is the Fe scrubbing step, where minimal Pd loss has to be achieved, along with complete Fe scrubbing generating minimum amount of aqueous effluents. One of the interesting features of the malonamide technology is that no extra scrubbing or stripping agent is required: only careful control of the HNO₃ concentration in the aqueous phase is required. The distribution coefficients (D_M) of both Pd and Fe directly depend on aqueous HNO₃ concentration, and as long as final aqueous HNO₃ concentration is kept above 1,5 M, Pd distribution coefficient is well above 1, and Pd/Fe selectivity well above 100 (Table 4). This enables quantitative Pd extraction, along with residual Fe, as this metal can be in much higher concentration in the initial aqueous phase than Pd. This residual Fe has to be scrubbed from organic phase to ensure recovery of pure Pd. The concentrations of metals back-extracted from the organic
phase into the aqueous phase depend on distribution coefficients, along with the organic to aqueous (O/A) phase volume ratio, according to equation (1):

\[ [M]_{aq,f} = \frac{[M]_{org,ini} \cdot O/A}{1 + O/A \cdot D_M(HNO_3)} \]  

(1)

As a consequence, for a metal with a high distribution coefficient such as Pd, its loss during a scrubbing step will directly depend on O/A and \( D_{Pd} \), following equation (2):

\[ Pd\ loss = \frac{[Pd]_{aq,f} \cdot V_{aq}}{[Pd]_{org,ini} \cdot V_{org}} = \frac{1}{1 + O/A \cdot D_{Pd}(HNO_3)} \approx \frac{1}{O/A \cdot D_{Pd}(HNO_3)} \]  

(2)

And for a metal with a very low distribution coefficient such as Fe, its scrubbing from organic phase will be almost quantitative, as long as its concentration in aqueous phase does not exceed saturation. Its final concentration in aqueous phase can be approached using equation (3):

\[ [Fe]_{aq,f} = \frac{[Fe]_{org,ini} \cdot O/A}{1 + O/A \cdot D_{Fe}(HNO_3)} \approx [Fe]_{org,ini} \cdot \frac{O/A}{1} \]  

(3)

From a practical point of view, there is a compromise to find between the O/A ratio and the nitric acid concentration of the aqueous phase employed for scrubbing. A high O/A ratio will enable a low Pd loss, along with low generation of effluents. A low O/A ratio will enable an optimal Fe scrubbing. A low aqueous HNO_3 concentration will enable efficient Fe scrubbing but will also increase Pd loss. In a first instance, we evaluated both Fe scrubbing (elimination) and Pd loss after contacting an organic phase loaded with both metals with an aqueous phase at different O/A ratios (Figure 3). Using only water leads to almost quantitative Fe scrubbing, albeit with important Pd loss (up to 5% at a O/A ratio of 5). Using 1,5 M HNO_3 leads to lower Pd loss (less than 2% when O/A ratio exceeds 7), but also lower Fe elimination (70 to 80% only). Altogether it appears clearly that at least two
stages have to be set in place, and different strategies based on sequential two stage scrubbing were evaluated (Figure 4). The best option consists in a first scrubbing with water only, followed by a 1 M aqueous HNO$_3$ scrubbing, both with an O/A ratio of 10. In these conditions Pd purity is 96% with 3% Pd loss. These screening results demonstrate that an efficient Fe scrubbing step can be obtained with minimum generation of effluents: the total volume of waste aqueous phase generated represents only 20% of the volume of the organic phase. The final organic phase containing Pd can then be processed in order to recover Pd as a Pd(II) salt with classical techniques.

3.4 Impact of chlorides and consequences for Pd recovery

Evaluation of the behavior of each metal in the solvent extraction step drove us also to evaluate the impact of the presence of chloride ions in the aqueous phase. Sn is poorly soluble in pure nitrate media, as Sn(IV) precipitates as mentioned beforehand. As a consequence it is difficult to evaluate its distribution coefficient with precision as concentration of Sn in the organic phase after extraction is below quantification limit. On the other hand, similar experiment performed with a Sn(IV) chloride solution leads to almost quantitative extraction of Sn. The influence of chloride ions was evaluated on 4 key metals (Pd, Ag, Fe and Sn, Table 5). It is clear that chloride have a negative impact on the process: i. they inhibit the leaching of Pd (see above) and lead to the precipitation of Ag, ii. they decrease the efficiency of Pd extraction, and the Pd/Fe selectivity as Fe is extracted more easily into organic phase, iii. they increase the solubility of Sn and the subsequent extraction of Sn in the organic phase. Altogether, the use of aqua regia is not only poorly suitable for leaching, but also for Pd recovery. Of course other extraction agents could be envisioned (Fontana et al., 2018), but Sn will require deeper studies as it is employed in the extraction of platinum group metals to increase their extraction efficiency: Sn(II)
chloride is a labilizing agent which is easily co-extracted with Pd or Pt in chloride media (Mojski, 1980). Furthermore, the use of a chloride solution to strip Pd from organic phase appears as a very interesting option for malonamides: With low distribution coefficient in the presence of chloride no specific Pd complexing agent will be required to strip Pd, from organic phase. Afterwards, Pd(II) salts can be easily precipitated from aqueous chloride solutions as Pd(NH$_3$)$_2$Cl$_2$ salt through classical process.

Altogether, the complete sequence is the following: i. chemical de-soldering, ii. Pd leaching from components, iii. Pd isolation through solvent extraction, iv. Pd precipitation as Pd(NH$_3$)$_2$Cl$_2$. The two last points are detailed in Figure 5 and Figure 6. A selected solution containing a high amount of Fe and Cu (along with other metals Ag, Ni, Pb, Sn, Zn and traces Al, Ba, Nd, Ti and Y, discarded for clarity) was employed and led to an aqueous solution containing 85% of the initial Pd amount with a 99.4% purity: traces of Fe were still quantified in this final Pd solution, Cu was below quantification limit, and other metals were not detected (Figure 6). This aqueous solution was further processed through successive addition of an ammonia solution and hydrochloric acid solution to lead to quantitative precipitation of Pd(NH$_3$)$_2$Cl$_2$ of characteristic yellow color. SEM, X-EDS and powder X-ray diffraction (PXRD) analysis confirmed the structure and the purity of the salt (Figure 5). No residual Fe was detected in the solid.

3.5 Regeneration of solvent

We chose not to fully back-extract (strip) Pd from the organic phase in order to minimize the volume of aqueous phase employed: 15% of the Pd remains in the organic phase. Theoretically, a 15% Pd hold-up in the extraction solvent should lead to a maximum 17% $(1 - 1 / 0.85)$ increase in the Pd loading in the organic phase after re-use of the organic phase for a new solvent-extraction cycle. Such a slight increase in Pd concentration
should not modify distribution coefficient nor extraction yield. Actually, re-use of this solution for a new extraction cycle led to quantitative Pd extraction from same initial aqueous phase. Organic phase Pd content is higher, and those of Fe and Cu do not vary significantly. Interestingly, no regeneration of the organic phase was required: usually, stripping the metal of interest with a strong chelator requires washing of the organic phase in order to perform a new extraction cycle. In the present case, possible traces of chloride did not alter Pd extraction. No other aqueous effluents are thus generated. Altogether, starting from one volume of aqueous phase, the same volume of organic phase is needed and can be re-employed in successive cycles, and effluents generated account for only 30% of the initial volume to be treated.

The choice of solvent is the direct consequence of our former studies on such systems (Mastretta et al., 2019; Poirot et al., 2014). Using BDMA in toluene, we were able to tackle key issues related to the development of a solvent extraction process, i.e. low generation of effluents and solvent regeneration. Working on the worst possible case, i.e. a leaching solution of high Fe concentration, we obtained very satisfactory results. Our previous results demonstrate that the use of aromatic diluent is only motivated by the optimization of Pd/Fe selectivity (Poirot et al., 2016), and that otherwise Pd distribution coefficient and solubility in the diluent is marginally affected by shift to an aliphatic diluent (Poirot et al., 2014). As toluene is volatile, it would be much safer to use a higher boiling point diluent, such as an aromatic cut (e.g. Solvesso 150). Mixed aliphatic-aromatic cuts could also be employed, and it would also be interesting to investigate malonamide in purely aliphatic diluents when physical sorting of the waste guarantees low Fe content in the leachate. Any of these solutions would also definitely limit inhalation exposure to the toluene, a harmful substance.
5. Conclusion

Through this study, we demonstrated that efficient Pd recovery from waste PCBs can be performed at laboratory scale via an approach based on successive de-soldering, Pd leaching with dilute nitric acid, solvent extraction then precipitation. This approach takes profit of the quasi-exclusive location of Pd in MLCCs, and the fact that it is alloyed with Ag. It demonstrates that the systematic recourse to shredding and aqua regia is inappropriate for the recovering of Pd, as it will lead to more complex mixtures and leaching difficulties. Furthermore, the process benefits from previous work, e.g. regeneration of de-soldering baths, and complements existing strategies performed at small industrial scale to recover Au and Cu. Usually, when WEEE are processed through hydrometallurgy, principal target metal is Au, and other precious metals and base metals are eliminated during a preliminary step in order to maximize Au leaching yield (Figure 7). The proposed process generates a final solid residue which contains still all (or almost all) the Au initially present in the product. This solid residue can be processed according to existing techniques, either directly in the Au leaching step, or with classical base metals dissolution (or even through pyrolysis and grinding for smelting processes). The process also enables selective recovery of Sn as a solid precipitate after dissolution of the solders. We demonstrated that the organic solvent can be re-employed without loss of performance and that the amount of aqueous waste generated is low (ca. 30% of the initial volume to be treated). We have not explored the possibility to recover Ag from this waste, but this option will be explored in
a near future. Pd is isolated as a Pd(II) salt, dichlorodiammine palladium(II) Pd(NH$_3$)$_2$Cl$_2$, with an excellent purity (no other trace metals detected). This salt is a key intermediate in Pd chemistry as its burning at ca. 1000°C leads to Pd sponge, basis for Pd fine chemistry.

To our knowledge, this study is the first one to detail each step from waste PCBs to a key Pd intermediate at the laboratory scale, including outcome of by-products and effluents.

Considering the forecasted increasing demand in Pd, such a process could be further developed and implemented at small industrial scale, i.e. on 10-100 kg of waste PCBs. This is the scale at which regional industrial players operate in the sector of precious metals recovery from waste. These are fully complementary to bigger actors that operate pyrometallurgical processes (Cu smelters). Of course further scale-up of the proposed process is conceivable, and operation of the solvent extraction steps with counter-current continuous mixer-settlers will lead to better performances. But the technological investment is higher, and the access to available waste PCBs may be a limit for cost-effective operation rate. Thus we suggest in a first instance not to start at a large industrial scale. Finally, this work, along with others mentioned in this article, strongly suggest players to seek for alternatives to systematic shredding and complete leaching. This approach, inspired by extraction of metals from natural ores, is not adapted to the management of wastes of high content in several metals, of much lower tonnage and diversity.

Acknowledgements

The authors are grateful to the LaBex ChemiSyst for funding the PhD thesis grant of V. Lacanau (ANR-10-LABX-05-01), and to the Commissariat à l’Energie Atomique et aux
Energies Alternatives (CEA) for financial support of the study.
Table 1: Summary of previously published studies dedicated to palladium recovery from waste PCBs.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Physical treatment</th>
<th>Chemical pre-treatment</th>
<th>Leaching step</th>
<th>Pd purification</th>
<th>Pd compound obtained</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disassembled components from waste PCBs.</td>
<td>Crushing, enrichment of metallic components with centrifugal air separator, grinding into metallic particles (94% Cu, 304 mg/kg Pd).</td>
<td>Enrichment through Cu dissolution with CuSO₄ and NaCl.</td>
<td>CuSO₄ + NaCl (Cu/Cu²⁺ &lt; 0.9) Solution obtained: Pd 20 mg/L, Cu 7260 mg/L + traces Pb, Zn, Fe, Al, Ni.</td>
<td>SX with di-isooamyl sulfide, stripping with NH₃ solution</td>
<td>Pd(II) solution in ammonia (ca. 100 mg/L)</td>
<td>97% Pd recovery during the dissolution-extraction-stripping process, possibility to regenerate the solvent demonstrated.</td>
<td>(Zhang and Zhang, 2014)</td>
</tr>
<tr>
<td>Disassembled components from waste PCBs.</td>
<td>Shredding into metallic particles (18.5% Cu, 97 mg/kg Pd, 86 mg/kg Au).</td>
<td>none</td>
<td>CuSO₄ + NaCl + H₂SO₄.</td>
<td>Not performed</td>
<td>Multimetallic solution (Cu, Fe, Ni, Ag, Pd).</td>
<td>58% Pd leaching.</td>
<td>(Yazıcı and Deveci, 2013)</td>
</tr>
<tr>
<td>MLCCs.</td>
<td>Grinding, sieving</td>
<td>Base metals leaching with concentrated HCl, then with HCl/H₂O₂.</td>
<td>Concentrated HCl/HNO₃ at 80°C.</td>
<td>Au precipitation with urea and Na₂S₂O₅, then Pd precipitation with Zn dust. Then aqua regia redissolution, and sodium formate precipitation.</td>
<td>Not mentioned, probably metallic Pd</td>
<td>Max. 90% Pd leaching.</td>
<td>(Prabaharan et al., 2016)</td>
</tr>
<tr>
<td>MLCCs.</td>
<td>Grinding</td>
<td>None</td>
<td>Concentrated HCl/HNO$_3$ at 25°C. Solution obtained: Pd 108 mg/L, Cu 500 mg/L, Fe 250 mg/L, Pb 700 mg/L, Mn 120 mg/L, Ni 8260 mg/ L, Ba 19 g/L + traces Ag. SX with quaternary ammonium chloride (Aliquat336) in limonene, then precipitation with NaBH$_4$. Precipitate of metallic Pd and Ag, Ba and other metals. Purity depends on SX efficiency: best results given 98.8% Pd purity for 83% Pd recovery yield. Regeneration of extraction solvent not evaluated. The authors mention the use of a 10% w/w NaBH$_4$ solution in water, but in these conditions NaBH$_4$ decomposes with release of H$_2$.</td>
<td>(Fontana et al., 2018)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste PCBs.</td>
<td>Shredding, grinding.</td>
<td>Two steps base metals leaching with H$_2$SO$_4$/H$_2$O$_2$. Then Au leaching with acidic thiourea. 2 M HCl + H$_2$O$_2$ and NaOCl. Precipitation of both Au and Pd with NaBH$_4$. Metallic Pd and Au precipitate. Safety concerns regarding the process are not discussed, e.g. Mixing HCl with NaOCl generates Cl$_2$, and adding solid NaBH$_4$ to an aqueous acidic solution leads to a violent reaction generating H$_2$.</td>
<td>(Behnamfard et al., 2013)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>'Blast powder' (industrial waste from a semiconductor processing unit)</td>
<td>None</td>
<td>None Composition of powder: metallic Ag/Pd alloy, with Al₂O₃.</td>
<td>No leaching</td>
<td>Liquid-liquid-powder extraction with dodecyl amine acetate in kerosene.</td>
<td>Enriched Pd/Ag particles</td>
<td>The technique focuses on the physical separation between Pd/Ag particles and Al₂O₃ particles.</td>
<td>(Ponou et al., 2018)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Waste PCBs.</td>
<td>Shredding and crushing.</td>
<td>Supercritical water oxidation, then 0.1 M HCl leaching of base metals.</td>
<td>KI-I₂ in acetone and supercritical CO₂.</td>
<td>Not performed</td>
<td>Mixture of Ag(I) and Pd(II) iodides in partially iodinated acetone.</td>
<td>Up to 94% extraction of Pd. Concentration of Pd containing solution not given.</td>
<td>(Liu et al., 2016)</td>
</tr>
<tr>
<td>Waste PCBs from mobile phones.</td>
<td>Shredding and grinding.</td>
<td>Supercritical water oxidation using H₂O₂, then leaching of base metals with diluted HCl.</td>
<td>Iodine-iodide (KI/I₂ at pH = 9)</td>
<td>Not performed</td>
<td>Mixture of Ag(I), Au(I) and Pd(II) iodides in water.</td>
<td>Detailed optimisation of process parameters. Concentration of Pd containing solution not given.</td>
<td>(Xiu et al., 2015)</td>
</tr>
</tbody>
</table>
Table 2: Summary of concentrations (mg/L) of principal metals of interest found during the dissolution/leaching steps of the process (Al, Ba, Nd, Ti, and Y were all found below quantification limit and were removed for clarity).

<table>
<thead>
<tr>
<th>Composition of solution</th>
<th>Ag</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>Pd</th>
<th>Sn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantification limit (LoQ)</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.15</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>0.25</td>
</tr>
<tr>
<td>Bath after dissolution of solders</td>
<td>&lt;LoQ</td>
<td>1400</td>
<td>70</td>
<td>180</td>
<td>730</td>
<td>&lt;LoQ</td>
<td>40</td>
<td>&lt;LoQ</td>
</tr>
<tr>
<td>After leaching of selected non-magnetic MLCC</td>
<td>205-968</td>
<td>0-4</td>
<td>0-135</td>
<td>5-41</td>
<td>59-300</td>
<td>38-193</td>
<td>2-24</td>
<td>&lt;LoQ</td>
</tr>
<tr>
<td>After dissolution of selected magnetic components</td>
<td>1</td>
<td>2500</td>
<td>2650</td>
<td>3500</td>
<td>700</td>
<td>&lt;LoQ</td>
<td>5</td>
<td>&lt;LoQ</td>
</tr>
<tr>
<td>After leaching of components recovered after dissolution of solders</td>
<td>481</td>
<td>1940</td>
<td>970</td>
<td>350</td>
<td>172</td>
<td>98</td>
<td>33</td>
<td>37</td>
</tr>
</tbody>
</table>
Table 3: Distribution coefficients and maximum concentrations expected in organic phase after solvent extraction for unwanted metals present in leaching solution, of which HNO$_3$ concentration is 3 M.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Distribution coefficient (D)</th>
<th>Maximum organic concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.04</td>
<td>7</td>
</tr>
<tr>
<td>Cu</td>
<td>0.015</td>
<td>32</td>
</tr>
<tr>
<td>Fe</td>
<td>0.24</td>
<td>88</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td>2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.02</td>
<td>12</td>
</tr>
<tr>
<td>Sn</td>
<td>(0.04)$^a$</td>
<td>&lt;LoQ</td>
</tr>
<tr>
<td>Zn</td>
<td>0.03</td>
<td>1</td>
</tr>
</tbody>
</table>

Note: $^a$. Solubility of tin is very limited in pure nitrate media
Table 4: Distribution coefficients of Pd and Fe between a 0,6 M BDMA in toluene organic phase and aqueous phases of variable HNO$_3$ concentrations, and corresponding Pd/Fe selectivity.

<table>
<thead>
<tr>
<th>Aqueous [HNO$_3$]</th>
<th>1 mol/L</th>
<th>1,2 mol/L</th>
<th>1,5 mol/L</th>
<th>2 mol/L</th>
<th>3 mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(Pd)</td>
<td>1,7</td>
<td>2,5</td>
<td>3,7</td>
<td>6,1</td>
<td>27</td>
</tr>
<tr>
<td>D(Fe)</td>
<td>&lt;LoQ$^a$</td>
<td>0,001</td>
<td>0,003</td>
<td>0,024</td>
<td>0,24</td>
</tr>
<tr>
<td>$S_{\text{Pd}/\text{Fe}}$</td>
<td>n.a.</td>
<td>2500</td>
<td>1230</td>
<td>250</td>
<td>110</td>
</tr>
</tbody>
</table>

Notes: a. LoQ = 0,001 in the determination of Fe distribution coefficient.
Table 5: Impact of the presence of chloride anions on the distribution coefficients of key metals present in leaching solution. Conditions: a controlled quantity of NaCl was added to a 3 M aqueous HNO₃ phase containing dissolved ions.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>D(Pd)</th>
<th>D(Fe)</th>
<th>D(Ag)</th>
<th>D(Sn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No chloride</td>
<td>27</td>
<td>0.24</td>
<td>0.04</td>
<td>(0.04)</td>
</tr>
<tr>
<td>1 M chloride</td>
<td>0.06</td>
<td>1.0</td>
<td>n.a.</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Notes: a. Solubility of tin is very limited in pure nitrate media; b. precipitation of silver chloride.
Figure 1: Malonamide extractants: BDMA (also referred to as DMDBTDMA), employed in the study, and OEMA (also referred to as DMDOHEMA), employed in actinide(III)/lanthanide(III) separation.
Figure 2: Details of printed circuit boards (PCBs) employed in the study, and location of palladium in multi-layer ceramic capacitors (MLCC) with electron microscope imaging of a MLCC transversal cut. Pictures of leaching step of the process and solids and solution obtained.

Waste printed circuit boards

Dissolution of solders & Recovery of components by filtration

Dissolution of components

80°C 4 h

Leaching solution

Plastics & processors
Figure 3: Results of iron elimination and palladium loss during scrubbing. Initial organic phase based on 0.6 M BDMA in toluene, containing Pd (196 mg/L) and Fe (97 mg/L), scrubbed with different aqueous solutions (H$_2$O or 1.5 M HNO$_3$) at different organic to aqueous phase volume ratios (O/A).
Figure 4: Detailed results of the scrubbing sequence optimization. Initial organic phase: 0.6 M BDMA in toluene, containing Pd (95 mg/L) and Fe (79 mg/L), scrubbed with different aqueous solutions (H₂O or 1 M HNO₃) at different organic to aqueous phase volume ratios (O/A). Two scrubbing stages were performed, at same O/A ratio but with possibly different solutions.
Figure 5: Flowsheet of the palladium recovery section of the process, along with obtained Pd(II) salt analysis (electron-dispersion analysis and powder X-ray diffractogram). N = number of stages; A/O = aqueous to organic feed ratio; O/A = organic to aqueous feed ratio.

Palladium recovery section

- **Extraction**
  - Leaching solution
  - \( N = 2, A/O = 2 \)
  - \( L \) to Scrubbing

- **Scrubbing**
  - H\(_2\)SO\(_4\) solution (Cu, Fe…)
  - \( N = 2, O/A = 10 \)
  - \( L \) to Stripping

- **Stripping**
  - Waste solution
  - \( N = 1, O/A = 10 \)
  - \( L \) to Palladium precipitation

- **Palladium precipitation**
  - \( L \) to Solvent re-use
  - \( L \) to Pd\((\text{NH}_3)_2\text{Cl}_2\)

**Notes:**
- Exp Pd\((\text{NH}_3)_2\text{Cl}_2\)
- Ref peaks

**Analytical Data**

<table>
<thead>
<tr>
<th>Element</th>
<th>AT. NO.</th>
<th>Line C</th>
<th>Nett N</th>
<th>Mass %</th>
<th>Mass F.W.</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>17</td>
<td>k, kα1</td>
<td>16.39</td>
<td>31.75</td>
<td>42.79</td>
<td>57.21</td>
</tr>
<tr>
<td>Palladium</td>
<td>46</td>
<td>k, kα1</td>
<td>4.83</td>
<td>23.42</td>
<td>26.09</td>
<td>73.91</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>7</td>
<td>k, kα1</td>
<td>8.14</td>
<td>28.00</td>
<td>72.00</td>
<td>28.00</td>
</tr>
</tbody>
</table>
Figure 6: Detailed results of the solvent-extraction processing section of the palladium recovery process (data for other metals not shown for clarity).

**INITIAL AQUEOUS FEED**

<table>
<thead>
<tr>
<th>Aq. phase content</th>
<th>Org. phase content</th>
<th>Extraction yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>&lt; LoQ</td>
<td>Pd &gt;99%</td>
</tr>
<tr>
<td>Fe</td>
<td>795 mg/L</td>
<td>Fe 19%</td>
</tr>
<tr>
<td>Cu</td>
<td>1916 mg/L</td>
<td>Cu 1,4%</td>
</tr>
</tbody>
</table>

**Fe EXTRACITON: 2 stages, cross-current, A/O = 2**

<table>
<thead>
<tr>
<th>Aq. phase content</th>
<th>Org. phase content</th>
<th>Extraction yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>98 mg/L</td>
<td>Pd 102 mg/L</td>
</tr>
<tr>
<td>Fe</td>
<td>972 mg/L</td>
<td>Fe 184 mg/L</td>
</tr>
<tr>
<td>Cu</td>
<td>1942 mg/L</td>
<td>Cu 27 mg/L</td>
</tr>
</tbody>
</table>

**Fe (and Cu) SCRUBBING H₂O: O/A = 10**

<table>
<thead>
<tr>
<th>Aq. phase content</th>
<th>Org. phase content</th>
<th>Loss/Extraction yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>16 mg/L</td>
<td>Pd 101 mg/L</td>
</tr>
<tr>
<td>Fe</td>
<td>1644 mg/L</td>
<td>Fe 20 mg/L</td>
</tr>
<tr>
<td>Cu</td>
<td>250 mg/L</td>
<td>Cu 2 mg/L</td>
</tr>
</tbody>
</table>

**Fe SCRUBBING 1 M HNO₃: O/A = 10**

<table>
<thead>
<tr>
<th>Aq. phase content</th>
<th>Org. phase content</th>
<th>Loss/Extraction yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>30 mg/L</td>
<td>Pd 99 mg/L</td>
</tr>
<tr>
<td>Fe</td>
<td>168 mg/L</td>
<td>Fe 3 mg/L</td>
</tr>
<tr>
<td>Cu</td>
<td>5 mg/L</td>
<td>Cu &lt; LoQ</td>
</tr>
</tbody>
</table>

**Pd STRIPPING 0,5 M NaCl: O/A = 10**

<table>
<thead>
<tr>
<th>Aq. phase content</th>
<th>Org. phase content</th>
<th>Stripping yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>854 mg/L</td>
<td>Pd 14 mg/L</td>
</tr>
<tr>
<td>Fe</td>
<td>5 mg/L</td>
<td>Fe 2 mg/L</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt; LoQ</td>
<td>Cu &lt; LoQ</td>
</tr>
</tbody>
</table>

**NEW EXTRACTION CYCLE: 2 stages, cross-current, A/O = 2**

<table>
<thead>
<tr>
<th>Aq. phase content</th>
<th>Org. phase content</th>
<th>Extraction yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>&lt; LoQ</td>
<td>Pd 116 mg/L</td>
</tr>
<tr>
<td>Fe</td>
<td>753 mg/L</td>
<td>Fe 222 mg/L</td>
</tr>
<tr>
<td>Cu</td>
<td>1922 mg/L</td>
<td>Cu 23 mg/L</td>
</tr>
</tbody>
</table>
Figure 7: Comparison between existing processes and proposed process: the proposed process dedicated to Pd recovery can fit into existing processes with recycling of Au-containing solid waste.
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