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

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1 ABSTRACT: An efficient process for the recovery of palladium from waste printed circuits  
2 boards (PCBs) is detailed. Palladium is employed as an electrode material in multi-layer  
3 ceramic capacitors (MLCCs). These components can be easily removed from PCBs by de-  
4 soldering. As palladium is alloyed with silver, its dissolution is readily achieved using dilute  
5 nitric acid. As a result, a solution containing palladium along with base metals, mostly  
6 copper and iron, is obtained. This solution is then processed through solvent extraction  
7 (SX) with a solvent based on *N,N*-dimethyl,*N,N*-dibutyltetradecylmalonamide (BDMA), a  
8 robust extracting molecule previously developed in the frame of the reprocessing of waste  
9 nuclear fuel. The volume of effluents generated during the SX sequence is limited: iron  
10 scrubbing is operated with a very low aqueous to organic phase volume ratio, no specific  
11 metal chelator is required for palladium stripping, and no shift from acidic to basic media is  
12 required. Finally, a ca 1 g/L Pd(II) aqueous solution with 99,4% purity is obtained, from  
13 which palladium is directly isolated as dichlorodiammine palladium(II) salt ( $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ )  
14 after precipitation with ammonia. Overall, palladium is quantitatively recovered from the  
15 leaching solution, and no palladium was detected in the remaining solid residue. Purity is  
16 high, as no contaminating metal could be detected in the final palladium salt. The  
17 proposed approach is simple and complementary to existing hydrometallurgical processes  
18 dedicated to gold and copper recovery.

19

20 *Keywords:*

21 *Palladium; e-waste; Solvent extraction; Malonamide*

## 22 1. Introduction

23 Palladium is a precious metal which is principally employed in autocatalysts. The  
24 increasing demand in palladium for this application combined with stable production has  
25 recently led to a sharp rise in palladium price as the market remains tight (Cowley, 2019).  
26 Palladium price more than doubled over the last three years, and even, in January 2019,  
27 reached that of gold. Since then, palladium price regularly reaches ca. 45 k€/kg  
28 (1600 \$/oz). Palladium market is expected to go further in deficit and production from other  
29 secondary resources becomes a key to fulfil palladium needs (Sverdrup and  
30 Ragnarsdottir, 2016). Supply from the so-called urban mine appears as a very attractive  
31 alternative to traditional mining, especially for Western countries, poorly endowed with  
32 natural mineral ores (Sun et al., 2016). Collected waste volume is increasing, and largely  
33 unexploited resources are regularly disclosed, such as printed circuits boards (PCBs)  
34 contained in end of life vehicles (Xu et al., 2019). Gold represents the principal value  
35 fraction of metals contained in waste of electric and electronic equipment (WEEE) (Diaz et  
36 al., 2016). Copper and silver represent respectively the highest base-metal and semi-  
37 precious metal contents and are present in important quantity. Processes dedicated to the  
38 recovery of metals from WEEE have been widely investigated, and mostly optimized for  
39 gold and copper recovery (Hsu et al., 2019; Işıldar et al., 2018; Kaya, 2018). Precious  
40 metals apart from gold have been generally much less detailed in these studies (Lu and  
41 Xu, 2016). Existing copper smelters have been successfully adapted for the reprocessing  
42 of WEEE, and several industrial companies claim to recover palladium along with gold and  
43 copper from WEEE (Cui and Zhang, 2008). This technical solution is well-adapted to the  
44 reprocessing of used autocatalysts, as precious metals are supported on an inert aluminosilicate (cordierite) (Ding et al., 2019). But reprocessing of used PCBs in copper smelters

46 necessitates complicated off-gas treatments (Cui and Zhang, 2008; Li et al., 2018). In  
47 complement, hydrometallurgical processes have been developed to recover valuable  
48 metals from waste PCBs: These are generally soaked in acidic baths to remove unwanted  
49 base metals (copper, iron, nickel...), which leaves a solid residue, enriched in gold, further  
50 processed through dissolution/isolation sequences (Birloaga and Vegliò, 2018). Very often,  
51 the outcome of palladium in these processes is not detailed. Efficient techniques targeting  
52 palladium recovery from secondary resources are scarce to our knowledge. Detailed  
53 analysis of the proposed approaches reveals the difficulty to design a simple process  
54 which enables isolation of pure palladium (Table 1). All approaches rely on poorly selective  
55 halide based precious metals leaching agents (chloride or iodide media), and (when  
56 operated) the purification of palladium can be tedious. Proposed processes often end up  
57 with a mixture, of low or unspecified palladium concentration, and isolation of pure  
58 palladium is seldom performed. Finally, some proposed processes clearly raise safety  
59 issues (Table 1). As 8 to 9% of the total palladium demand is employed in electronic goods  
60 manufacturing, it is clearly understandable that palladium recycling from waste PCBs  
61 deserves a much deeper consideration.

62 Available data suggest that palladium concentration in waste PCBs ranges between 10  
63 and 100 mg/kg (Yazici and Deveci, 2013; Zhang and Zhang, 2014). Higher concentrations  
64 have been found in specific cases, though on quite old samples (Cui and Zhang, 2008). In  
65 PCBs, palladium is principally employed in multi-layer ceramic capacitors (MLCCs)  
66 because of its electrical conductivity and its durability (Işıldar et al., 2018; Prabakaran et  
67 al., 2016). Palladium is found in the conductive electrode material sandwiched between  
68 insulating ceramic layers. Apart from very old MLCCs (more than 20 years old), where  
69 100% Pd electrode material was employed, palladium is found in an alloy with silver (Lee,  
70 2010; Wang et al., 1994). A cheaper alternative to the use of silver-palladium alloys is the

71 use of nickel electrodes, which leads to heavier and less durable MLCCs. As nickel is a  
72 ferromagnetic metal, different MLCC classes can be easily discriminated with a simple  
73 magnet: Base metal electrodes (BME) MLCCs are magnetic, whereas precious metal  
74 electrodes (PME) MLCCs are not. Most of precious metals recovery processes from waste  
75 PCBs start with a shredding or grinding step (Table 1). The purpose of this step is to  
76 ensure access to the metallic parts for the leaching/dissolving agent, and is directly  
77 inspired from the comminution step of natural ores processing. In the case of waste PCBs,  
78 a different approach is also sometimes considered as i. metallic parts are often easily  
79 accessible (surface layers, continuous contact...) and ii. reducing PCBs into powder also  
80 leads to total mixing of the metals. Several studies focusing on gold and copper suggest  
81 removing electronic components from boards prior to leaching in order to lower the amount  
82 of leaching agent required (Choudhary et al., 2017; Fontana et al., 2018). Components are  
83 connected to the boards through solders, mostly made of Sn-Pb based alloys in waste  
84 PCBs, which can easily be removed either via thermal or chemical treatment (Kaya, 2018).  
85 This simple step enables obtaining electronic components separated from naked boards.  
86 The location of palladium in MLCCs pushes towards such an approach, which enables  
87 simple separation of palladium and gold/copper flows.

88 In this work, we describe a complete detailed study which enables the recovery of  
89 palladium from used PCBs, through a hydrometallurgical process based on chemical de-  
90 soldering of components, including MLCCs, followed by selective leaching with nitric acid,  
91 selective palladium extraction with a malonamide (*N,N*-dimethyl,*N,N'*-  
92 dibutyltetradecylmalonamide, BDMA, Figure 1) based solvent, and precipitation of a pure  
93 palladium salt using standard techniques. The choice of the extracting molecule was  
94 motivated by our previous results which demonstrated its excellent performance in the  
95 processing of complex aqueous nitrate solutions containing palladium (Mastretta et al.,

96 2019; Poirot et al., 2016), along with the consequent technical knowledge gathered during  
97 process development studies dedicated to spent nuclear fuel reprocessing with same  
98 molecule (Modolo et al., 2007). The adaptation of an existing technology for a new  
99 application thus only deserves proof of concept at the laboratory scale, as most process  
100 issues have already been tackled out. Overall, the proposed process generates a solid  
101 residue which contains most initial gold and copper content, and a controlled volume of  
102 aqueous effluents, which can be in part reemployed in the leaching step.

103

104

## 105 **2. Experimental**

### 106 2.1 Materials and reagents

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

113

### 114 2.2 Dissolution of solders

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

120

### 121 2.3 Complete digestion of components

122 With aqua regia: Components were weighed and placed in a glass vessel. A mixture of  
123 32% HCl and 69% HNO<sub>3</sub> 2/1 (v/v) at a 25 g/L solid/liquid ratio (S/L = 1/40) was then  
124 added, and the vessel was covered with a glass slip. The resulting mixture was stirred at  
125 80°C for 24 h using an IKA-Mag magnetic stirrer and a teflon coated bar. The resulting  
126 suspension was filtered with a 0.20µm filter and the resulting solution analyzed by  
127 ICP/AES. The residual solid was analyzed by SEM.

128 With aqueous nitric acid solution: The same procedure was applied, using a 3 M aqueous  
129 HNO<sub>3</sub> solution.

130

### 131 2.4 Palladium leaching from MLCCs

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

137

138

### 139 2.5 Solvent Extraction

140 Extractions were carried out in 50 mL glass vials by putting in contact the aqueous solution  
141 resulting from leaching of components with an organic phase containing BDMA in toluene.  
142 The two phases were vigorously shaken at 1000 vibrations per min with an IKA-Vibrax  
143 VXR basic shaker in a 20-22°C environment during 1 h. The vials were removed and let to  
144 stand for 5 min and the phases were separated. Scrubbing and stripping stages were



145 performed in 50 mL glass vials by putting in contact the organic phase resulting from  
146 previous stage, with an adequate aqueous solution (diluted nitric acid solution, pure water  
147 of sodium chloride solution, see text). The volume of the aqueous phase was chosen  
148 according to the A/O ratio detailed in the text. The two phases were vigorously shaken at  
149 1000 vibrations per min with an IKA-Vibrax VXR basic shaker in a 20-22°C environment  
150 for 1 h. The vials were removed and let to stand for 5 min and the phases were separated.  
151 When necessary, 500 µL of each phase were taken for analysis.

152

## 153 2.6 Palladium precipitation

154 To the aqueous sodium chloride solution containing Pd(II) was added dropwise an  
155 aqueous 28% ammonia solution until the solution became clear and colorless and the  
156 medium became basic (ca. 5% of the initial volume needed). To the resulting solution, a  
157 6 M aqueous hydrochloric solution was added dropwise under constant stirring until  
158 precipitation of a yellow solid. The resulting suspension was stirred until it cooled to room  
159 temperature, and filtered. The resulting solid was washed with water and dried in an oven  
160 at 40°C overnight.

161

## 162 2.7 Determination of metal concentration in solutions

163 Aliquots of aqueous phases were directly diluted into a 2% HNO<sub>3</sub> aqueous solution. Metals  
164 contained in the aliquots of the organic phases were back-extracted with 800 µL of an  
165 aqueous 0.1 M thiourea solution at 20-22°C for 1 h. Both phases were separated, and  
166 500 µL of the resulting aqueous solution were taken and diluted into a 2% HNO<sub>3</sub> aqueous  
167 solution. Concentrations of each metal in both aqueous phases (extraction and stripping  
168 phases) were determined by inductively coupled plasma atomic emission spectroscopy  
169 (ICP/AES, SPECTRO ARCOS ICP Spectrometer, AMETEK Materials Analysis). Given

170 concentrations are calculated as the means of three replicates on three different  
171 wavelengths for each metal; relative standard deviations were determined and lie between  
172 1 and 4%. Quantification limits (LoQ) in each analyzed phase were determined for each  
173 metal from the dilution factor applied and from the background equivalent concentration  
174 (BEC), calculated by the spectrometer for each optical line.

175

## 176 2.8 Powder X-ray diffraction (PXRD)

177 The PXRD pattern of the obtained solid was recorded at ambient temperature on a Bruker  
178 D8 ADVANCE powder diffractometer using Ni filtered  $\text{CuK}_{\alpha 1}$  ( $\lambda=1.5406 \text{ \AA}$ ) radiation. Data  
179 was collected in the range  $5\text{-}60^\circ$  ( $2\theta$ ), with a step of  $0.01^\circ$ , and a scanning rate of  $0.1^\circ/\text{min}$ .

180

## 181 2.9 Scanning Electronic Microscopy (SEM) and elemental analysis

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

187

188

# 189 3. Results and discussion

## 190 3.1 Chemical de-soldering and isolation of MLCCs

191 Thermal de-soldering of components from PCBs has been implemented at the industrial  
192 scale. Its application requires specific equipment and temperature control to enable  
193 complete melting without emission of toxic lead fumes. On smaller scale, it may be

194 interesting to turn to chemical de-soldering (Zhang et al., 2015). Several media have been  
195 employed, and the most efficient technique appears to be immersion into an aqueous nitric  
196 acid bath (Yang et al., 2011; Yoo et al., 2012). We evaluated at laboratory scale the  
197 removal of electronic components from boards after immersion into 3 M aqueous nitric  
198 acid solution. Small pieces (ca. 2 x 2 cm<sup>2</sup>) of different PCBs were cut off and immersed  
199 into 3 M nitric acid. According to the board studied, complete dissolution was either  
200 observed after a few minutes at room temperature, or after 10 to 15 min of gentle heating.  
201 This behavior may be related to the composition of solders employed and/or the presence  
202 of varnish. Altogether, a 3 M aqueous nitric acid bath was prepared and heated at 50°C in  
203 order to achieve removal of components from all PCBs studied. Most small components  
204 fall to the bottom of the bath, while some pinned components remain on the board.  
205 Interestingly, MLCCs are not pinned on the boards (Figure 2), and pinned components are  
206 generally memory bars or processors, which often contain gold. De-soldered components  
207 are then recovered after simple filtration.

208 Chemical de-soldering has several advantages. First of all, it is a safe operation. Only  
209 dilute aqueous nitric acid is employed, no brown NO<sub>x</sub> fume could be observed. It is a rapid  
210 process, as tin, lead and Sn-Pb alloys dissolutions are very easy in nitric acid. Secondly,  
211 no gold is leached into nitric acid in the absence of chloride ions, and copper is almost not  
212 attacked during this process. The de-soldering solution was analyzed (Table 2) and  
213 contains **Cu at a g/L level**, but this does not represent an important quantity considering  
214 the large amount of Cu contained in PCBs. A rough estimate based on an average weight  
215 Cu content of 15% in PCBs suggests that more than 95% of Cu remains on the board.  
216 Thirdly, tin can be easily recovered in the process. A white precipitate was observed in the  
217 filtrate after few minutes, and its isolation followed by X-EDS analysis revealed that it is  
218 exclusively composed of Sn. Actually, oxidation of metallic tin by nitric acid has been

219 described to lead to complete oxidation into Sn(IV) species, which are soluble only in the  
220 presence of chloride ions. Otherwise, hydrolysis of the metallic cation occurs, and leads  
221 eventually to precipitation of Sn(IV) oxide (as SnO<sub>2</sub> or H<sub>2</sub>SnO<sub>3</sub>), as long as concentrated  
222 nitric acid is not employed (Yoo et al., 2012). Finally, no Ag nor Pd were detected in the  
223 solution, so that it is relatively uncomplicated, and contains only Cu, Pb, Ni and Fe as  
224 major metallic salts (Table 2). Re-use and reprocessing of such solutions have been  
225 already successfully investigated by several authors (Lee et al., 2003; Yang et al., 2017).  
226 As a consequence, we have not fully optimized this step.

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

### 233 234 3.2 Location of Pd in waste PCBs and consequences for leaching

235 Several non-magnetic MLCCs were selected and collected after de-soldering, and  
236 analyzed with optical and scanning electronic microscopy (SEM). The multilayer structure  
237 is well visible at low magnification with optical microscopy, but the electrode can only be  
238 seen thanks to SEM as its thickness is only in order of 1 μm (Figure 2). Chemical analysis  
239 by X-ray Energy dispersive spectrometry (X-EDS) revealed the presence of both Ag and  
240 Pd, in a ratio varying between 4/1 and 2/1 according to the considered sample. Pd was  
241 always found along with silver, confirming the use of Ag-Pd alloys. Barium and titanium  
242 were the main elements found in the thick layer, in full agreement with the well-described  
243 use of a BaTiO<sub>3</sub> ceramic as the dielectric material. Ag was also detected in the connecting

244 terminations of the MLCCs, pure in most cases, containing a small amount of Pd in some  
245 cases (up to 5% respective to Ag). Similar analysis performed on magnetic MLCCs  
246 revealed the use of Ni or Ni-Sn based electrodes, with Ni or Cu based connecting  
247 terminations.

248 In order to evaluate the amount of palladium present in MLCCs, we tried to perform  
249 complete digestion with aqua regia of one MLCC reduced to coarse powder after manual  
250 grinding in a mortar. Almost no Pd was detected in the leaching solution (4 mg/L). A white  
251 solid residue was left, and its analysis by X-EDS revealed the presence of both Ag and Pd  
252 in the solid, along with Ti from the ceramic. This result is quite surprising since aqua regia  
253 is often proposed for complete dissolution of precious metals present in waste PCBs.  
254 Previous studies give however contradictory information about the leaching of Pd and Ag  
255 by aqua regia: Metallic palladium leads to soluble chloro complexes in aqua regia even in  
256 the presence of Ag (Jung et al., 2009; Prabakaran et al., 2016). The reduction of nitric acid  
257 into  $\text{NH}_4^+$  could lead to the precipitation of stable red  $\text{Pd}(\text{NH}_4)_2\text{Cl}_6$  without the need for  
258 stronger oxidizing agent to stabilize the Pd(IV) in the system. This has been observed in  
259 the presence of Zn(II) or Ni(II) ions (Park and Fray, 2009). Ni(II) has been quantified in our  
260 study (550-1100 mg/L), but no red precipitate was observed. Silver is not soluble in dilute  
261 chloride media, but can be solubilized by concentrated aqua regia as  $\text{AgCl}_2^-$ , and this has  
262 been observed also using a low 2/1 (v/v) ratio of hydrochloric to nitric concentrated acids  
263 (Wang et al., 2016). Surface passivation by AgCl has also been described during attack of  
264 metallic Ag alone in aqua regia even at low concentration, using a 1/40 S/L ratio (Park and  
265 Fray, 2009). It is thus reasonable to assume that no dissolution of the Ag-Pd alloy  
266 occurred, and that Pd dissolution was prevented by the presence of Ag. Two hypotheses  
267 can be put forward: the temperature may be too low, as sometimes complete digestion is  
268 performed at higher temperature in pressure vessels, or the S/L ratio may be still too high.

269 We therefore turned to the use of nitric acid alone. Ag is readily soluble in nitric acid and 3  
270 to 6 M aqueous nitric acid solutions have been successfully employed for efficient Ag  
271 leaching from metals mixtures (Petter et al., 2014). Dissolution of Pd in the absence of  
272 chloride ions may be sluggish, but its oxidation is accelerated through alloying with Ag  
273 (Cole, 1985). Although available literature regarding selective leaching of palladium alloys,  
274 especially Ag-Pd alloys, is scarce, we were pleased to find that dissolution using 3 M  
275 aqueous nitric acid instead of aqua regia led to efficient Pd dissolution, even after only 4 h.  
276 Although it is not possible to state whether Pd leaching is complete, no Pd was detected in  
277 the remaining solid, and Pd content in the MLCCs studied was determined to be between  
278 0,5 and 3% wt (5 to 30 g/kg). Latter value demonstrates that Pd content in MLCCs can be  
279 very high, and that focusing a recovery process on MLCCs should enable to recover  
280 substantial Pd contained in waste PCBs. Finally, these results demonstrate that the use of  
281 aqua regia for the dissolution of complex matrices containing precious metals is not so  
282 simple. It would be possible, using a higher temperature or a lower S/L ratio (i.e. a higher  
283 volume of liquid), but this approach does not appear as a good process solution.

284 It is conceivable to use the same nitric acid solution to perform first chemical dissolution of  
285 solders then leaching of Pd from components. But such a strategy leads to a solution  
286 rather diluted in Pd (3 to 5 mg/L). It appears thus judicious to employ a first bath for de-  
287 soldering, regenerate it according to existing techniques, and then to perform leaching of  
288 Pd from components with another aqueous solution, of limited volume. It is also possible to  
289 select from the mixture of components obtained after de-soldering only non-magnetic  
290 MLCCs. Preliminary leaching experiments (not optimized) led to Pd containing solutions of  
291 relatively simple composition (Table 2). On the other hand, dissolution of magnetic  
292 components led to mixtures containing no Pd, but relatively important concentration of Cu,  
293 Fe and Ni instead (Table 2). As in both case contaminating metals are the same, and only

294 their concentrations differ, the selection of specific MLCCs from the components mixture is  
295 not necessary. Indeed, leaching of metals from a mixture of components not selected  
296 (Figure 2) led to a solution containing ca. 100 mg/L Pd along with Ag, Cu, Fe, Ni and Pb at  
297 higher concentration, and low amount of Sn and Zn (Table 2).

### 298 3.3 Separation and purification of Pd from a nitric acid solution

299 Palladium recovery from nitrate media resulting from the dissolution of used nuclear fuel in  
300 nitric acid has been largely documented (Kolarik and Renard, 2003). However, we recently  
301 highlighted that the proposed solutions are not adequate for a mixture containing common  
302 base metals such as Fe, Cu, Pb, Zn, Ni, etc..., and turned to the use of malonamide based  
303 solvents (Mastretta et al., 2019). Malonamides make up a family of extracting molecules  
304 developed in the frame of the reprocessing of spent nuclear fuel (Musikas, 1988). Although  
305 dedicated to the actinide(III)/lanthanide(III) separation in advanced purification process,  
306 e.g. DIAMEX (Facchini et al., 2000; Sypula et al., 2012), their affinity for Pd(II) was also  
307 evidenced (Poirot et al., 2014). The optimal process in the nuclear fuel cycle is based on  
308 *N,N*-dimethyl,*N,N*-dioctylhexylethoxymalonamide (OEMA, Figure 1), but the previous  
309 candidate, BDMA, showed a higher affinity for Pd(II) (Mastretta et al., 2019; Serrano-  
310 Purroy et al., 2005). Latter molecule is also simpler to prepare, as the tetradecyl chain is  
311 commercially available. Both molecules are very robust, stable after prolonged contact  
312 with concentrated nitric acid, and even resistant to radiolysis (Le Caër et al., 2012).  
313 Process studies performed with continuous feeds in mixer-settlers revealed nice phase  
314 splitting (Modolo et al., 2007), probably thanks to low viscosity of the solvent (less than  
315 10 cP). Benchmarking with commercially available extractants recently demonstrated that  
316 malonamides are very well positioned and should be considered for the recovery of  
317 palladium from complex mixtures such as those arising from the dissolution of electronic  
318 waste (Mastretta et al., 2019).

319 Regarding the present study, two key points need to be addressed in order to validate the  
320 malonamide technology in Pd recovery processes: i. the possibility to generate low amount  
321 of effluents during solvent extraction step, and ii. the effective isolation of Pd from waste  
322 PCBs at laboratory scale. Considering the composition of the leaching solution obtained  
323 beforehand, we evaluated the impact of each metal separately on the extraction step  
324 (Table 3). It is clear that Fe is the impurity of concern, and that Cu should be also  
325 controlled. All other metals have a lower distribution coefficient and/or a lower  
326 concentration in aqueous phase, so that their concentration in organic phase is lower, and  
327 that scrubbing of both Fe and Cu will guarantee their elimination from organic phase.

328 Suitable Pd distribution coefficients and Pd/Fe selectivity have been achieved using BDMA  
329 in toluene (Poirot et al., 2016). Modelling a counter current process based on Pd extraction  
330 step, Fe scrubbing step and Pd stripping step, each of one with 6 stages, leads to  
331 quantitative Pd recovery (Mastretta et al., 2019). As it is much simpler to operate cross-  
332 current processes at laboratory and pilot scale, we evaluated a cross-current process at  
333 the laboratory scale. The key step in the Pd isolation sequence is the Fe scrubbing step,  
334 where minimal Pd loss has to be achieved, along with complete Fe scrubbing generating  
335 minimum amount of aqueous effluents. One of the interesting features of the malonamide  
336 technology is that no extra scrubbing or stripping agent is required: only careful control of  
337 the HNO<sub>3</sub> concentration in the aqueous phase is required. The distribution coefficients  
338 ( $D_M$ ) of both Pd and Fe directly depend on aqueous HNO<sub>3</sub> concentration, and as long as  
339 final aqueous HNO<sub>3</sub> concentration is kept above 1,5 M, Pd distribution coefficient is well  
340 above 1, and Pd/Fe selectivity well above 100 (Table 4). This enables quantitative Pd  
341 extraction, along with residual Fe, as this metal can be in much higher concentration in the  
342 initial aqueous phase than Pd. This residual Fe has to be scrubbed from organic phase to  
343 ensure recovery of pure Pd. The concentrations of metals back-extracted from the organic



344 phase into the aqueous phase depend on distribution coefficients, along with the organic  
345 to aqueous (O/A) phase volume ratio, according to equation (1):

$$346 \quad [M]_{aq,f} = \frac{[M]_{org,ini} \cdot O/A}{1 + O/A \cdot D_M(HNO_3)} \quad (1)$$

347

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

$$350 \quad Pd \text{ loss} = \frac{[Pd]_{aq,f} \cdot V_{aq}}{[Pd]_{org,ini} \cdot V_{org}} = \frac{1}{1 + O/A \cdot D_{Pd}(HNO_3)} \approx \frac{1}{O/A \cdot D_{Pd}(HNO_3)} \quad (2)$$

351

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

$$356 \quad [Fe]_{aq,f} = \frac{[Fe]_{org,ini} \cdot O/A}{1 + O/A \cdot D_{Fe}(HNO_3)} \approx [Fe]_{org,ini} \cdot O/A \quad (3)$$

357

358 From a practical point of view, there is a compromise to find between the O/A ratio and the  
359 nitric acid concentration of the aqueous phase employed for scrubbing. A high O/A ratio  
360 will enable a low Pd loss, along with low generation of effluents. A low O/A ratio will enable  
361 an optimal Fe scrubbing. A low aqueous  $HNO_3$  concentration will enable efficient Fe  
362 scrubbing but will also increase Pd loss. In a first instance, we evaluated both Fe  
363 scrubbing (elimination) and Pd loss after contacting an organic phase loaded with both  
364 metals with an aqueous phase at different O/A ratios (Figure 3). Using only water leads to  
365 almost quantitative Fe scrubbing, albeit with important Pd loss (up to 5% at a O/A ratio of  
366 5). Using 1,5 M  $HNO_3$  leads to lower Pd loss (less than 2% when O/A ratio exceeds 7), but  
367 also lower Fe elimination (70 to 80% only). Altogether it appears clearly that at least two

368 stages have to be set in place, and different strategies based on sequential two stage  
369 scrubbing were evaluated (Figure 4). The best option consists in a first scrubbing with  
370 water only, followed by a 1 M aqueous HNO<sub>3</sub> scrubbing, both with an O/A ratio of 10. In  
371 these conditions Pd purity is 96% with 3% Pd loss. These screening results demonstrate  
372 that an efficient Fe scrubbing step can be obtained with minimum generation of effluents:  
373 the total volume of waste aqueous phase generated represents only 20% of the volume of  
374 the organic phase. The final organic phase containing Pd can then be processed in order  
375 to recover Pd as a Pd(II) salt with classical techniques.

376

#### 377 3.4 Impact of chlorides and consequences for Pd recovery

378 Evaluation of the behavior of each metal in the solvent extraction step drove us also to  
379 evaluate the impact of the presence of chloride ions in the aqueous phase. Sn is poorly  
380 soluble in pure nitrate media, as Sn(IV) precipitates as mentioned beforehand. As a  
381 consequence it is difficult to evaluate its distribution coefficient with precision as  
382 concentration of Sn in the organic phase after extraction is below quantification limit. On  
383 the other hand, similar experiment performed with a Sn(IV) chloride solution leads to  
384 almost quantitative extraction of Sn. The influence of chloride ions was evaluated on 4 key  
385 metals (Pd, Ag, Fe and Sn, Table 5). It is clear that chloride have a negative impact on the  
386 process: i. they inhibit the leaching of Pd (see above) and lead to the precipitation of Ag, ii.  
387 they decrease the efficiency of Pd extraction, and the Pd/Fe selectivity as Fe is extracted  
388 more easily into organic phase, iii. they increase the solubility of Sn and the subsequent  
389 extraction of Sn in the organic phase. Altogether, the use of aqua regia is not only poorly  
390 suitable for leaching, but also for Pd recovery. Of course other extraction agents could be  
391 envisioned (Fontana et al., 2018), but Sn will require deeper studies as it is employed in  
392 the extraction of platinum group metals to increase their extraction efficiency: Sn(II)

393 chloride is a labilizing agent which is easily co-extracted with Pd or Pt in chloride media  
394 (Mojski, 1980). Furthermore, the use of a chloride solution to strip Pd from organic phase  
395 appears as a very interesting option for malonamides: With low distribution coefficient in  
396 the presence of chloride no specific Pd complexing agent will be required to strip Pd, from  
397 organic phase. Afterwards, Pd(II) salts can be easily precipitated from aqueous chloride  
398 solutions as Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> salt through classical process.

399 Altogether, the complete sequence is the following: i. chemical de-soldering, ii. Pd leaching  
400 from components, iii. Pd isolation through solvent extraction, iv. Pd precipitation as  
401 Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. The two last points are detailed in Figure 5 and Figure 6. A selected solution  
402 containing a high amount of Fe and Cu (along with other metals Ag, Ni, Pb, Sn, Zn and  
403 traces Al, Ba, Nd, Ti and Y, discarded for clarity) was employed and led to an aqueous  
404 solution containing 85% of the initial Pd amount with a 99,4% purity: traces of Fe were still  
405 quantified in this final Pd solution, Cu was below quantification limit, and other metals were  
406 not detected (Figure 6). This aqueous solution was further processed through successive  
407 addition of an ammonia solution and hydrochloric acid solution to lead to quantitative  
408 precipitation of Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> of characteristic yellow color. SEM, X-EDS and powder X-ray  
409 diffraction (PXRD) analysis confirmed the structure and the purity of the salt (Figure 5). No  
410 residual Fe was detected in the solid.

411

### 412 3.5 Regeneration of solvent

413 We chose not to fully back-extract (strip) Pd from the organic phase in order to minimize  
414 the volume of aqueous phase employed: 15% of the Pd remains in the organic phase.  
415 Theoretically, a 15% Pd hold-up in the extraction solvent should lead to a maximum 17%  
416  $(1 - 1 / 0,85)$  increase in the Pd loading in the organic phase after re-use of the organic  
417 phase for a new solvent-extraction cycle. Such a slight increase in Pd concentration

418 should not modify distribution coefficient nor extraction yield. Actually, re-use of this  
419 solution for a new extraction cycle led to quantitative Pd extraction from same initial  
420 aqueous phase. Organic phase Pd content is higher, and those of Fe and Cu do not vary  
421 significantly. Interestingly, no regeneration of the organic phase was required: usually,  
422 stripping the metal of interest with a strong chelator requires washing of the organic phase  
423 in order to perform a new extraction cycle. In the present case, possible traces of chloride  
424 did not alter Pd extraction. No other aqueous effluents are thus generated. Altogether,  
425 starting from one volume of aqueous phase, the same volume of organic phase is needed  
426 and can be re-employed in successive cycles, and effluents generated account for only  
427 30% of the initial volume to be treated.

428 The choice of solvent is the direct consequence of our former studies on such systems  
429 (Mastretta et al., 2019; Poirot et al., 2014). Using BDMA in toluene, we were able to tackle  
430 key issues related to the development of a solvent extraction process, i.e. low generation  
431 of effluents and solvent regeneration. Working on the worst possible case, i.e. a leaching  
432 solution of high Fe concentration, we obtained very satisfactory results. Our previous  
433 results demonstrate that the use of aromatic diluent is only motivated by the optimization  
434 of Pd/Fe selectivity (Poirot et al., 2016), and that otherwise Pd distribution coefficient and  
435 solubility in the diluent is marginally affected by shift to an aliphatic diluent (Poirot et al.,  
436 2014). As toluene is volatile, it would be much safer to use a higher boiling point diluent,  
437 such as an aromatic cut (e.g. Solvesso 150). Mixed aliphatic-aromatic cuts could also be  
438 employed, and it would also be interesting to investigate malonamide in purely aliphatic  
439 diluents when physical sorting of the waste guarantees low Fe content in the leachate. Any  
440 of these solutions would also definitely limit inhalation exposure to the toluene, a harmful  
441 substance.

442

443  
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## 447 **5. Conclusion**

448 Through this study, we demonstrated that efficient Pd recovery from waste PCBs can be  
449 performed at laboratory scale via an approach based on successive de-soldering, Pd  
450 leaching with dilute nitric acid, solvent extraction then precipitation. This approach takes  
451 profit of the quasi-exclusive location of Pd in MLCCs, and the fact that it is alloyed with Ag.  
452 It demonstrates that the systematic recourse to shredding and aqua regia is inappropriate  
453 for the recovering of Pd, as it will lead to more complex mixtures and leaching difficulties.  
454 Furthermore, the process benefits from previous work, e.g. regeneration of de-soldering  
455 baths, and complements existing strategies performed at small industrial scale to recover  
456 Au and Cu. Usually, when WEEEs are processed through hydrometallurgy, principal target  
457 metal is Au, and other precious metals and base metals are eliminated during a  
458 preliminary step in order to maximize Au leaching yield (Figure 7). The proposed process  
459 generates a final solid residue which contains still all (or almost all) the Au initially present  
460 in the product. This solid residue can be processed according to existing techniques, either  
461 directly in the Au leaching step, or with classical base metals dissolution (or even through  
462 pyrolysis and grinding for smelting processes). The process also enables selective  
463 recovery of Sn as a solid precipitate after dissolution of the solders. We demonstrated that  
464 the organic solvent can be re-employed without loss of performance and that the amount  
465 of aqueous waste generated is low (ca. 30% of the initial volume to be treated). We have  
466 not explored the possibility to recover Ag from this waste, but this option will be explored in

467 a near future. Pd is isolated as a Pd(II) salt, dichlorodiammine palladium(II)  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ ,  
468 with an excellent purity (no other trace metals detected). This salt is a key intermediate in  
469 Pd chemistry as its burning at ca.  $1000^\circ\text{C}$  leads to Pd sponge, basis for Pd fine chemistry.  
470 To our knowledge, this study is the first one to detail each step from waste PCBs to a key  
471 Pd intermediate at the laboratory scale, including outcome of by-products and effluents.  
472 Considering the forecasted increasing demand in Pd, such a process could be further  
473 developed and implemented at small industrial scale, i.e. on 10-100 kg of waste PCBs.  
474 This is the scale at which regional industrial players operate in the sector of precious  
475 metals recovery from waste. These are fully complementary to bigger actors that operate  
476 pyrometallurgical processes (Cu smelters). Of course further scale-up of the proposed  
477 process is conceivable, and operation of the solvent extraction steps with counter-current  
478 continuous mixer-settlers will lead to better performances. But the technological  
479 investment is higher, and the access to available waste PCBs may be a limit for cost-  
480 effective operation rate. Thus we suggest in a first instance not to start at a large industrial  
481 scale. Finally, this work, along with others mentioned in this article, strongly suggest  
482 players to seek for alternatives to systematic shredding and complete leaching. This  
483 approach, inspired by extraction of metals from natural ores, is not adapted to the  
484 management of wastes of high content in several metals, of much lower tonnage and  
485 diversity.

486

487

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492

Table 1: Summary of **previously published** studies dedicated to palladium recovery from waste PCBs.

Starting material	Physical treatment	Chemical pre-treatment	Leaching step	Pd purification	Pd compound obtained	Remarks	Reference
Disassembled components from waste PCBs.	Crushing, enrichment of metallic components with centrifugal air separator, grinding into metallic particles (94% Cu, 304 mg/kg Pd).	Enrichment through Cu dissolution with $\text{CuSO}_4$ and NaCl.	$\text{CuSO}_4 + \text{NaCl}$ ( $\text{Cu}/\text{Cu}^{2+} < 0.9$ ) Solution obtained: Pd 20 mg/L, Cu 7260 mg/L + traces Pb, Zn, Fe, Al, Ni.	SX with di-isoamyl sulfide, stripping with $\text{NH}_3$ solution	Pd(II) solution in ammonia (ca. 100 mg/L)	97% Pd recovery during the dissolution-extraction-stripping process, possibility to regenerate the solvent demonstrated.	(Zhang and Zhang, 2014)
Disassembled components from waste PCBs.	Shredding into metallic particles (18.5% Cu, 97 mg/kg Pd, 86 mg/kg Au).	none	$\text{CuSO}_4 + \text{NaCl} + \text{H}_2\text{SO}_4$ .	Not performed	Multimetallic solution (Cu, Fe, Ni, Ag), Pd).	58% Pd leaching.	(Yazici and Deveci, 2013)
MLCCs.	Grinding, sieving	Base metals leaching with concentrated HCl, then with $\text{HCl}/\text{H}_2\text{O}_2$ .	Concentrated $\text{HCl}/\text{HNO}_3$ at $80^\circ\text{C}$ .	Au precipitation with urea and $\text{Na}_2\text{S}_2\text{O}_5$ , then Pd precipitation with Zn dust. Then aqua regia redissolution, and sodium formate precipitation.	Not mentioned, probably metallic Pd	Max. 90% Pd leaching.	(Prabaharan et al., 2016)



MLCCs.	Grinding	None	<p>Concentrated HCl/HNO<sub>3</sub> at 25°C.</p> <p>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.</p>	SX with quaternary ammonium chloride (Aliquat336) in limonene, then precipitation with NaBH <sub>4</sub> .	Precipitate of metallic Pd and Ag, Ba and other metals.	<p>Purity depends on SX efficiency: best results given 98.8% Pd purity for 83% Pd recovery yield.</p> <p>Regeneration of extraction solvent not evaluated.</p> <p>The authors mention the use of a 10% w/w NaBH<sub>4</sub> solution in water, but in these conditions NaBH<sub>4</sub> decomposes with release of H<sub>2</sub>.</p>	(Fontana et al., 2018)
Waste PCBs.	Shredding, grinding.	Two steps base metals leaching with H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O <sub>2</sub> . Then Au leaching with acidic thiourea.	2 M HCl + H <sub>2</sub> O <sub>2</sub> and NaOCl.	Precipitation of both Au and Pd with NaBH <sub>4</sub> .	Metallic Pd and Au precipitate.	<p>Safety concerns regarding the process are not discussed, e.g. Mixing HCl with NaOCl generates Cl<sub>2</sub>, and adding solid NaBH<sub>4</sub> to an aqueous acidic solution leads to a violent reaction generating H<sub>2</sub>.</p>	(Behnamfard et al., 2013)

'Blast powder' (industrial waste from a semi-conductor processing unit).	None	None Composition of powder: metallic Ag/Pd alloy, with Al <sub>2</sub> O <sub>3</sub> .	No leaching	Liquid-liquid-powder extraction with dodecyl amine acetate in kerosene.	Enriched Pd/Ag particles	The technique focusses on the physical separation between Pd/Ag particles and Al <sub>2</sub> O <sub>3</sub> particles.	(Ponou et al., 2018)
Waste PCBs.	Shredding and crushing.	Supercritical water oxidation, then 0.1 M HCl leaching of base metals.	KI-I <sub>2</sub> in acetone and supercritical CO <sub>2</sub> .	Not performed	Mixture of Ag(I) and Pd(II) iodides in partially iodinated acetone.	Up to 94% extraction of Pd. Concentration of Pd containing solution not given.	(Liu et al., 2016)
Waste PCBs from mobile phones.	Shredding and grinding.	Supercritical water oxidation using H <sub>2</sub> O <sub>2</sub> , then leaching of base metals with diluted HCl.	Iodine-iodide (KI/I <sub>2</sub> at pH = 9)	Not performed	Mixture of Ag(I), Au(I) and Pd(II) iodides in water.	Detailed optimisation of process parameters. Concentration of Pd containing solution not given.	(Xiu et al., 2015)

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).

Composition of solution	Ag	Cu	Fe	Ni	Pb	Pd	Sn	Zn
Quantification limit (LoQ)	0,2	0,1	0,2	0,15	0,2	0,3	0,2	0,25
Bath after dissolution of solders	<LoQ	1400	70	180	730	<LoQ	40	<LoQ
After leaching of selected non-magnetic MLCC	205-968	0-4	0-135	5-41	59-300	38-193	2-24	<LoQ
After dissolution of selected magnetic components	1	2500	2650	3500	700	<LoQ	5	<LoQ
After leaching of components recovered after dissolution of solders	481	1940	970	350	172	98	33	37

Table 3: Distribution coefficients and maximum concentrations expected in organic phase after solvent extraction for unwanted metals present in leaching solution, of which HNO<sub>3</sub> concentration is 3 M.

<b>Metal</b>	<b>Distribution coefficient (D)</b>	<b>Maximum organic concentration (mg/L)</b>
Ag	0,04	7
Cu	0,015	32
Fe	0,24	88
Ni	0,01	2
Pb	0,02	12
Sn	(0,04) <sup>a</sup>	<LoQ
Zn	0,03	1

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<sub>3</sub> concentrations, and corresponding Pd/Fe selectivity.

<b>Aqueous [HNO<sub>3</sub>]</b>	1 mol/L	1,2 mol/L	1,5 mol/L	2 mol/L	3 mol/L
<b>D(Pd)</b>	1,7	2,5	3,7	6,1	27
<b>D(Fe)</b>	<LoQ <sup>a</sup>	0,001	0,003	0,024	0,24
<b>S<sub>Pd/Fe</sub></b>	n.a.	2500	1230	250	110

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 HNO<sub>3</sub> phase containing dissolved ions.

<b>Conditions</b>	<b>D(Pd)</b>	<b>D(Fe)</b>	<b>D(Ag)</b>	<b>D(Sn)</b>
No chloride	27	0,24	0,04	(0,04) <sup>a</sup>
1 M chloride	0,06	1,0	n.a. <sup>b</sup>	11,2

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.

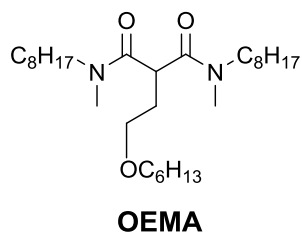
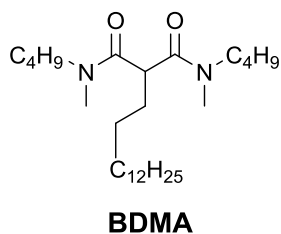


Figure 2: Details of printed circuit boards (PCBs) employed in the study, and location of palladium in multi-layer ceramic capacitors (MLCC) with electron microscope imaging of a MLCC transversal cut. Pictures of leaching step of the process and solids and solution obtained.

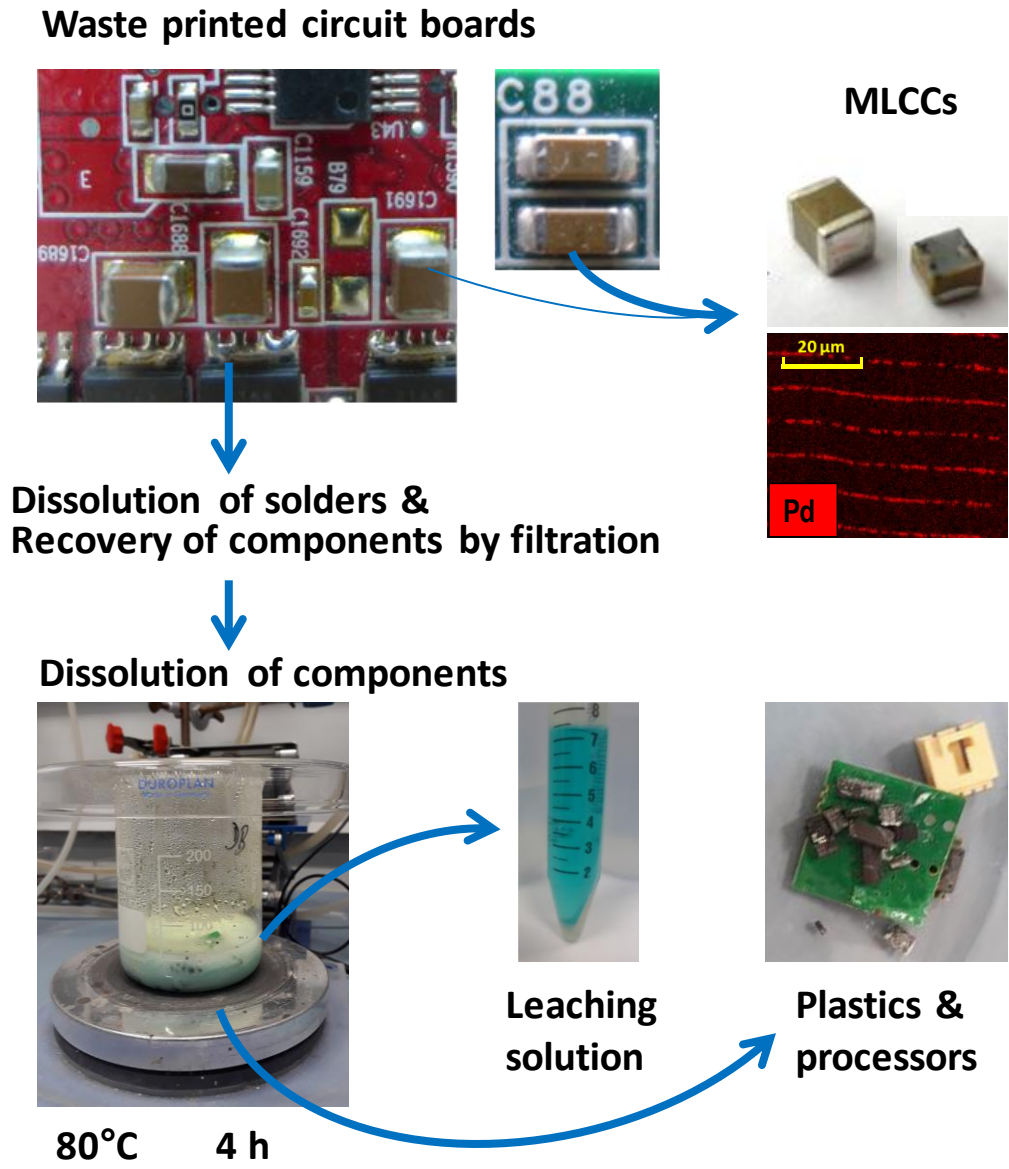




Figure 3: Results of iron elimination and palladium loss during scrubbing. Initial organic phase based on 0,6 M BDMA in toluene, containing Pd (196 mg/L) and Fe (97 mg/L), scrubbed with different aqueous solutions (H<sub>2</sub>O or 1,5 M HNO<sub>3</sub>) at different organic to aqueous phase volume ratios (O/A).

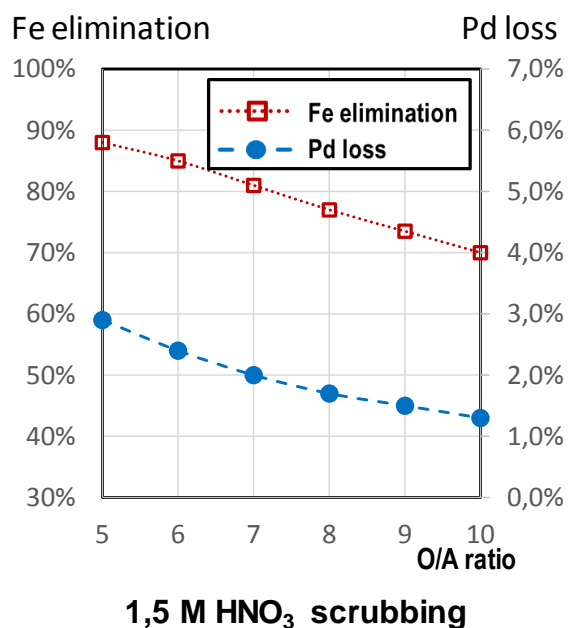
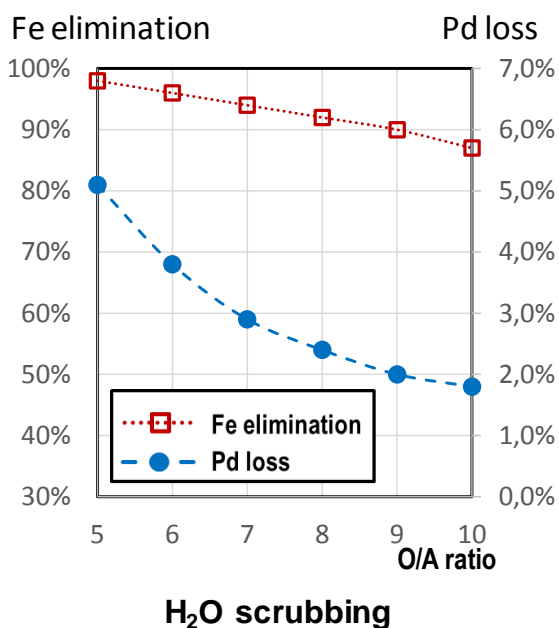


Figure 4: Detailed results of the scrubbing sequence optimization. Initial organic phase: 0,6 M BDMA in toluene, containing Pd (95 mg/L) and Fe (79 mg/L), scrubbed with different aqueous solutions (H<sub>2</sub>O or 1 M HNO<sub>3</sub>) at different organic to aqueous phase volume ratios (O/A). Two scrubbing stages were performed, at same O/A ratio but with possibly different solutions.

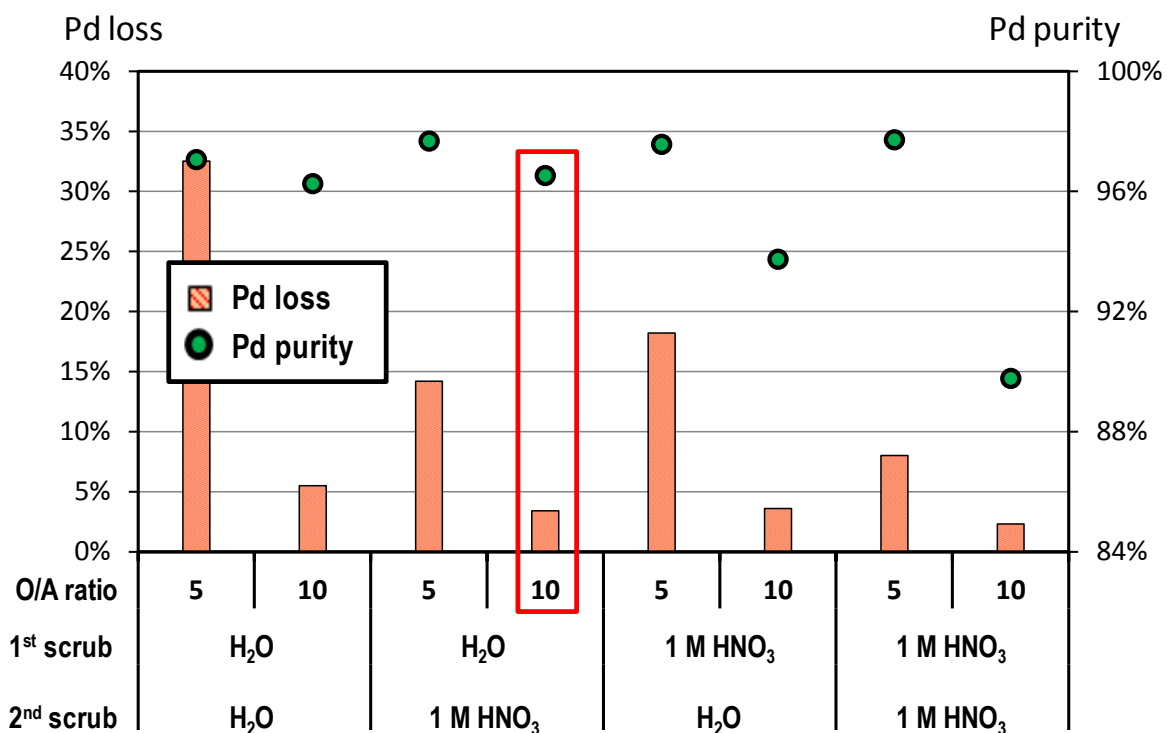


Figure 5: Flowsheet of the palladium recovery section of the process, along with obtained Pd(II) salt analysis (electron-dispersion analysis and powder X-ray diffractogram). N = number of stages; A/O = aqueous to organic feed ratio; O/A = organic to aqueous feed ratio.

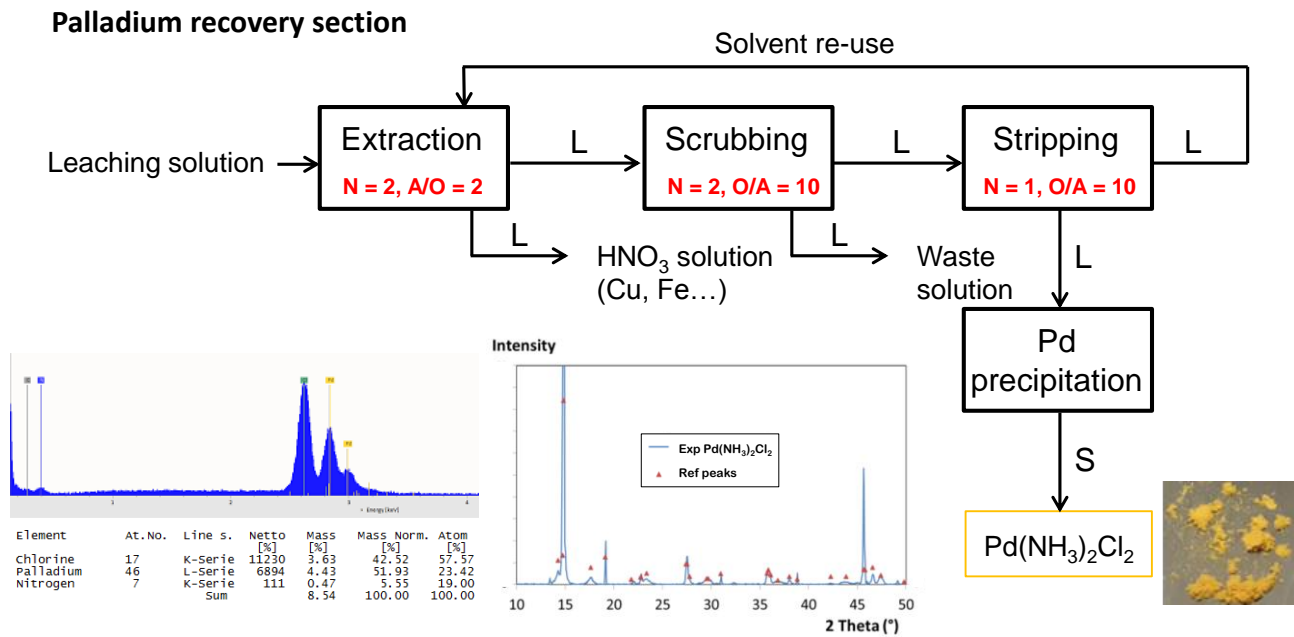


Figure 6: Detailed results of the solvent-extraction processing section of the palladium recovery process (data for other metals not shown for clarity).

**INITIAL AQUEOUS FEED**

**Aq. phase content**

Pd	98 mg/L
Fe	972 mg/L
Cu	1942 mg/L

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

Aq. phase content		Org. phase content	Extraction yield		
Pd	< LoQ	Pd	102 mg/L	Pd	>99%
Fe	795 mg/L	Fe	184 mg/L	Fe	19%
Cu	1916 mg/L	Cu	27 mg/L	Cu	1,4%

**Fe (and Cu) SCRUBBING H<sub>2</sub>O: O/A = 10**

Aq. phase content		Org. phase content	Loss/Extraction yield		
Pd	16 mg/L	Pd	101 mg/L	Pd	1%
Fe	1644 mg/L	Fe	20 mg/L	Fe	89%
Cu	250 mg/L	Cu	2 mg/L	Cu	93%

**Fe SCRUBBING 1 M HNO<sub>3</sub>: O/A = 10**

Aq. phase content		Org. phase content	Loss/Extraction yield		
Pd	30 mg/L	Pd	99 mg/L	Pd	4%
Fe	168 mg/L	Fe	3 mg/L	Fe	98%
Cu	5 mg/L	Cu	< LoQ	Cu	>99%

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

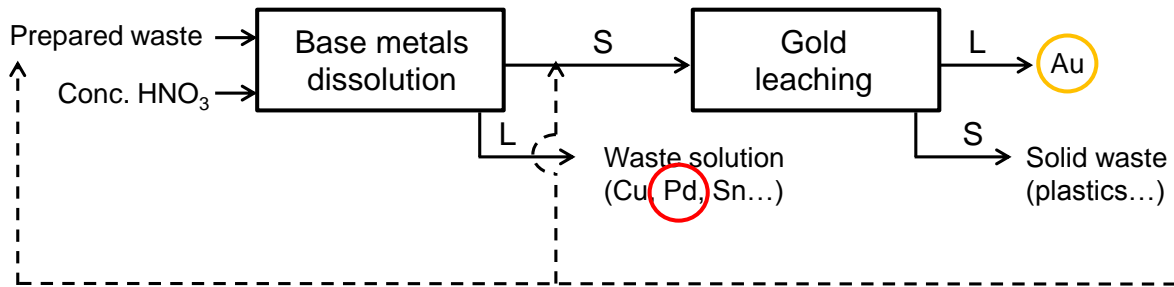
Aq. phase content		Org. phase content	Stripping yield		
Pd	854 mg/L	Pd	14 mg/L	Pd	85%
Fe	5 mg/L	Fe	2 mg/L		
Cu	< LoQ	Cu	< LoQ	<b>Pd purity</b>	<b>99,4%</b>

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

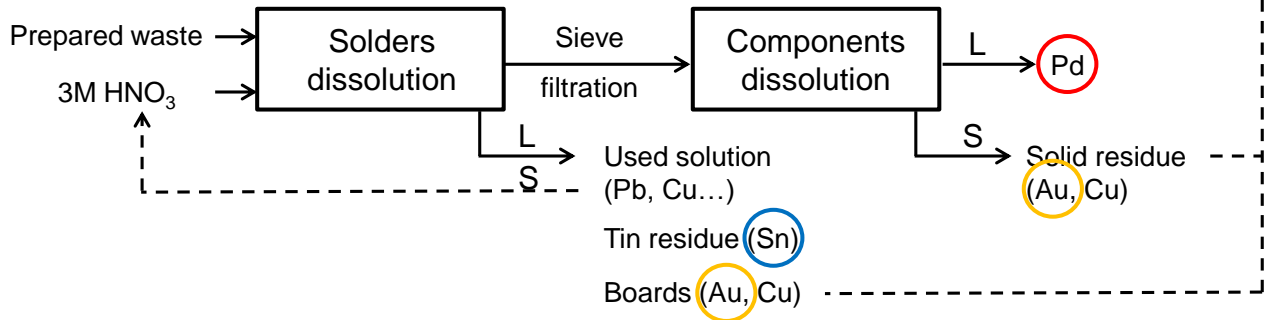
Aq. phase content		Org. phase content	Extraction yield		
Pd	< LoQ	Pd	116 mg/L	Pd	>99%
Fe	753 mg/L	Fe	222 mg/L	Fe	23%
Cu	1922 mg/L	Cu	23 mg/L	Cu	1,2%

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.

**Existing hydrometallurgical process**



**Proposed process for Pd recovery**



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