

# 1 Thermal Decomposition of Three Types of Copper Clad 2 Laminates Considering the Influence of an Iron-clay 3 Catalyst in the Production of Pollutants

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## 11 12 Abstract

13 Metal recovering through decomposition in the presence of steam of different wastes has  
14 been demonstrated to be an effective method. In the present work, three different types of  
15 copper clad laminates (FR4, CEM3 and ROGERS) were subjected to high temperature  
16 decomposition, analyzing their performance. Firstly, the samples were analyzed by  
17 thermogravimetry, both in the absence and in the presence of oxygen in the atmosphere; FR4  
18 and CEM3 showed a very strong interaction with oxygen, in contrast to ROGERS. Secondly,  
19 the laminates underwent oxidative pyrolysis in the presence of steam at 900 °C in a horizontal  
20 laboratory furnace; the experiments °were carried out in the presence and in the absence of an  
21 iron-clay catalyst, in order to evaluate its effect on the production of pollutants. Analyses of  
22 the produced gas and semivolatile species are shown, including polycyclic aromatic  
23 hydrocarbons (PAHs), bromophenols (BrPhs) and brominated dioxins and furans (PBDD/Fs).  
24 The gaseous emissions are almost limited to methane, hexane, toluene and xylene, and the  
25 production of PAHs and other semivolatile compounds is considerably reduced with the use  
26 of the iron-clay catalyst. The emissions of BrPhs and PBDD/Fs are also very limited.  
27 Comparing among the behavior of the three types of laminates, the emission of brominated  
28 compounds is much lower in the gasification of ROGERS, compared to FR4 and CEM3.

29 **Keywords:** copper clad laminates, printed circuit boards, dioxin, iron-clay catalyst,  
30 thermogravimetry.

31

## 32 **1. Introduction**

33 Nowadays a rapid technological development is observed in all kinds of sectors. For this  
34 purpose, engineers design composite materials which provide superior quality and long life  
35 span. The features of these materials contribute to many applications: electrical and  
36 electronic, defense and aerospace, automotive industries, ... Some of the most commonly  
37 used are laminates based on reinforcement of glass fiber, such as FR-4, CEM-3 and  
38 ROGERS4003 [1].

39 FR-4 are mainly composed of glass fiber combined with epoxy resin and with outer layers  
40 of copper, and are mainly used as a base of printed circuit boards in all types of electrical and  
41 electronic equipment, especially in mobile phones [2]. CEM-3, which are very similar to the  
42 most commonly used FR-4 ones, consist of a core of vitreous felt (non-woven glass fiber)  
43 with an outer layer of woven glass impregnated with epoxy resin, and coated copper on the  
44 base plates [3]. However, the amount of brominated epoxy resins (BERs) is lower compared  
45 to FR-4. The structure and composition of ROGERS4003 are also similar to FR-4, but consist  
46 of a woven glass reinforced hydrocarbon resin with ceramic filler, without brominated flame  
47 retardants (BFRs). Worldwide, there is a huge generation of scrap laminates from obsolete  
48 and discarded equipment, which are mainly landfilled, with the increasing problems  
49 associated to this practice [1]. Additionally, due to its heterogeneous structure and the  
50 presence of BFRs, waste printed circuit boards are problematic to recycle. Consequently,  
51 appropriate treatment approaches are being sought for these types of materials.

52 The process of thermal decomposition of laminates composed of multilayer plastics, resins  
53 and metals has been studied with the objective of extracting the metals without melting the  
54 system [4,5]. Decomposition in the presence of steam enables almost complete elimination of  
55 char from metals/inorganic structure and reduction (by catalytic conversion) of condensing  
56 oils and tars content in the product gas. PVC cables have been studied in this sense,  
57 presenting a good recovery of copper through decomposition of plastics at high temperature  
58 [6].

59 Currently, other methods to transform e-waste are being considered, but attention is mainly  
60 focused on thermal methods, which have been developed with printed circuit boards (PCBs)  
61 that mainly consist of FR-4 laminates with TBBPA (tetrabromobisphenol-A) acting as binder  
62 and flame-retardant [7-9]. Some researchers conducted conventional combustion process and

63 others used pyrolysis for the treatment of waste PCBs [10-15], focusing mainly on the  
64 characterization of solid residue and liquid.

65 Quan et al. [10] investigated the characterization of two products: pyrolytic oil and solid  
66 residue after pyrolysis of PCB waste, performed on a fixed bed reactor at 700 °C. De Marco  
67 et al. [11] conducted a pyrolysis process in an autoclave at 500 °C with four different  
68 electronic devices. Solid and liquid yields were also determined. They noticed polymer-free  
69 metals could be separated and recycled, and the liquids may be used as fuels or chemical  
70 source. Guo et al. [12] reported a thermogravimetric analysis and kinetic study on plastic  
71 particles of printed circuit boards. A fluidized bed reactor was also used for the pyrolysis of  
72 the samples, analyzing gas, liquid and solid residue yields. Hall et al. [13] achieved the  
73 separation of the organic, metallic, and glass fiber fractions of PCBs by means of pyrolysis in  
74 a fixed bed reactor at 800 °C. When heated, the organic fraction decomposed to form volatile  
75 oils and gases, whereas the metal and glass fiber fractions remained in the pyrolyzed residue,  
76 and were easy to separate. Vasile et al. [14] carried out runs with PCBs from obsolete  
77 computers using combined procedures of thermal and catalytic pyrolysis. Pyrolysis was  
78 performed by semi-batch operation at 300-540 °C. Two catalysts were used: CaCO<sub>3</sub>/cracking  
79 catalyst or CaCO<sub>3</sub>/cracking catalyst/Red Mud in 2.5:1 and 2.5:1:1 weight ratios, respectively.  
80 They noticed that catalytic pyrolysis decreased the amount of all heteroatoms (Br, Cl, N and  
81 O) in PCB oils. Besides, Guan et al. [15] investigated the co-pyrolysis of PCBs with calcium-  
82 basic compounds. The authors noticed that adding various calcium based waste, the copper  
83 foil was not corroded and the additive absorbed the HBr generated during the process.

84 Other authors focused on the pollutant production during the thermal decomposition of  
85 these materials. Tue et al. [16] pointed out the importance of avoiding uncontrolled recycling  
86 processes, due to the formation of hazardous dioxin-related compounds. Duan et al. [17]  
87 studied the formation of chlorinated and brominated dibenzo-p-dioxins and furans associated  
88 with the low temperature thermal processing of scrap printed circuit boards (PCBs). An  
89 important formation of brominated dioxins and furans (PBDD/Fs) was found at 250 and 275  
90 °C, both under N<sub>2</sub> and air atmospheres. Further research was reported by Ortuño et al. [7],  
91 who analyzed the pollutant emissions during pyrolysis and combustion of PCBs (without and  
92 with metal) at high temperatures: 600 and 850 °C. The extensive research provided  
93 information on the generation of halogen gases and hydrogen halides, gases and volatile  
94 compounds, semivolatile compounds (including bromophenols and PAHs) and PBDD/Fs.

95 Nowadays, studies on elimination of e-waste concentrate on decomposition in the presence  
96 of steam, which has been used for biomass either without catalyst [18,19] or with various

97 kinds of catalyst: Ni catalyst [20], Fe/olivine [21], dolomite [22-24], untreated olivine [22],  
98 clay catalyst with precursors [6,25]. Based on this knowledge, recycling methodologies of  
99 waste electrical and electronic equipment (WEEE) are being developed. Potential technology  
100 should aim to obtaining valuable solid residue with metals in its original form, the reduction  
101 of tars, oils and volatile compounds and production of a clean gas enriched with hydrogen.

102 Mońka et al. [26] dealt with the steam decomposition process of RAM memory waste  
103 under a steam flow at high temperature (750 °C for 1 hour, 790 °C for 20 minutes). The  
104 treatment was carried out on solid residue in its original form. The study showed that this  
105 process may be considered as a promising technology for WEEE recycling.

106 Salbidegoitia et al. [27] carried out the pyrolysis of phenolic boards in the presence of  
107 LNK-carbonate mixture ( $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  plus nickel powder) at different  
108 temperatures (550, 600 and 675 °C) to produce clean hydrogen. They observed that the  
109 addition of metal powder lead to a decrease of the organic matter content in the solid residue.  
110 Moreover, rates of hydrogen formation were accelerated when nickel powder was used.

111 Zabłocka-Malicka et al. [6] discussed the copper recovery from PVC multi-wire cable  
112 waste during thermal decomposition in steam atmosphere. They found that the organic  
113 fraction was completely removed from the wires after the treatment. Furthermore, copper was  
114 preserved in unmodified form and the rate of copper recovery was close to 100 %.

115 In the present study, three laminates: FR4, CEM3 and ROGERS4003 were analyzed in the  
116 thermobalance in order to characterize their thermal decomposition. Then, the samples were  
117 subjected to thermal decomposition, without and with iron-clay catalyst. This procedure has  
118 been demonstrated to be effective in the recovery of metals, but the pollutant production has  
119 not been considered so far. For this purpose, the gases, light hydrocarbons, polycyclic  
120 aromatic hydrocarbons (PAHs), brominated phenols (BrPhs) and brominated dioxins and  
121 furans (PBDD/Fs) were analyzed, with special attention to examine the influence of the  
122 presence of catalyst in the emissions of pollutants.

123

## 124 **2. Materials and methods**

### 125 *2.1. Laminates*

126 Three types of laminates were studied in the present work, FR4, CEM3 and  
127 ROGERS4003, supplied by an international company. To homogenize them, the samples  
128 were crushed by a vibratory disc mill by Herzog, HSM 100 (Osnabruch, Germany).

129 A CHNS analyzer (FlashEA 1112 Series, ThermoFinnigan) was used for elemental  
130 analysis, and the oxygen was obtained by difference. Also, the heating values of the samples  
131 were measured, using an AC-350 calorimetric bomb from Leco. Table 1 presents these  
132 results.

133 Equally, a semi-quantitative X-Ray fluorescence analysis was also performed using a  
134 Philips PW2400 X-ray fluorescence (XRF) Spectrometer. The results are shown in Table 2. In  
135 all materials, the main elements found were silica, calcium, aluminum and copper.

136 In order to obtain information about the content of halogens in FR4, CEM3 and  
137 ROGERS4003, EPA Method 5050 [28] was used, analyzing the obtained solutions by ion  
138 chromatography (Dionex DX-500). The amount of bromine (Br) was: 5.28, 3.77 and 0.004 wt  
139 %, for chlorine (Cl): 0.054, 0.035 and, 0.003, and fluorine (F): 0.038, 0.036 and 0.010,  
140 respectively. As expected, the amount of bromine is much higher in FR4 and CEM3, because  
141 of the presence of brominated flame retardants.

## 142 2.2. *Catalyst*

143 Natural alumino-silicate was gained from a small, local deposit in Dzierżoniów County  
144 (south-west Poland). Original raw clay was dried at ambient temperature and pulverized  
145 below 0.25 mm, and this was used for the formation of wet granules followed by drying and  
146 calcination. Preparation procedure was based on the one described by Miao at al. [29]. The  
147 clay and precursor powder: iron (III) oxide, Fe<sub>2</sub>O<sub>3</sub>, CAS 1309-37-1, pure POCH S.A. Poland  
148 (fractions below 0.25 mm) were mixed with polyethylene glycol (Carl Roth GmbH, ROTH  
149 600, molar mass: 570-630 g/mol) and distilled water in weight proportions of 22/44/12/22.  
150 The mixture was homogenized and granules with 5-6 mm diameter were formed and dried for  
151 24 hours at 105°C, then heated (in Nabertherm GmbH N 150 furnace) from ambient  
152 temperature to 950°C for 9 h, calcined for 3 h at 950°C and cooled down gradually to ambient  
153 temperature. Weight losses during drying and calcination were equal to 20 % and 30 %. The  
154 characterization of iron-clay granules (elemental composition and basic properties of catalyst)  
155 was described in the literature [25].

## 156 2.3. *Experimental setup*

157 On the one hand, thermogravimetric runs of samples were carried out on a Mettler Toledo  
158 TGA/SDTA851e/SF/1100 Thermal Gravimetric Analyzer. The decomposition temperatures  
159 were measured under dynamic conditions in pyrolysis (N<sub>2</sub> atmosphere) and oxidative  
160 pyrolysis (air atmosphere) with a total flow rate of 100 mL min<sup>-1</sup>. Dynamic runs were

161 performed at heating rates of 5, 10 and 20 K min<sup>-1</sup> for each atmosphere, from room  
162 temperature up to 1173 K. For each run 10 ± 0.3 mg of sample were used.

163 Besides, experiments were performed in a moving tubular quartz reactor located inside a  
164 horizontal laboratory furnace, described in detail elsewhere [30]. In all runs the temperature of  
165 the oven was 900 °C. The carrier gas (nitrogen) flow rate was 500 mL/min, maintaining a  
166 relative humidity of 85 % (details on the system have been previously reported [23]). Before  
167 each run started, the reactor was flushed for 0.5 h with the mix of steam and nitrogen.

168 Eight runs were conducted: three samples without catalyst and three with iron-clay  
169 catalyst, apart from one blank without and with catalyst. The catalyst was placed at the end of  
170 the reactor and maintained at the same temperature, 900 °C. The mass of the catalytic bed for  
171 each run was about 4.8 g, being the space of quartz tube occupied by catalyst ~8 cm.

172 In each experiment, fine powdered sample of laminates, in the amount of approximately 1  
173 g, was placed in two quartz boats and fed into the reactor at a constant speed (1 mm/s), once  
174 the set temperature had been reached. The samples were kept at this high temperature: 80 min  
175 for FR4 and CEM3, and 40 min for ROGERS4003. This was done in order to keep constant  
176 the ratio between the total amount of steam available and the carbon content of the sample, as  
177 the C content of ROGERS laminate halved that of FR4 and CEM3.

178 Gases were sampled every 10 min into Tedlar<sup>®</sup> bags (Restek, USA) and analyzed by two  
179 gas chromatographs, one equipped with flame ionization detector (FID) for light  
180 hydrocarbons between C1 and C8, and one with a thermal conductivity detector (TCD) to  
181 determine CO, CO<sub>2</sub> and N<sub>2</sub>.

182 Volatile products leaving the reactor were trapped into a quartz tube filled with Amberlite<sup>®</sup>  
183 XAD-2 resin (Sigma Aldrich, USA). After each run, the extraction of the resin was performed  
184 using a mixture of dichloromethane/acetone, 1:1 vol, as presented in previous work [7]. The  
185 analysis of the concentrated extracts was performed with HRGC-MS in the SCAN mode  
186 (m/z=35–550) with an Agilent HP5-MS (30 m × 0.25 mm i.d. × 0.25 μm) capillary column,  
187 using the U.S. EPA method 8270D for reference [31]. The results of polycyclic aromatic  
188 hydrocarbons (PAHs) and semivolatile compounds were quantified according to this method.  
189 Brominated phenols (BrPhs) were specifically analyzed in the SIR mode, and quantified by  
190 internal standard calibration, in a similar way to the 16 PAHs. The identification of each  
191 isomer was confirmed by checking the ratio between the areas of the primary and the  
192 secondary ions.

193 Furthermore, polybrominated dioxins and furans (PBDD/Fs) were also analyzed by  
194 collecting them in XAD-2 resin. <sup>13</sup>C-labeled internal standards were added to the resin prior to

195 extraction, which was performed with two different solvents (dichloromethane and toluene) in  
196 subsequent steps [32]. The extracts were concentrated in a rotary evaporator, diluted in n-  
197 hexane and purified in an automated Power-Prep system with silica, alumina and activated  
198 carbon pre-packed columns. Finally, the samples were analyzed in a HRGC-HRMS  
199 Micromass Autospec Ultima-NT, equipped with an Agilent DB5-MS (15 m × 0.25 mm i.d. ×  
200 0.10 μm) capillary column.

201 Before the decomposition runs, a control containing no sample was done using the same  
202 experimental condition (blank). This procedure was similar to that used in previous work [7],  
203 where it can be found the accuracy, precision and recovery of the methods used.

204

### 205 **3. Results and discussion**

#### 206 *3.1. Thermogravimetry*

207 Figure 1 presents the decomposition of the three laminates both in pyrolytic (nitrogen) and  
208 oxidative pyrolysis conditions (air). The runs were performed at three heating rates for each  
209 atmosphere and material. Note that for the mass fraction (y axis), the scale goes from 1 to 0.5,  
210 because the mass loss for these materials is not very high.

211 Thermal decomposition in inert atmosphere presents two different processes in the case of  
212 CEM3 laminate (centered around 275 °C and 400 °C), but only one process for FR4 (centered  
213 at around 320 °C) and ROGERS (approx. at 400 °C). The effect of the heating rate is similar  
214 in all samples, presenting a displacement to higher temperatures as the heating rate increases.  
215 This has been explained for other materials, being the kinetic law responsible for this behavior  
216 [23,33].

217 The effect of the presence of oxygen is also different for the different materials. The first  
218 stages of the decomposition of CEM3 in the presence of oxygen coincide with those presented  
219 in inert atmosphere. Nevertheless, the oxygen appears to strongly react with the pyrolytic  
220 residue of CEM3 decomposition, producing a fast weight loss.

221 The presence of oxygen strongly accelerates the decomposition of ROGERS laminates,  
222 although the weight loss at time infinity is similar both in the presence and absence of oxygen,  
223 so the oxygen does not interact very much with the solid residue.

224 FR4 laminate presents a decomposition in air that is accelerated with respect to the  
225 pyrolysis, but it seems that the decomposition is split into two different processes, one

226 centered at approx. 320 °C and the other at 400 °C. The similarity in the behavior of FR4 and  
227 CEM3 laminates indicates their similar composition, as mentioned before.

228 The total mass loss at the final temperature in the presence of air is an indicative of the ash  
229 content of the material, and correlates well with the data presented in Table 1.

### 230 *3.2. Analysis of gases evolved during the decomposition of laminates.*

231 During the decomposition runs in the reactor, gases were conveniently collected and  
232 analyzed. The analysis of the hydrocarbons by FID shows a very small amount of methane, n-  
233 hexane, toluene and xylene. Other compounds of low molecular weight present nil emission  
234 or close to zero (ethylene, propylene, benzene, among others). Details on the measured  
235 compounds are found in Figure 2. Note that the concentration is expressed in grams of  
236 compound per volume of gas, as the analyses were performed over different small samples of  
237 the gas sampled at different times along the experimental runs. As can be seen, the emissions  
238 are centered in the first part of the experiments, being the emissions of all species very small  
239 at time higher than 20 min. Figure 2 shows clearly that the presence of the catalyst reduces the  
240 emissions of hydrocarbons in almost all runs. Only the run performed with the ROGERS  
241 laminate does not present a clear decrease of the emissions in the presence of the iron catalyst.

242 TCD chromatography was used to analyze hydrogen and carbon oxides (CO and CO<sub>2</sub>). The  
243 amount of hydrogen produced during pyrolysis is very low (in the range 0.2-0.5 g/m<sup>3</sup>), and in  
244 most cases was not detected. The levels of carbon oxides found were in most cases near 2  
245 g/m<sup>3</sup> for CO and 5 g/m<sup>3</sup> for CO<sub>2</sub>, without a clear variation along time.

246 During the decomposition of the laminates presented, the formation of HBr and Br<sub>2</sub> is  
247 expected and is necessary to implement a system to eliminate it in a possible commercial  
248 system. Nevertheless, the formation of such pollutants has been studied before, especially  
249 from FR4 laminates [7], and does not present great difficulties to be eliminated.

250

### 251 *3.3. PAHs and semivolatile compounds*

252 The results of the emission of PAHs for the six runs (with and without catalyst) are  
253 illustrated in Figure 3; the experiments with iron-clay catalyst are marked in the Figure as 'C'.  
254 In these analyses, the whole amount of each compound is collected in the XAD-2 resin, so the  
255 emission is expressed as milligram of compound per kilogram of laminate decomposed.

256 In all runs, formation of PAHs was observed. In the first run of FR4 the total amount of  
257 PAHs was equal to 9950 mg/kg sample. The addition of calcined iron-clay catalyst led to a

258 decrease of pollutants in 1520 mg/kg. Laminate CEM3 produced around 14000 mg/kg PAHs  
259 during the decomposition, but the presence of iron increased effectively the conversion, and  
260 the total concentration dropped to 8300 mg/kg sample. The same situation was observed with  
261 ROGERS laminate, and after catalytic treatment with iron-clay granules the total  
262 concentration dropped from 11380 to 6380 mg/kg.

263 In each run, the most abundant PAHs detected were naphthalene, acenaphthylene,  
264 phenanthrene and fluorene. These compounds are identified in class 4 tars (light  
265 polyaromatic), as defined by Devi et al. [22]. As can be seen, after thermal decomposition at  
266 900 °C, the contribution of naphthalene is more than 30 % and 45 %, for CEM3 and  
267 ROGERS respectively, whereas the amount of naphthalene in FR4 is much lower (230  
268 mg/kg). The conversion of naphthalene over calcined iron-clay catalyst reaches a 14 %  
269 (CEM3-C) and 42.5 % (ROGERS-C). According to Devi [22] this low conversion may be due  
270 to the fact that naphthalene is a very stable compound, or also that the decomposition of PAHs  
271 with a higher ring number leads to the formation of naphthalene.

272 The amount of acenaphthylene decreased by a factor of 14 in FR4-C, twice in CEM3-C.  
273 Moreover, the smaller yields of fluorene and phenanthrene after the catalytic process led to a  
274 decrease in light PAH amounts. In this way, calcined iron-clay is reactive with respect to tar  
275 decomposition. This can be explained by the steam reforming reactions in the reactor, that  
276 reduces the tar in the exiting gas [22].

277 Table 3 shows semivolatile compound distribution. The decomposition process resulted in  
278 high yields of semivolatile compounds in the experiments without catalyst. The highest  
279 amounts were observed for FR-4 and CEM3 samples (5680 and 5550 mg/kg respectively), in  
280 contrast to ROGERS which only emitted 3390 mg/kg. The most abundant semivolatile  
281 compounds in each run were biphenyl, dibenzofuran, benzene and naphthalene derivatives,  
282 benzo[a]fluorene and benzo[c]fluorene.

283 As can be seen, in the presence of catalyst a great decrease is observed in the total amount  
284 of semivolatile compounds for FR4-C, CEM3-C, and a slight decrease for ROGERS-C.  
285 Semivolatile yields are 2760 mg/kg lower for FR-4, 2400 mg/kg lower for CEM3 and only  
286 470 mg/kg lower for ROGERS. These data show that oxidative atmosphere, which was  
287 described by Ortuño et al. [7] and also catalytic cracking lead to the destruction of these  
288 compounds.

289 *3.4. Bromophenols and PBDD/Fs*

290 As commented above, specific analyses of brominated phenols and brominated dioxins and  
291 furans were performed during the eight runs performed in the laboratory reactor.

292 Regarding the analyses of the brominated dioxins and furans (PBDD/Fs), the recoveries  
293 obtained for the labelled standards were within the ranges established for the chlorinated  
294 analogues [34], namely, 50 – 130 % for tetra- to hexachlorinated congeners, and 40 – 130 %  
295 for hepta- and octachlorinated congeners.

296 However, any of the samples presented detectable amounts of the brominated congeners.  
297 Considering the limits of detection (based on the response of congeners of the same  
298 bromination level present in the calibration solutions), the amounts of PBDD/F congeners, if  
299 released, would be less than 5 pg/g for tetra- and penta-BDD/F congeners, 20 pg/g for hexa-  
300 and hepta-BDD/Fs and 40 pg/g for OBDD/Fs.

301 When taking a conservative approach, and setting all nondetects to their detection limits, a  
302 total PBDD/F emission value of 210 pg/g is obtained, which corresponds to 18.6 pg  
303 WHO<sub>2005</sub>-TEQ/g in toxicity units. In order to calculate this last value, the Toxic Equivalency  
304 Factors (TEFs) for PBDD/Fs were assigned as those of their PCDD/Fs equivalents [35,36].  
305 This emission factor is more than 6 times lower than the observed during combustion of waste  
306 printed circuit boards at 850 °C in a similar horizontal laboratory reactor [7], and nearly 10  
307 times lower when comparing the toxicity of the emissions. In this sense, it seems that the  
308 presence of water at this high temperature produces the degradation of PBDD/Fs.

309 With respect to the emission of bromophenols, Figure 4 presents a summary with the  
310 evolution of these compounds at the different experimental conditions. The emission of total  
311 brominated phenols is quite low, in the range of 0.06 – 4.87 mg/kg in all runs. The more  
312 abundant congeners are mono-bromophenols (with bromine in the positions 2-, 3- and 4-),  
313 followed by di-bromophenols (2,4- and 2,6-congeners) and 2,4,6-tribromophenol. Laminate  
314 ROGERS presents a very low emission, as expected because it does not contain brominated  
315 flame retardants.

316 In previous studies [7], emissions of bromophenols in the pyrolysis and combustion of FR4  
317 printed circuits in the presence and in the absence of metals were studied in our laboratory. In  
318 these runs, the emissions of bromophenols during the pyrolysis at 850 °C was 830 mg/kg  
319 sample for the non-metallic fraction, and 4.7 mg/kg when the whole sample was used. In the  
320 case of combustion runs, 0.25-0.35 mg/kg were detected, similar to those measured in the

321 present work. These results point out the importance of the metals in the formation of such  
322 compounds, as well as the easy decomposition that is produced in oxidative atmosphere (both  
323 oxygen and steam). Nevertheless, the small values of bromophenols emitted are slightly  
324 increased in the presence of the iron-clay catalyst. Different authors[37] observed PCDD  
325 formation reactions on clay surfaces at much lower temperatures (< 200 °C) but these  
326 reactions could be also involved in the thermal decomposition conditions.

#### 327 **4. Conclusions**

328 The thermal decomposition and high temperature decomposition of three types of  
329 laminates (FR4, CEM3 and ROGERS) has been studied.

330 The thermogravimetric study reveals important differences in the form that the oxygen acts in  
331 the polymer matrices: on the one hand, FR4 and CEM3 show a very strong interaction with  
332 oxygen, whereas the weight loss in ROGERS laminates is similar both in inert and oxygen  
333 atmosphere.

334 When treating the laminates with steam at 900 °C, the gaseous emissions are reduced to  
335 methane, hexane, toluene and xylenes, with nil production of other hydrocarbons. It has been  
336 proved that the production of PAHs and semivolatile compounds is considerably reduced if  
337 iron-clay catalyst is used in the reactor. The emission of bromophenols is in any case very low  
338 (< 5 mg/kg sample), and can be somewhat affected by the presence of iron-clay, but no  
339 important differences were found. The emission of PBDD/Fs is in all runs well below 200  
340 pg/g. In general, the emission of brominated compounds is much lower in the thermal  
341 decomposition of ROGERS, compared to FR4 and CEM3.

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412 **Figure legends and Table captions**

413

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415 Table 2. X-ray fluorescence analysis of the laminates used in the present work.

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426

427 Table 1. Ultimate analysis of each type of laminate.

428

wt%	FR4	CEM3	ROGERS4003
C	24.5	25.1	12.6
H	2.1	3.1	1.4
N	0.6	1.1	nd
S	nd	nd	nd
O and ash (by difference)	72.8	70.7	86.0
HHV (MJ/kg)	10.48	9.68	5.94

429

nd: not detected

430

431

432 Table 2. X-ray fluorescence analysis of the laminates used in the present work.

wt%	FR4	CEM3	ROGERS4003
Si	16.26	13.52	30.30
Ca	9.81	4.00	3.28
Cu	5.87	3.81	10.24
Al	4.31	12.00	1.57
Mg	1.00	2.14	0.09
Ti	0.28	0.21	0.07
Fe	0.26	0.28	0.24
K	0.17	0.09	0.02
Na	0.14	0.09	nd
As	0.09	nd	nd
P	0.08	0.10	0.02
Ba	0.06	nd	nd
Sr	0.04	0.04	0.02
Zn	0.02	0.01	0.05
Zr	0.02	0.01	0.004
W	nd	nd	nd
Ce	nd	nd	nd
Cr	nd	nd	0.02

nd: not detected

433

434 Table 3. Distribution of semivolatiles during thermal decomposition.

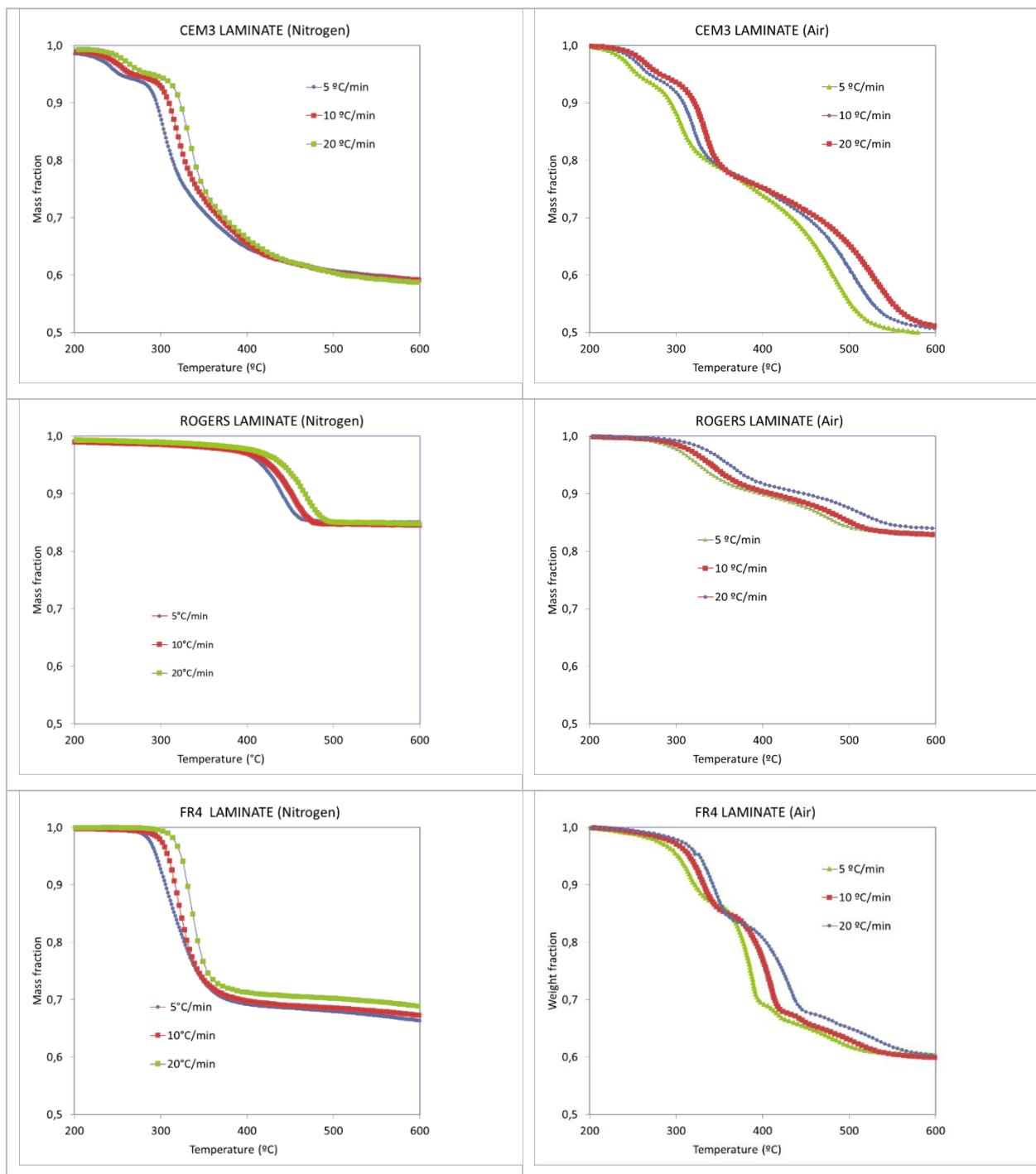
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Compound	FR4	FR4 C	CEM3	CEM3 C	ROGERS	ROGERS C
	mg compound/kg sample (ppm)					
2-pentanone, 4-hydroxy-4-methyl-	90	180	220	380	10	140
benzofuran	-	-	70	-	-	-
benzene, 1-propynyl-	-	-	140	130	160	290
benzofuran, 7-methyl-	-	-	20	20	-	-
benzofuran, 2-methyl-	-	-	50	50	-	-
benzene, 1,3-diethenyl-	-	-	-	-	20	-
benzene, 1,4-diethenyl-	-	-	-	-	20	-
indene, 3-methyl-	-	-	-	-	30	-
naphthalene, 1,2-dihydro-	-	-	-	-	20	-
1-methylene-1H-indene	-	-	-	-	30	-
1,4-dihydronaphthalene	-	-	-	-	10	-
naphthalene, 1-methyl-	60	90	280	150	190	470
naphthalene, 2-methyl-	100	70	280	150	100	290
biphenyl	470	640	530	410	550	330
1,1'-biphenyl, 2-methyl-	-	-	-	-	20	10
naphthalene, 2,6-dimethyl-	10	-	10	-	30	30
naphthalene, 1,7-dimethyl-	10	-	10	-	20	20
naphthalene, 2-ethenyl-	80	-	-	30	-	-
1,1'-biphenyl, 3-methyl-	80	30	60	40	50	40
1-isopropenylnaphthalene	40	50	50	40	40	20
1,1'-biphenyl, 4-methyl-	50	10	30	20	30	20
2-naphthalenecarbonitrile	60	30	90	50	-	-
2-naphthalenamine	30	-	20	10	-	-
dibenzofuran	250	340	310	230	10	30
9H-fluorene, 9-methyl-	90	20	50	-	100	70
phenalene	90	-	70	-	40	30
2-hydroxyfluorene	50	-	40	40	100	-
phenanthrene, 9,10-dihydro-	-	-	-	-	10	140
9H-fluorene, 1-methyl-	50	-	-	-	40	50
1,2-diphenylethylene	-	-	-	-	90	-
9H-fluorene, 2-methyl-	20	-	50	20	10	-
9H-fluoren-9-one, hydrazone	110	-	30	-	-	-
phenanthridine	50	-	60	-	-	-
naphthalene, 1-phenyl-	180	-	110	60	200	80
phenanthrene, 1-methyl-	70	20	60	30	60	40
phenanthrene, 2-methyl-	90	30	90	40	80	50
benzo[def]fluorene	310	40	270	100	190	100
phenanthrene, 3-methyl-	100	20	70	30	60	40
2-phenylnaphthalene	400	330	260	160	320	170
benzo[a]fluorene	440	-	340	140	140	90
triphenylene	50	50	40	20	30	20

benzo[c]fluorene	380	10	310	120	160	60
pyrene, 1-methyl-	70	-	80	20	110	10
benzo[c]phenanthrene	330	360	280	150	100	60
11H-benzo[a]fluoren-11-one	170	180	140	30	-	130
chrysene, 2-methyl-	90	10	80	10	50	-
phenanthrene, 2-phenyl-	130	130	100	10	130	-
9-phenylanthracene	100	40	70	30	30	10
13H-dibenzo[a,h]fluorene	120	-	110	-	-	-
11H-indeno[2,1-a]phenanthrene	200	-	150	-	-	-
pyrene, 1-phenyl-	130	20	80	30	-	-
benzo(a)chrysene	90	10	60	30	-	-
benzo[b]triphenylene	180	100	120	50	-	-
dibenzo(a,e)fluoranthene	130	70	140	50	-	-
dibenzo[a,e]pyrene	130	40	120	30	-	-
<b>Total</b>	<b>5680</b>	<b>2920</b>	<b>5550</b>	<b>3150</b>	<b>3390</b>	<b>2920</b>

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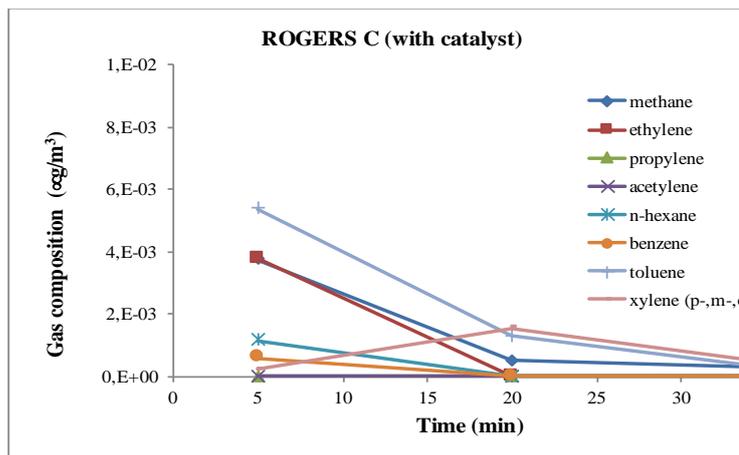
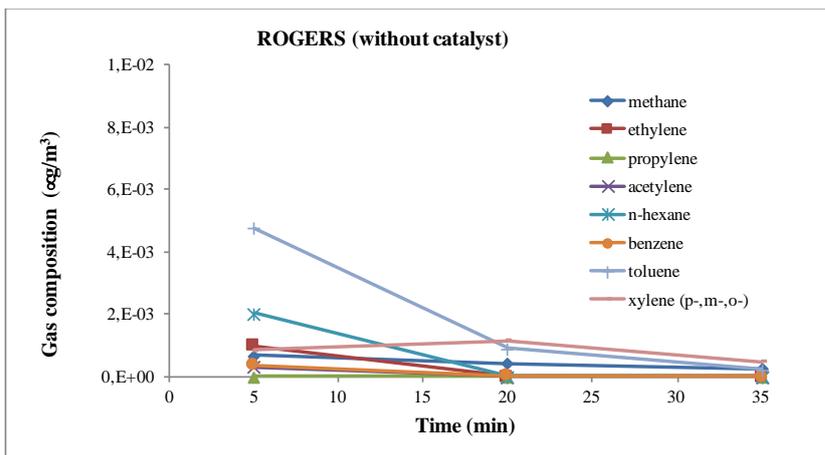
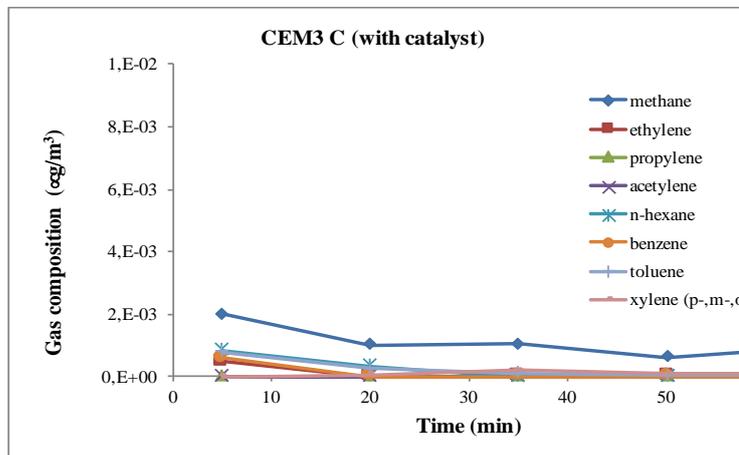
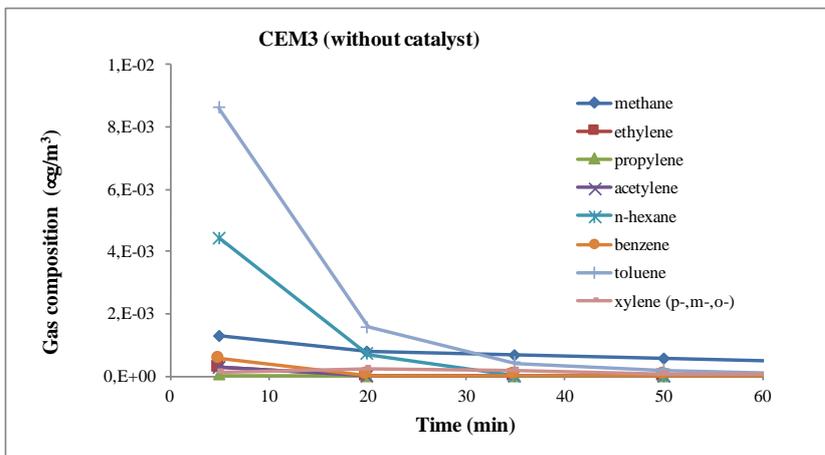
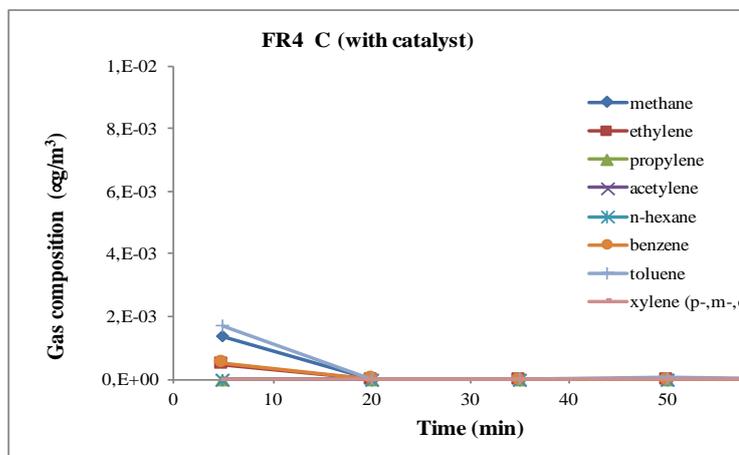
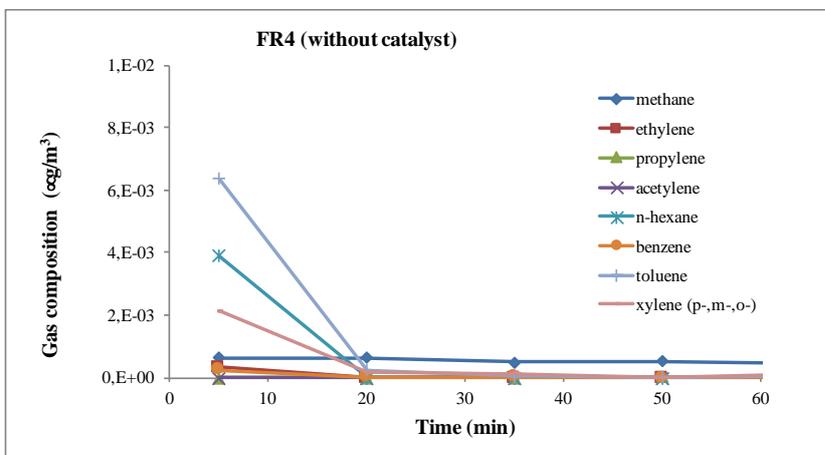
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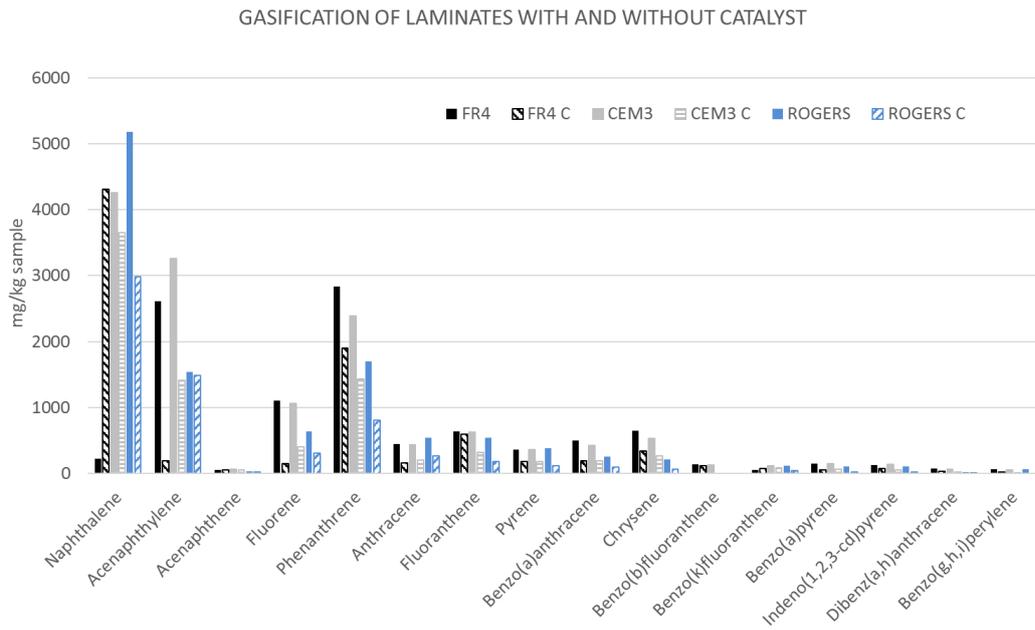


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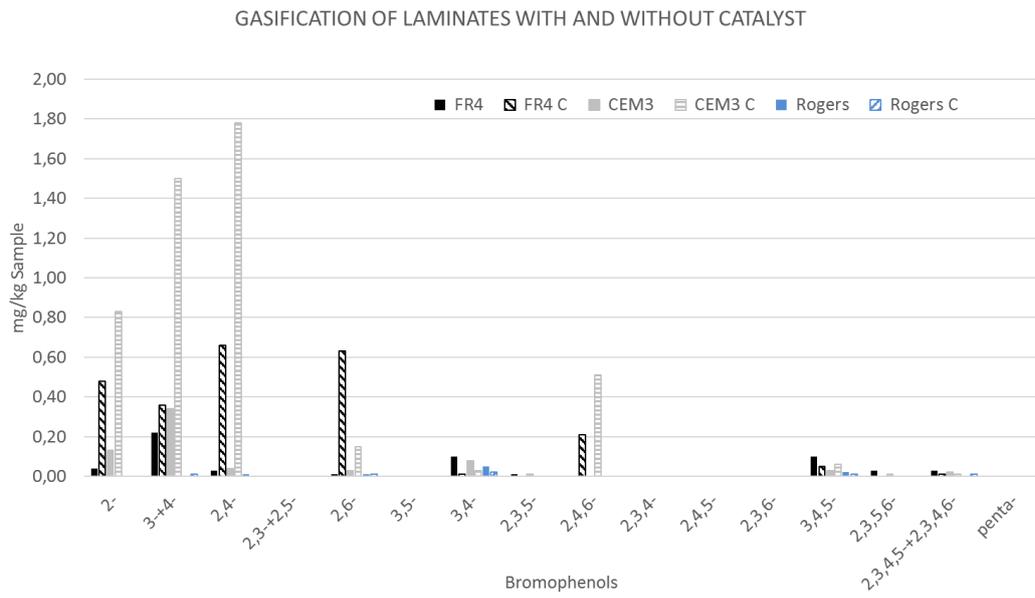


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456

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