Degradation products of the process of thermal recovery of copper from lamina scraps in lab-scale fluidized bed reactor

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Abstract

This paper presents experimental results dealing with a process for recovering copper in the scrap composite materials issued from electronic laminas industry. This environment-friendly process consists in the thermal treatment of scrap in a fluidized bed whose particles fix the harmful gases emitted by the organic glue gasification. A series of experiments was carried out in a thermobalance coupled to FTIR spectrometer and GC/MS with small lamina samples. These experiments demonstrated the thermal behavior of scrap composite materials, and identified the major degradation reaction gases. A series of experiments was performed with bigger scrap samples hung in a laboratory-scale fluidized bed coupled to FTIR and MS, at 350 °C; the results confirmed those obtained in thermobalance. Experiments showed that a residence time lasting less than 5 min is sufficient to recover the metallic copper, and exhaust gases are not harmful.
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1. Introduction

A lot of scrap materials are produced during the manufacturing of copper laminas or printed circuit boards production. These scrap materials, which represent about 8–10% of the total production, have to be discarded and the total world-wide production of copper lamina scraps can be estimated currently as thousands of tons annually. Until now, the problem of disposal was apparently solved, either by dumping or by incinerating these wastes with other industrial wastes, but the problem is now becoming critical. On the one hand, dumping will clearly become more and more difficult, especially in the EC because of the soon-to-be-applied regulations concerning residues. On the other hand, incineration is a technique leading to ashes, which contain many metals among other materials. These ashes must be disposed in costly controlled dumps since they are toxic, which is mainly due to the presence of metals, although the latter are in rather low concentrations which hinder their recovery. With no doubt, it is worth to develop recycling processes

since almost 30% of the scrap is metallic copper; moreover, in some cases there are several precious metals that might be retrieved also.

The literature survey shows that only a few processes attempting to recover copper and other worthy metals from electronic industry residues have been proposed. They can be classified into three main types: mechanical processes, chemical and electrochemical processes, and thermal processes [1–4]. Mechanical processes include erosion processing, splitting into small pieces, crushing, etc. Proposed chemical processes consist in dialysis inside chemical solutions, and electrochemical process consists in electrolytic Cu separation from printed circuit boards [5–7]. These two types of processes are rather costly. They only lead to a partial recovery of worthy metals, and they do not permit to recover other components such as resin and fiberglass, thus leading to a final residue which has to be dumped. So, they do have an impact on the environment, which may even be strong in some cases. Thermal processes developed for treating composite scrap materials are considered as the more classical ones [8–12]. They involve several heat transfer modes for destroying the cohesion between the metal plate surface and the insulating material surface: the scrap is superficially heated by radiation/convection, then the heat

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is transferred to the inner mass of the scrap by conduction. For example, a German-patented process [9] involves two flames, located opposite to each other, which heat up for a short time the moving lamina scrap surfaces. The lamina surface temperature reaches 400–500 °C, but the support material does not burn and the glue burns partially only. The result is a detached metallic plate that can be recycled, but since the technique does not permit to control precisely the inner temperature of the scrap, the burning of the organic compounds present in it cannot be controlled, and therefore the valorization of the recovered materials is more difficult.

Moreover, without an accurate temperature control, the scrap temperature may reach the critical value of 550 °C beyond which explosion risks exist.
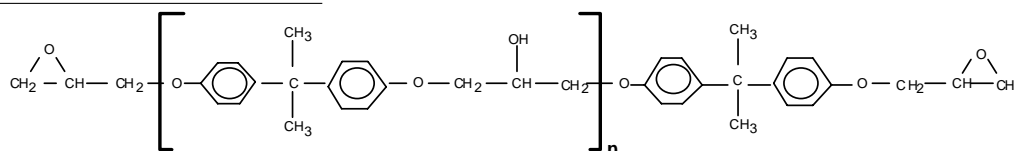

This paper presents the experimental results dealing with a new environment-friendly process for recovering copper from the scrap composite materials. This process consists in the pyrolysis of scrap inside a fluidized bed whose particles fix the emitted harmful gases due to the organic glue gasification. First, a series of experiments was performed in thermobalance with small lamina samples to get a better understanding of their thermal behavior and to identify the main degradation gases. Then, experiments were run in a laboratory-scale fluidized bed with bigger samples hung in a bed of selected material, in order to confirm the previous findings and to determine the required residence time in the reactor to recover the metallic copper.

2. Description of the lamina samples

A schematic view of a typical lamina sample is given in Fig. 1. Sandwich-type samples are composed of two 40 μm-thick copper plates, containing between them two 80 μm-thick glass fiber linens embedded in epoxy resin; the total resulting thickness of the lamina is 280 μm. Treated

samples were pieces of edges of new laminas, i.e. residues from a European manufacture of laminas for circuit boards; their average composition was (wt.%): 60% copper, 20% glass fiber and 20% organic material (epoxy resin). The resin involved in the manufacturing process is especially designed for electronic and electric applications that require a low level of polar impurities (inorganic chlorine, hydrolizable chlorine, α-glycol, etc.). It is synthesized from epichlorohydrin (C_3H_5ClO) and bisphenol A ($C_{15}H_{16}O_2$), and its main constituent is the bisphenol A diglycidyl ether ($C_{21}H_{24}O_4$; formula weight: 340.23 g) of formula:
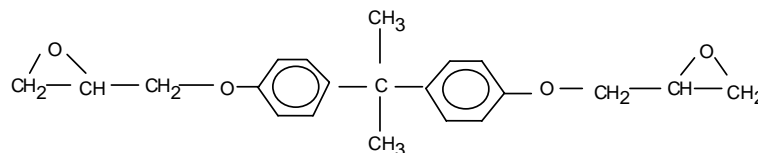
In fact, this resin is characterized by some distribution of molecular weight, and it can be symbolized best by the general formula:
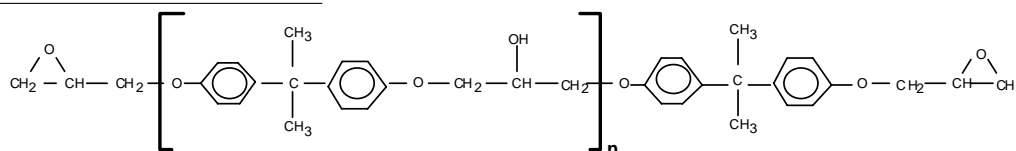
3. Experiments in electrical furnaces

3.1. Experimental setup

Two types of small-scale experiments were developed in electrical furnace, which involved respectively a thermobalance coupled to FTIR spectrometer and a tubular furnace combined to GC/MS.

3.1.1. Thermobalance coupled to FTIR spectrometer

The thermobalance was a TG-DTA 92 manufactured by SETARAM, coupled online by a insulated tubing to a Fourier transform infrared spectrometer (NICOLET, type MAGNA 550) equipped with a DTGS/KBr detector for gas analysis. The gas cell temperature was 200 °C, and the domain of wavenumbers 4000–650 cm^{-1} was studied. Coupling the thermobalance with an FTIR spectrometer appears to be a good way for studying the thermal behavior of scrap composite materials and for identifying the major degradation

Fig. 1. Schematic view of the lamina samples.

reaction gases. Experiments were carried out in the thermobalance under air (flow rate: 55 ml min^{-1}). The heating procedure was as follows: stabilization at 30 °C for 10 min, then increase up to 900 °C according to a 5 °C min^{-1} ramp.

3.1.2. Tubular furnace combined to GC/MS

A copper-free sample (weighing 40 g) was put in a quartz vessel that was set in the center of a quartz tubing heated by an electrical furnace. Gases due to the sample degradation were entrained by a nitrogen stream that was going through a series of two scrubbers (scrubber 1: 1% HNO$_3$ solution; scrubber 2: 1% NaOH solution). At the end of the experiment, both liquid solutions and the glassware washing solution were analyzed to determine the volatile compounds. Analyses were done on a chromatograph (HEWLET PACKARD, type 5890 II) coupled to a mass spectrometer (HEWLET PACKARD, type 5971). The chromatographic analysis was carried out in a HP-S-type column (30 m × 0.25 mm), and the carrier gas was helium (flow rate: 1 ml min^{-1}).

The injector temperature was 250 °C, and the GC/MS interface temperature was 300 °C. The heating procedure of the sample was as follows: stabilization at 40 °C for 5 min, increase up to 300 °C at 5 °C min^{-1}, then stabilization at 300 °C for 10 min.

3.2. Experimental results

3.2.1. Experiments in thermobalance

The results of the experiments carried out on scrap composite under air and at 5 °C min^{-1} consist in thermograms. Data processing of the thermograms shows that the degradation is a one-step exothermic reaction. The reaction begins at 288 °C and it ends up at 362 °C. At this temperature, the weight loss ranges between 18 and 22%.

3.2.2. Experiments in thermobalance coupled to FTIR

Experiments coupled to the FTIR spectrometer, carried out on a scrap composite material, pointed out the existence of a gas release phenomenon, which begins at 280 °C and ends up at 430 °C, with maximal intensity at 310 °C.

In this temperature range, all infrared spectra are identical, except for a slight fluctuation of the intensity of the different absorption lines. Four main gases were identified from the infrared spectra obtained at 310 °C; they were: phenol, 4,4′-isopropylidenediphenol ("bisphenol A"), water traces and carbon dioxide (representing totally 92 wt.%). Dichloromethane may be present, but there exists some uncertainty since the wave numbers of its two characteristic bands are very close to some bands existing in the IR spectra of phenol and bisphenol A. In a few experiments at T lower than 370 °C, HCl was found in small quantity.

3.2.3. Experiment in tubular furnace combined to GC/MS

The gas chromatography permitted to isolate 27 peaks corresponding to 27 compounds, as shown on the spectra displayed in Fig. 2 (glassware washing solution). Thirteen peaks (corresponding to 83.95% of the detected gases) were identified by the mass spectrometry analysis, whereas 14 peaks (16.05% of the detected gases) were not. Table 1 shows that among the detected compounds, phenol and its derivatives (74%) were found as major components, as expected, since they are components of the epoxy resin. Three brominated compounds were identified (7.56%) by the analysis of the TIC (total ion chromatogram) spectra, although the resin manufacturer did not mention the use of brominated precursors. Actually, this presence could be expected since classically the epoxide resin used for printed circuit boards is flame-retarded with some brominated compounds, such as brominated bisphenol A. Another series of experiments was performed on the cokefied residues obtained after thermal treatment of lamina scrap. In most cases, the residue
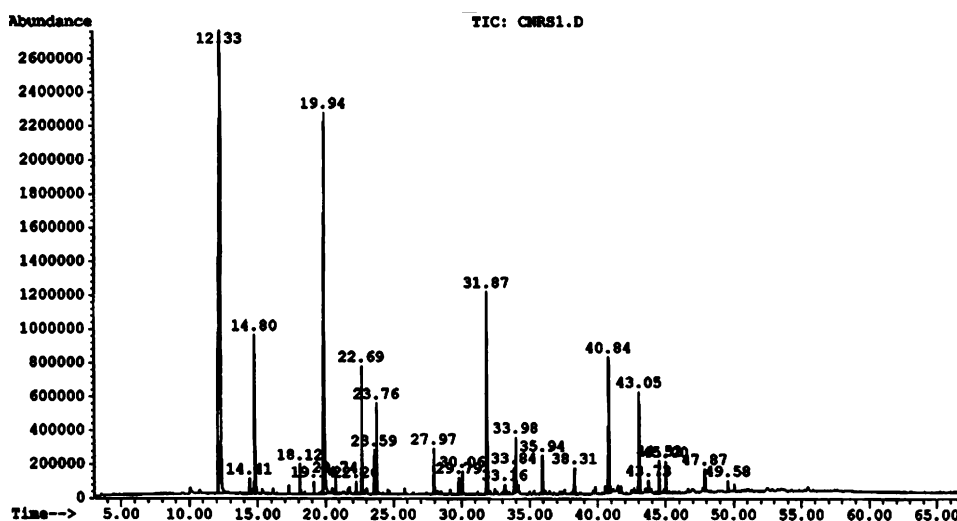

Fig. 2. Total ion chromatogram (TIC) spectra of the glassware washing solution.

Table 1
Summary library search report of the MS analysis of the spectra of the glassware washing solution

Peak no.	Retention time (min)	Area (%)	Library/ID	Quality
1	12.33	40.25	C:\DATABASE\NBS75K.L/Phenol	95
2	14.41	0.56	C:\DATABASE\NBS75K.L/2-Propanol, 1,3-dibromo-	90
3	14.80	4.49	C:\DATABASE\NBS75K.L/Phenol, 2-bromo-	97
4	18.12	0.93	C:\DATABASE\NBS75K.L/Phenol, 4-ethyl-	91
			Phenol, 2-ethyl-	91
5	19.14	0.29	C:\DATABASE\NBS75K.L/Phenol, 2-(1-methylethyl)-	94
6	19.93	18.53	C:\DATABASE\NBS75K.L/Phenol, 4-(1-methylethyl)-	95
7	20.74	0.44	C:\DATABASE\GCDEVAL.L/No matches found	
8	22.26	0.33	C:\DATABASE\NBS75K.L/Phenol, 4-(1-methylpropyl)-	91
9	22.69	3.21	C:\DATABASE\GCDEVAL.L/No matches found	
10	23.59	1.48	C:\DATABASE\NBS75K.L/2H-1-benzopyran-3-ol, 3,4-dihydro-	90
11	23.76	2.51	C:\DATABASE\NBS75K.L/Phenol, 2,4-dibromo-	96
12	27.97	1.41	C:\DATABASE\GCDEVAL.L/No matches found	
13	29.79	0.54	C:\DATABASE\GCDEVAL.L/No matches found	
14	30.06	0.59	C:\DATABASE\GCDEVAL.L/No matches found	
15	31.86	7.20	C:\DATABASE\NBS75K.L/*p*-Hydroxybiphenyl	97
16	33.17	0.70	C:\DATABASE\GCDEVAL.L/No matches found	
17	33.84	0.62	C:\DATABASE\GCDEVAL.L/No matches found	
18	33.98	1.58	C:\DATABASE\GCDEVAL.L/No matches found	
19	35.94	1.08	C:\DATABASE\GCDEVAL.L/No matches found	
20	38.31	0.90	C:\DATABASE\NBS75K.L/Phenol, 2-[1-(4-hydroxyphenyl)]-1-meth	91
21	40.83	5.61	C:\DATABASE\NBS75K.L/Phenol, 4,4′-(1-methylethylidene)bis-	98
22	43.05	3.43	C:\DATABASE\GCDEVAL.L/No matches found	
23	43.72	0.59	C:\DATABASE\GCDEVAL.L/No matches found	
24	44.52	0.87	C:\DATABASE\NBS75K.L/Phosphoric acid, triphenyl ester	99
25	45.00	0.87	C:\DATABASE\GCDEVAL.L/No matches found	
26	47.87	0.63	C:\DATABASE\GCDEVAL.L/No matches found	
27	49.58	0.34	C:\DATABASE\GCDEVAL.L/No matches found	

Search libraries: C:\DATABASE\NBS75K.L (minimum quality: 90); C:\DATABASE\GCDEVAL.L (minimum quality: 0).

releases a negligible quantity of adsorbed gases since the sample mass loss is not significant. Dioxins were never detected, although their presence in very small quantities might be expected (treatment temperature, catalytic properties of copper [13]). Indeed, in a few cases, several compounds, which may be precursors of dioxins, were found by mass spectrometry in very small quantity, too small to be detected by FTIR technique. So, the residue itself traps a part of the degradation gases.

4. Experiments in fluidized bed

4.1. Experimental setup

As shown on Fig. 3, the fluidized bed reactor developed by IMP-CNRS is a 0.0889 m i.d. and 0.4 m high refractory stainless steel tube. The gas distributor (porosity: 10%) consists in a metallic grid welded over a 1 mm thick perforated plate; in addition, the cone at the lower part of the reactor is filled with metallic chips to obtain a uniform distribution of the air over the reactor surface. The bed is heated by a set of two electrically heated collars, its temperature is measured by 4 K thermocouples, located at various heights, and it is controlled by a PID temperature controller. Collars heat the outside reactor wall, which transmits the heat to the fluid

bed by conduction/convection. The whole reactor is insulated with a 0.1 m thick rock-wool layer.

The fluidizing gas is air, issued from the laboratory-compressed air network, and it is heated up before entering the fluidized bed reactor through an electric resistance located after a rotameter, and pressure and temperature are measured for gas flow rate calculation. The bed is composed of narrow cut 450 μm mean diameter particles (400 μm < d < 500 μm) and the fixed bed height is 0.11 m. In this study, sand particles were mainly used, but other types of particles, such as lime or feldspar, were also considered. The pressure drop across the fluid bed is measured by means of pressure taps located at the reactor wall, which indicate the quality of fluidization during the experiments.

The reactor is equipped with a special device, which permits to introduce and hang the sample in the bed when at steady state. Finally, a system including a valve and a pump is set in the outlet gas circuit to maintain good conditions for gas analysis.

The carrier gas enriched with gases produced from the degradation reaction is transferred into the nearby FTIR spectrometer (NICOLET, type PROTÉGÉ 460 E.S.P.) through a 1 m-long heated and insulated tube in order to be analyzed. A DTGS/KBr detector is used for analysis, the gas cell temperature is 185 °C and the maximum flow is 181 min^{-1}. Like in the first series of experiments in-
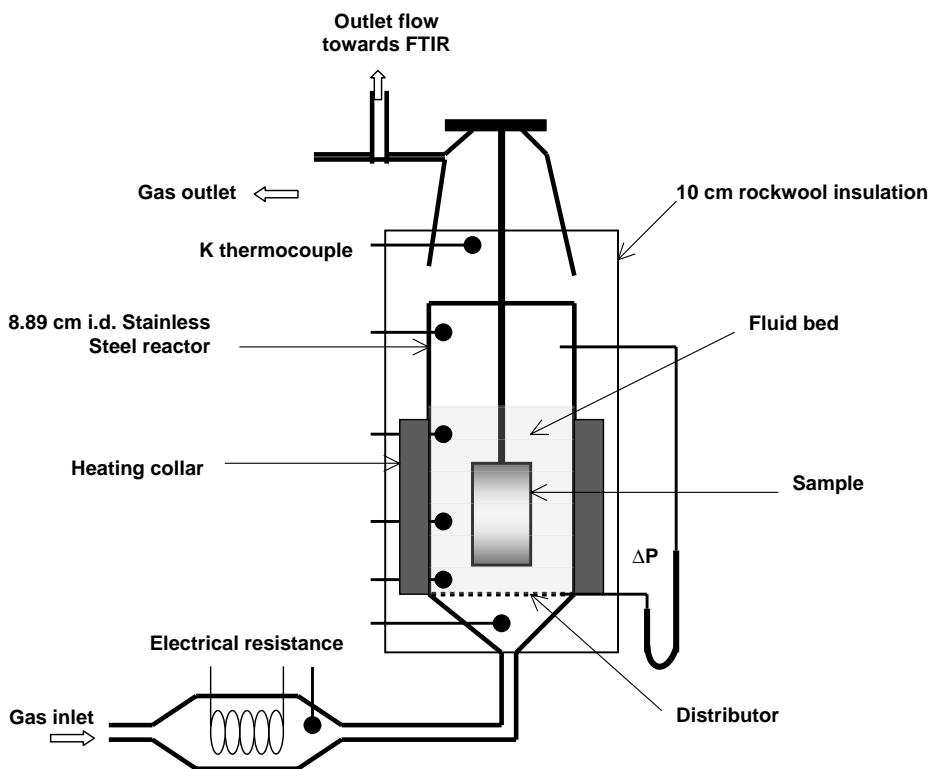
Fig. 3. Scheme of the lab-scale fluidized bed reactor.

volving the thermobalance coupled to FTIR, the domain of wavenumbers 4000–650 cm^{-1} is studied.

In another series of experiments, the outlet gas from the fluidized bed flows into a mass spectrometer (BALZERS, type QMG 511) that is set after the heated and insulated tube instead of the FTIR spectrometer. This technique, which consists in monitoring several specific mass peaks, is useful to study the kinetics of the release of harmful gaseous species.

4.2. Experimental results

4.2.1. Evolution of the sample temperature

Fig. 4 shows the temperature profile of a sample when introduced in the bed at 350 °C. The temperature is indicated
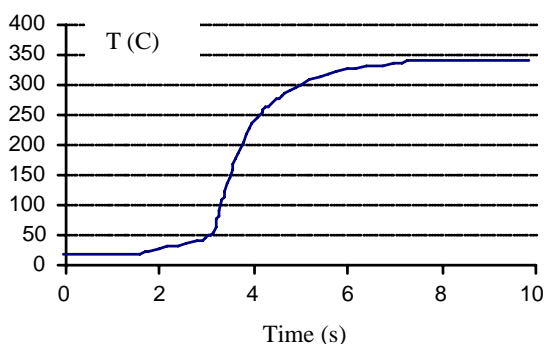

Fig. 4. Measured temperature profile of the sample.

by a K thermocouple welded on the lamina sample. Initially ($t < 0$), the sample is at ambient temperature ($T = 18$ °C); it starts increasing after a 2–3 s delay, then it reaches the bed temperature (350 °C) after nearly 5 s. The mean temperature ramp is about 60 °C s^{-1}, but the maximal slope, recorded between 3.2 and 4.2 s, is much higher (192 °C s^{-1}).

4.2.2. Influence of the residence time

All experiments were run at the same gas velocity equal to the minimum fluidization velocity ($U_{mf} = 0.52$ m s^{-1}), that is to say at constant gas flow rate (3.6 N m^3 h^{-1}); three residence times were considered: 2.5, 5 and 10 min.

The FTIR analysis confirmed the results from the study previously developed in thermobalance, independently of the sample residence time. Indeed, the major degradation gases were identified as (Fig. 5): phenol, 4,4′-isopropylidenediphenol (bisphenol A), water traces and carbon dioxide (totally 93 wt.%). Again, dichloromethane presence is possible but not sure, because of the uncertainty on the peaks existing at its characteristic wave numbers, as shown on the spectra given in Fig. 5.

Moreover, the intensity of infrared spectra proves that the degradation reaction is complete for a residence time shorter than 5 min (in our experimental conditions).

The study was then focused on the phenol since it is the main possibly harmful gaseous species released by the resin degradation. The kinetics of the phenol release and of the chlorine release are shown in Figs. 6 and 7, respectively,
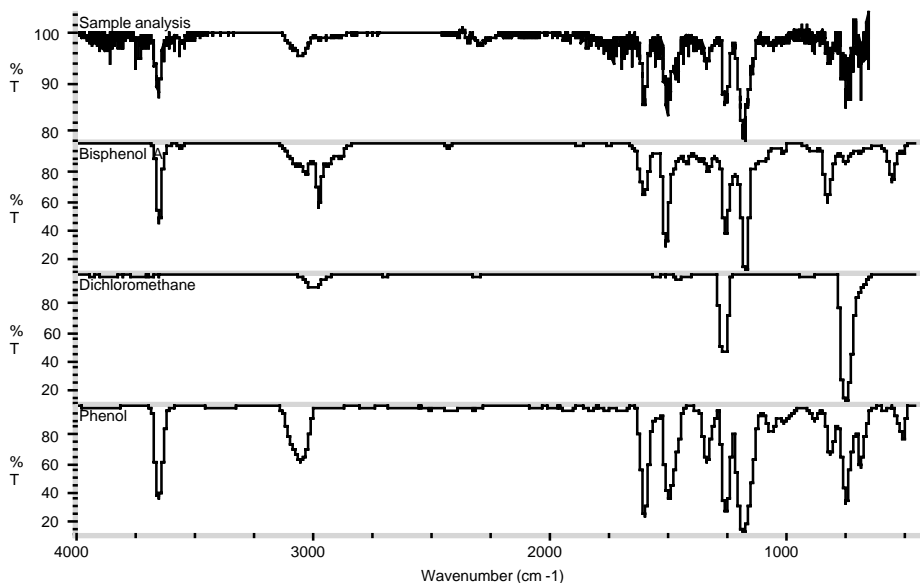
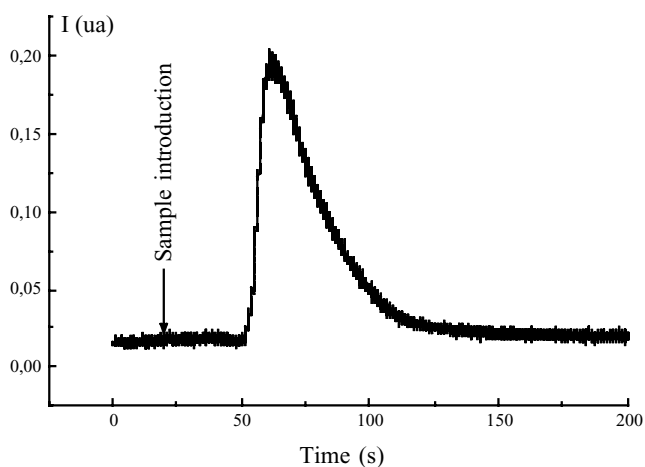Fig. 5. Infrared spectra: (1) experimental; (2) phenol; (3) 4,4′-isopropylidenediphenol.

obtained by coupling the mass spectrometer to the fluidized bed reactor gas outlet. Taking into account the time required for gases to go from the reactor to the mass spectrometer, phenol is detected first 15 s after introducing the lamina sample into the bed, and the detection lasts almost 2 min (110 s). Molecular chlorine is detected first 20 s after the sample introduction and the detection lasts a little bit longer (145 s). Afterwards, none of them is detected.

Fig. 8 shows a series of pictures of a lamina sample: before treatment (A), after thermal treatment in fluidized bed (B) and after separating the two copper sheets from the glass fiber sheets (C). As can be seen in Fig. 8B, at the end of the thermal treatment, sand particles are clustered on the edges of the sample with some organic glue (epoxy resin) rests. Then, the copper sheets can be very easily peeled off from the glass fiber sheets (Fig. 8C).

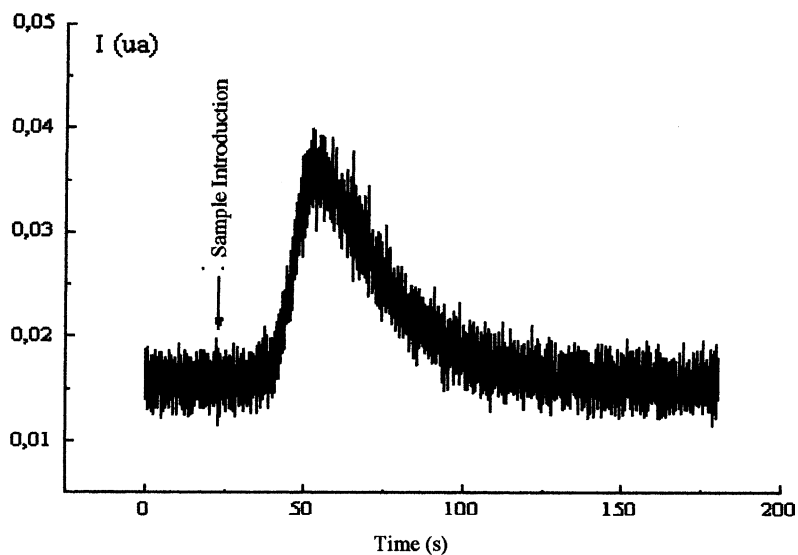Fig. 6. Kinetics of the phenol release (monitoring of the mass 94 peak).

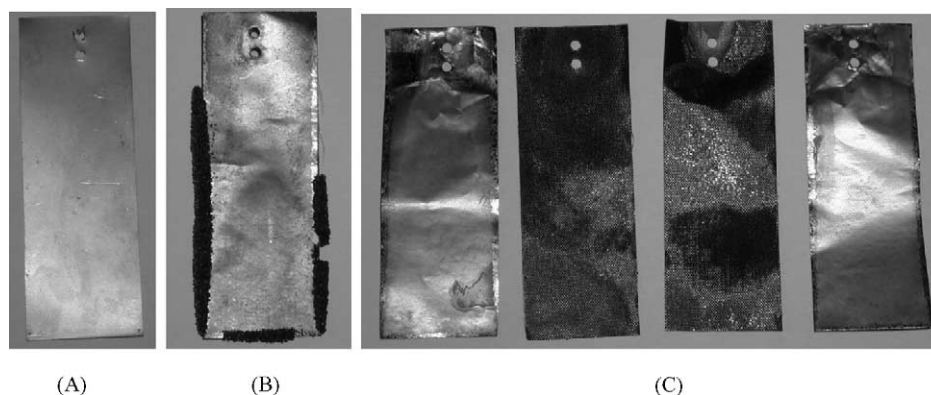Fig. 7. Kinetics of the chlorine release (monitoring of the mass 35 peak).

Fig. 8. Photographs of a lamina sample before treatment (A), after treatment (B) and after separating copper plates from glass fiber linens (C).

4.2.3. Influence of the gas velocity

Another series of experiments was run for a given residence time (5 min), and three gas velocities were considered (0, $1.5U_{mf}$ and $2U_{mf}$). The same five gases were found again by FTIR analysis: the gas velocity seems to have no influence on the degradation gas composition. For industrial application, the lowest possible gas velocity will be chosen in order to reduce the size of the post-process gas treatment device.

4.2.4. Influence of the bed material

The influence of the fluid bed material on the volume of released gas is important, as it was shown by a series of experiments with adsorbents such as lime and feldspar particles instead of sand with the same mean diameter (450 μm). When using feldspar, the reduction of gas release is 20% whatever be the treatment temperature. When using lime, the reduction ranges between 5 and 29% when the temperature varies between 350 and 450 °C.

5. Conclusion

The objective of this study was to set up an environment-friendly process to recover copper from lamina scraps. Experiments were performed both in electrical furnace (thermobalance and tubular furnace) and in lab-scale fluidized bed.

The thermobalance study showed that the degradation reaction begins at 288 °C and it is completed at 362 °C, with a 18–22% weight loss.

In the series of experiments performed both in thermobalance and fluidized bed, the identification of the main gases due to the degradation reaction was done jointly by FTIR and GC/MS or MS techniques. The released gases are mostly phenol and several derivatives (74%), and possibly dichloromethane. In addition, compounds which may be dioxin precursors (8%) are also released, although dioxins were never detected. Brominated compounds were put into evidence by GC/MS in several experiments: such com-

pounds are classically used as flame retardant in epoxy resin. The amount of phenol is high, as expected, since it is the main epoxy resin compound. The temperature ramp (5–30 °C min^{-1} in thermobalance and 360 °C min^{-1} in fluidized bed) has a slight influence on the characteristic temperatures, but no significant influence was observed on the degradation reaction (released gases are the same) and on the final weight loss.

Experiments in fluidized bed at 350 °C confirmed the results of the study in thermobalance. The best residence time of samples in the fluidized bed for copper recovery is less than 5 min.

This study is a first step towards a process for copper recovery from lamina scraps. A study is currently in progress to select the best type of particles for fixing by adsorption the harmful gases emitted by the organic glue gasification, and experiments are also run on a pilot-scale fluid bed reactor [14].

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