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Waste electric and electronic equipment (WEEE) melting and resulting gases processing in microwave field

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Abstract: The recycling of waste electric and electronic equipment (WEEE) is of great interest due to the large amounts of such wastes and to their contents of useful and precious metals. After reaching the end of its service lifetime, WEEE is collected and recycled through various processing methods, depending on the waste type.

Pyrometallurgy is currently the most used method for the recovery of the metallic fractions from WEEE such as printed circuit boards (PCBs). This type of processing raises major issues because of the generated gas emissions. The non-metallic fraction of the PCBs, which account for a large proportion (50-70 wt.%), contains brominated flame retardants, thermosetting resin, reinforced materials and other toxic and hazardous organic substances. The combustion of these chemicals during the pyrometallurgical processes may cause serious health-related and environmental problems. In this paper, the treatment in microwave field of the toxic gases resulted from the melting of crushed PCBs has been preliminarily investigated. During the waste melting in a microwave furnace, toxic compounds such as benzene (3.2-6.5 $mg \times m^{-3}$), toluene (15.3-17.8 $mg \times m^{-3}$), ethylbenzene (2.8-5.7 $mg \times m^{-3}$), styrene (21.5-24.3 $mg \times m^{-3}$), m/pXilen (1.4-2.8 $mg \times m^{-3}$), naphthalene (1.1-1.3 $mg \times m^{-3}$) and 1,3,5 trimethylbenzene (15.2-23.5 $mg \times m^{-3}$) have been detected in the effluent gases. The treatment was carried out by passing the resulting gases through a filter fabricated from a microwave susceptor granular material (SiC), placed in a microwave transparent tube (fused quartz, 5 cm diameter). For heating the filter, a number of 3 magnetrons (2.45 GHz frequency and 850 W power each) were mounted outside the fused quartz tube at an angle of 120 degrees and in different geometrical planes. The influence of the process parameters (heating response of the susceptor materials, temperature, gas flow, gas pressure) was investigated. It was observed that the temperature of the filter (i.e. the power density in the microwave susceptor material) has a major influence on the neutralization of the toxic compounds while the gas flow and pressure had a minor influence. At a temperature of 1350-1400˚C (power density of 5000 $W \times kg^{-1}$), a gas flow of 150 $m^3 \times h^{-1}$ and a pressure of 800-1000 mbar, the content of such substances in the gases was reduced below the legal limits.These results confirm the feasibility of the process of treating the gases resulting from the melting of e-waste in a microwave furnace.

1. Introduction

The rapid technological advancements in the consumer electronics industry lead to the faster replacement of current products, generating high amounts of electrical and electronic equipment waste (20 to 50 million tones/year worldwide). The recycling of waste electric and electronic equipment (WEEE) is of great interest due to the large amounts of such wastes and to their contents of useful and precious metals. After reaching the end of its service lifetime, WEEE are collected and recycled through various processing methods, depending on the waste type.

Amongst WEEE, the printed circuit boards (PCBs) represent a very important source of nonferrous (Cu, Al, Fe, Ni, Pb), rare and precious metals (Au, Ag, In, Sr, Ta, etc.), but especially of Cu and Au [1,2,3]. The frame of the printed circuits represents approximately 23% of the PCB's weight [4,5]. The copper (20%) and gold (250 g/t) contents in a printed circuit board used in common computers are much higher than those existing in an ore, respectively 20-40 times (Cu) and 25-250 times (Au) higher [4,5]. Printed circuits are present in a wide range of electronic equipment and small-sized home appliances: electronic instruments, toys, sports gear, etc. The frame boards have an inhomogeneous chemical composition and a complex structure, containing approximately 50÷55% organic components and 45÷50 % metallic fraction.

As e-waste also contains toxic metals (cadmium, mercury, etc.) and organic pollutants, their processing represents an important issue in respect to the EU environmental policies. WEEE processing for the recovery of the component metals is a subject which generated various studies and which also led to the development of technologies for metals separation/obtaining.

Pyrometallurgy is currently the most used method for the recovery of the metallic fractions from WEEE such as printed circuit boards (PCBs) [6-8]. This type of processing raises major issues because of the generated gas emissions. The non-metallic fraction of the PCBs, which account for a large proportion (50-70 wt.%), contain brominated flame retardants, thermosetting resin, reinforced materials and other toxic and hazardous organic substances. The combustion of these chemicals during the pyrometallurgical processes may cause serious health-related and environmental problems [9-12].
In this paper, the treatment in microwave field of the toxic gases resulted from the melting of crushed PCBs has been preliminarily investigated.

2. Experimental

The electronic wastes used in the experiments came from the dismantling and grinding of printed circuit boards (PC, radio, TV, mobile phones etc). The comminuted material was melted in a microwave field in inert atmosphere (Ar). Microwave melting presents a series of advantages, such as rapid heating cycles with energy savings of approximately 35%, compared to conventional melting methods; an improved process control; no direct contact with the heating materials; the possibility of processing various nonferrous metals containing wastes (WEEE, Al and brass, etc.) for the recovery of constituent metals with high efficiencies (94÷96% for the multi-component alloy). This innovative method allowed the complete and efficient separation of the metallic fraction and the organic components.

The printed circuit boards were grinded down to sizes of approximately 0.5÷2 cm and melted in an experimental installation, in the following conditions:
- Three microwave generators of 800 W capacity each, placed circularly on the furnace casing;
- Working temperatures of 1000÷1200°C;
- Temperature measurement using a Pt/Pt-Rh wire thermocouple;
- Time: approx. 30 minutes;

The technological flow-chart is presented in figure 1.

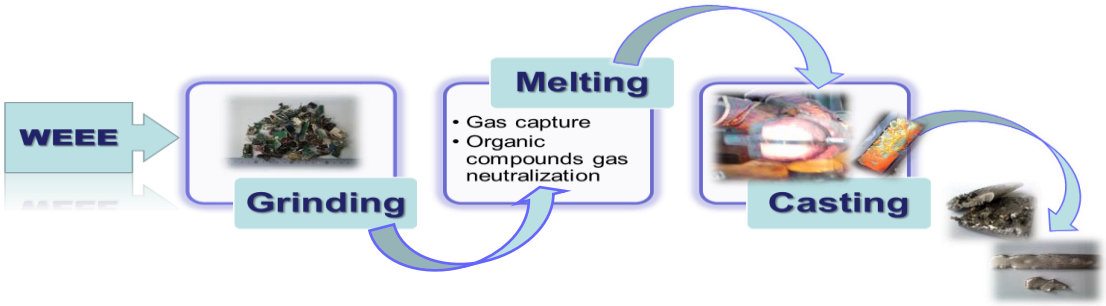

Figure 1. Technological flow-chart of the WEEE microwave melting.

The experimental melting installation is composed from the steel casing, on which three microwave generators are placed outwardly (figure 2). The microwave susceptor silicon carbide crucible, in which the metallic waste is placed, is situated inside the furnace.

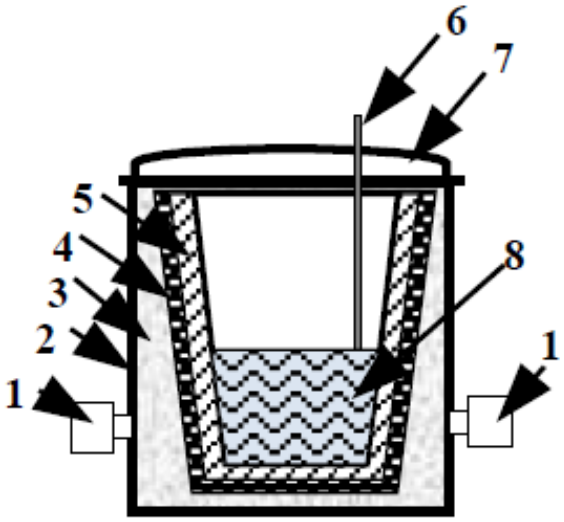

Figure 2. Microwave melting furnace: **1**– Microwave generator; **2** – Furnace casing; **3** – Thermal insulation; **4** – Layer of microwave susceptor material; **5** - Crucible; **6** – Thermocouple; **7** – Furnace lid; **8** – Raw material (WEEE).

For eliminating the heat loses through the chamber walls, a thermal insulation (3) layer fabricated of super-aluminous ceramic fiber, which can resist to temperatures of up to 1600°C, is inserted between the exterior wall of the crucible (5) and the furnace chamber (2). The material is heated using three microwave generators (1) of 800 W capacity each, mounted on the furnace walls. Flux (NaCl+KCl mix in a 1:1 ratio) is added to diminish the risk of metal oxidation during melting, in an amount which represents 5-10 wt% of the waste quantity. The chemical composition of the resulting multi-component alloy, cast as ingots, is given in table 1.

Table 1. Chemical composition of the multi-component alloy.

Element	Cu	Sn	Pb	Zn	Fe	Ni	Al	Ag	Au	Other*
%	55 - 70	10-20	5-15	5-10	0.5-2	0.5-3	0.5-4	0.5-0.8	0.05-0.2	0.3-1

*Other: Sb, Mn, Mo, Cr, Ti, V, Ta

The multi-metallic bulk is subsequently processed for the extraction of the contained base and precious metals through various hydro- and electrometallurgical methods. The general technological flow-chart of the recovery process is presented in figure 3.

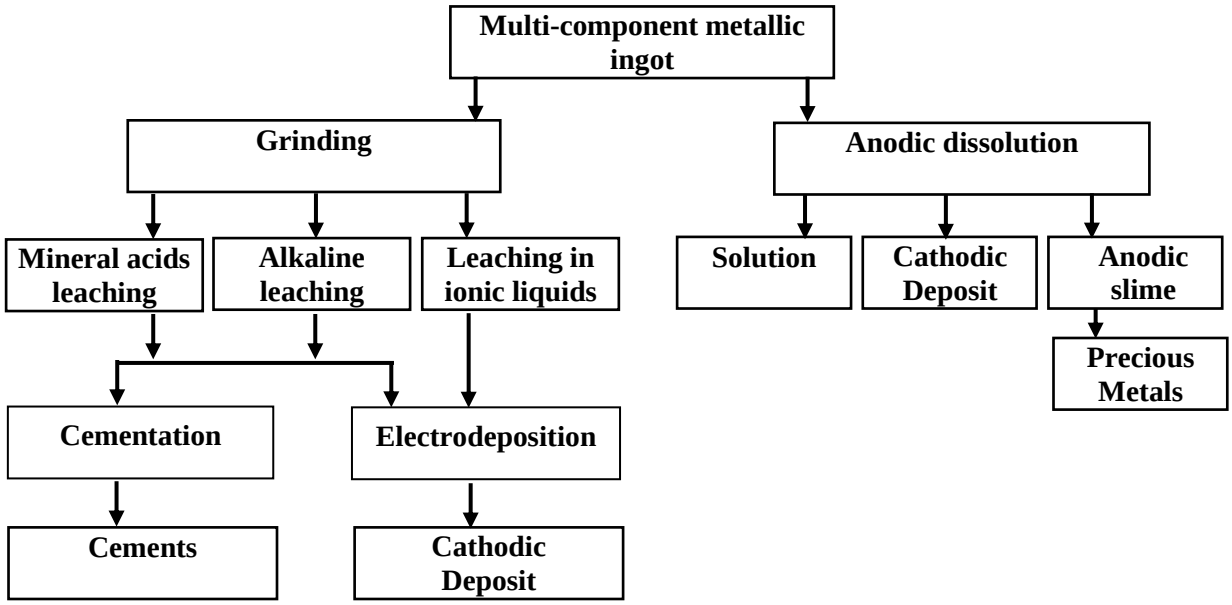

Figure 3. Technological flow-chart of the multi-component metallic bulk processing.

During the waste melting in the microwave furnace toxic compounds such as benzene, toluene, ethylbenzene, styrene, m/pXilen, naphthalene and 1,3,5 trimethylbenzene are generated in the effluent gases (table 2).

Table 2. Composition of the gases resulting from the melting process.

Compound	Benzene	Toluene	Ethylbenzene	Styrene	m/pXilen	Naphthalene	1,3,5 trimethylbenzene
Quantity [mg×m^{-3}]	3.2-6.5	15.3-17.8	2.8-5.7	21.5-24.3	1.4-2.8	1.1-1.3	15.2-23.5

These compounds are treated in a system which consists of a microwave irradiated chamber containing a microwave susceptor granular material for controlling the gas atmosphere. The emissions resulting from the WEEE pyrolysis process are directed through the thermal filter and mixed with an oxidizing agent to ensure the transformation of the organic compounds mainly into carbon dioxide. The working temperature of the filter is attained exclusively by using microwave energy. Cavities in which microwave generating systems (consisting of the magnetron unit, the waveguide and the power transformer) are mounted are designed in the body of the thermal filter.

The drawing of the thermal filter is presented in figure 4. It is formed by the cylindrical shaped body of the filter, fitted with a flange (2) and a fashioned support pad (3) at the bottom, and at the top with a lid (4) and a gas intake cone (5). In the body of the filter (1) there are rectangular cavities (6) of a length equal to the wavelength of the microwave frequency used. The quartz tube (7) is fastened to the support pad (3) and passes through the lid (4), which contains a quartz sieve (8) at the bottom part. A granular material (9) made of microwave susceptible materials is placed in the quartz tube (7), for high temperatures. A microwave transparent thermal insulation (10) is placed between the quartz tube (7) and the body of the filter (1). The microwave irradiation system consists of an adaptation flange (11) on which the waveguide (12) is mounted, and a magnetron unit (13) operating at the frequency of 2.45 GHz. The temperature measurement in the thermal filter is carried out with pyrometers located at

the bottom (14) and at the top (15) of the quartz tube, as well as before the entrance (16) and exit (17) of the heat treatment chamber. The control of the temperature in the granular material is achieved using temperature regulators (18). The pressure at the inlet of the thermal filter is measured with pressure sensors (19) which can operate at high temperatures.

The flow of exhaust gas is kept constant using a Venturi tube (20), which can be mounted after the thermal filter to obtain a controlled entrainment of the gaseous emissions. A pressure regulator (21) is mounted on the compressed air line before the tube to ensure a constant flow of compressed air for operating the Venturi tube.

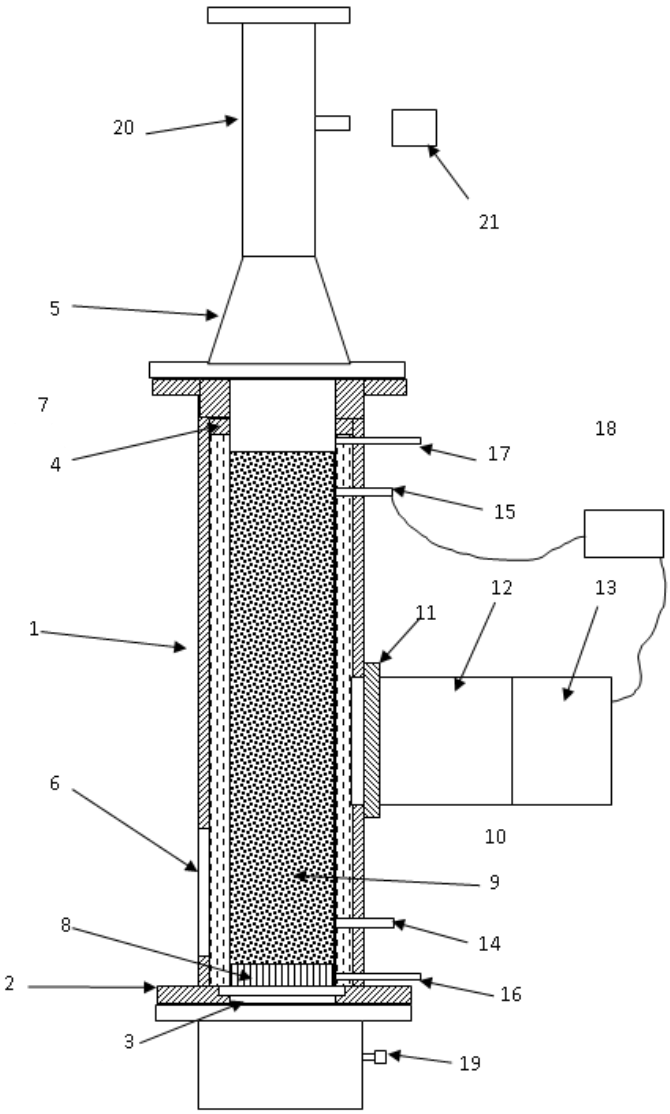

Figure 4. Drawing of the gas treatment system.

The irradiation of the microwave susceptible granular material generates the thermal decomposition temperatures of the combustion gases, using power densities ranging from 50 to 5500 W/kg of granular material. The microwave system is connected to a thermostatic system, in order to achieve the isothermal regime necessary for the thermal decompositions to take place.
The influence of the process parameters (heating response of the susceptor materials, temperature, gas flow, gas pressure) was investigated.

3. Results and discussion

The mean values of the chemical compositions of the exhaust gases, measured at the outlet of the thermal filter, are given in tables 3-5. The gas flow values were 450, 300 and 150 $m^3 \times h^{-1}$, at a gas pressure of 800-1000 mbar. The temperature of the filter was measured at 800, 1100 and 1400˚C.

The emissions were measured at the exhaust outlet located behind the thermal filter that is positioned at the top of the melting furnace. The sampling was performed using the non-extractive method that did not require sample absorption and was limited to the gas flow existing in the pipe. The sampling plane was located in a section of the waste gas pipeline where homogeneous flow conditions and concentrations are expected, away from any fluctuation which could result in a change in effluent direction (a pipe section with a right line length of at least 5 hydraulic diameters upstream and 2 hydraulic diameters downstream of the sampling plane).

A TESTO 435 analyser was used for the determination of the exhaust gas physical parameters (rate, temperature, pressure). The gas flow was determined using the following equation (1):

$$F_{ex} = S \times v \times 3600 \quad (1)$$

where

F_{ex} - exhaust gas flow, $m^3 \times h^{-1}$

S - section of the measurement point, in mp

v - exhaust gas rate, in m/s.

The temperature of the thermal treatment filter was measured using a Pt-PtRh thermocouple. A Tiger PhoCheck photoionization analyser (PID) was used to determine the emissions of volatile organic compounds in the gases resulting from WEEE melting. This method allows the determination of a wide range of organic gases and vapours and also some inorganic compounds. In order to obtain a response, the photon energy of the PID lamp must be higher than the ionizing energy of the compound. In this work the 9.8 eV, 10.0 eV, 10.6 eV, and 11.7 eV lamps were used for experimental determinations. The reference standard gas used for the PID calibration, was isobutylene.

Table 3. Chemical composition of the effluent gases at a gas flow of 450 $m^3 \times h^{-1}$ and a pressure of 800-1000 mbar.

	Filter Temperature [°C]			
Components $mg \times m^3$	800ºC	1100ºC	1400ºC	Legal limit * [mg/m^3]
Benzene	6.5	3.3	1.4	5
Toluene	17.1	16.8	15.4	100
Ethylbenzene	5.5	2.9	1.3	5
Styrene	23.8	21.6	18.7	100
m/pXilen	2.7	2.7	2.3	100
Naphthalene	1.2	1.1	1.1	100
1,3,5 Trimethylbenzene	17.8	6.3	4.2	5

* National legislation, Government order 462/1993.

Table 4. Chemical composition of the effluent gases at a gas flow of 300 $m^3 \times h^{-1}$ and a pressure of 800-1000 mbar.

	Filter Temperature [°C]			
Components $mg \times m^3$	800°C	1100°C	1400°C	Legal limit $[mg/m^3]$
Benzene	6.3	3.5	1.9	5
Toluene	17.8	16.3	14.9	100
Ethylbenzene	5.6	2.5	1.5	5
Styrene	25.8	20.6	17.6	100
m/pXilen	2.8	2.4	2.4	100
Naphthalene	1.1	1.1	1.0	100
1,3,5 Trimethylbenzene	18.3	6.1	3.3	5

Table 5. Chemical composition of the effluent gases at a gas flow of 150 $m^3 \times h^{-1}$ and a pressure of 800-1000 mbar.

	Filter Temperature [°C]			
Components $mg \times m^3$	800°C	1100°C	1400°C	Legal limit $[mg/m^3]$
Benzene	6.4	3.2	1.5	5
Toluene	17.9	16.5	14.2	100
Ethylbenzene	5.4	2.7	1.1	5
Styrene	26.8	22.6	15.3	100
m/pXilen	2.7	2.8	2.3	100
Naphthalene	1.2	1.0	1.1	100
1,3,5 Trimethylbenzene	16.6	5.8	3.1	5

The variation of the benzene, ethylbenzene and 1,3,5 trimethylbenzene contents in the exhaust gases treated in the thermal filter, depending on the filter temperature, is presented in figure 5, for a gas flow of 150 $m^3 \times h^{-1}$. The variation of the benzene, ethylbenzene and 1,3,5 trimethylbenzene contents depending on the gas flow, is presented in figure 6, at a filter temperature of 1400°C.

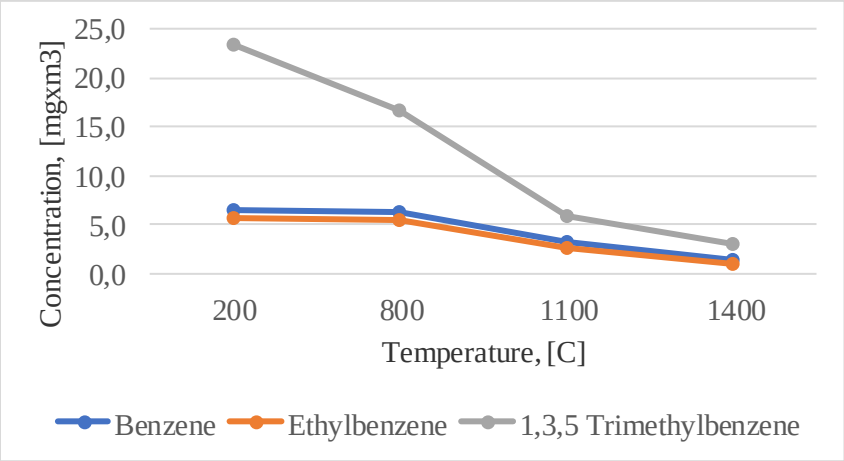

Figure 5. Variation of the benzene, ethylbenzene and 1,3,5 trimethylbenzene contents in the exhaust gases treated in the thermal filter, depending on the filter temperature.

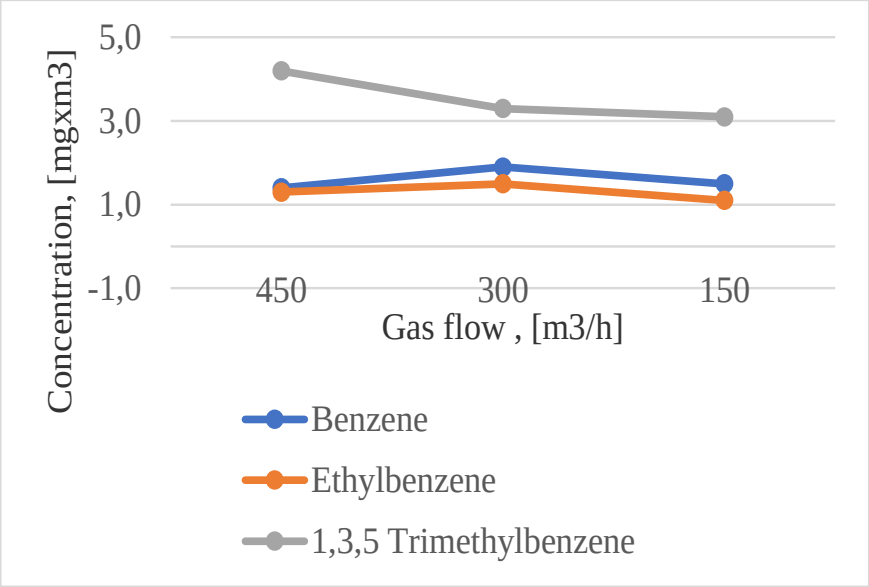

Figure 6. Variation of the benzene, ethylbenzene and 1,3,5 trimethylbenzene contents in the exhaust gases treated in the thermal filter, depending on the gas flow.

The values at 200°C are those recorded at the outlet of the melting furnace and before entering the gas thermal treatment filter. At a filter temperature of 800°C, the concentrations of benzene and ethylbenzene are basically the same to those at the filter inlet, as the concentration of 1,3,5-trimethylbenzene dropped from about 23 mg/m^3 to 16.6-18.3 mg/m^3. With the increase of the filter temperature to 1100 - 1400°C there can be observed a linear decrease of the concentration of benzene and ethylbenzene at values below the legal limit of 5 mg/m^3. The 1,3,5-trimethylbenzene content drops to about 5-6 mg/m^3 at 1100°C and at 3-4 mg/m^3 at 1400°C (also below the legal limit).

Depending on the gas flow through the thermal filter (heated to 1400°C), there are very few variations in the benzene and ethylbenzene content, which are in the concentration range 1.4-1.9 mg/m^3.

The content of 1,3,5-trimethylbenzene in the treated gases decreases with the reduction of the flow, which denotes another mechanism of decomposition for this gas.

4. Conclusions

This paper demonstrated the feasibility of the treatment in microwave field of the toxic gases resulted from the melting of e-waste. Toxic compounds such as benzene, toluene, ethylbenzene, styrene, m/pXilen, naphthalene and 1,3,5 trimethylbenzene were circulated through a filter fabricated from a microwave susceptor granular material, placed in a microwave transparent tube. The influence of the process parameters (heating response of the susceptor materials, temperature, gas flow, gas pressure) was investigated. It was observed that the temperature of the filter had a major influence on the neutralization of the toxic compounds while the gas flow and pressure had a minor influence. At a temperature of 1350-1400˚C (power density of 5000 W× kg^{-1}), a gas flow of 150 m^3 × h^{-1} and a pressure of 800-1000 mbar, the content of such substances in the gaseous emissions was reduced below the legal limits.

These promising results confirmed the remarkable potential of this innovative method for the recovery of useful and precious metals from WEEE.

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5. References

[1] Luda M P 2011 *Integrated Waste Management* **2** (InTech: Rijeka) p 285
[2] Kamberovic Z, Korac M and Ranitovic M 2011 *Metalurgija* **17** 139
[3] Duan H, Hou K, Li J and Zhu X 2011 *J. Environ. Manage.* **92** 392
[4] Deveci H, Yazıcı E Y, Aydın U and Akçil A U 2010 *Proc. of the 5th Going Green: CARE INNOVATION Conf. (Vienna)* (Vienna: Austria) 8
[5] Hagelüken C 2006 *A.M.S* **12** p111
[6] Yang X, Sun L, Xiang J, Hu S and Su S 2013 *Waste Management* **33**(2) 462
[7] Wang H, Zhang S, Li B, Pan D, Wu Y and Zuo T 2017 *Resources, Conservation & Recycling* **126** 209
[8] Wang R and Xu Z 2014 *Waste Management* **34**(8) 1455
[9] Badger G M 1995 *Progress in physical organic chemistry* (Ed. Cohen S) p 1
[10] Van Krevelen D W 1990 *Thermal Decomposition. Properties of Polymers* (Elsevier, The Netherlands)
[11] Acomb J C, Nahil M A and Williams P T 2013 *Journal of Analytical and Applied Pyrolysis* **103** 320
[12] Martinho G, Pires A, Saraiva L and Ribeiro R 2012 *Waste Management* **32**(6) 1213