Microwave treatment of electric arc furnace dust with Tetrabromobisphenol A: Dielectric characterization and pyrolysis-leaching

Mohammad Al-harahsheh*[1], Sam Kingman[2], Ian Hamilton

[1] Chemical Engineering Department, Jordan University of Science and Technology, Irbid, 22110, Jordan

* msalharahsheh@just.edu.jo

[2]Faculty of Engineering, University of Nottingham, Nottingham, NG7-2RD, UK

Abstract

In the present work microwave treatment of electric arc furnace dust (EAFD) mixed with tetrabromobisphenol A (TBBPA) was investigated. A range of characterization techniques were used to understand the thermal behaviour of TBBPA-EAFD mixtures under microwave pyrolysis conditions. Dielectric and thermal properties of EAFD, TBBPA and their mixtures were determined. Both the dielectric constant and loss factor of the mixture were found to vary considerably with temperature and subsequently it was found that the mixtures of these materials absorbed microwaves effectively, especially at temperatures above 170^0C. The high loss tangent of EAFD-TBBPA mixture above 170^0C resulted in fast heating and high temperatures (above 700^0C) resulting in reduction of Fe, Pb and Zn to their metallic form. This resulted in low recoveries of both Zn and Pb when the residue was leached in water. The recovery of Zn varied between 14 and 52 wt.%, while Pb recovery varied between 3 and 31 wt.% depending on microwave treatment efficiency. The low recovery of Zn and Pb could be ascribed by the reduction of metal oxides into their metallic form. More importantly this work has shown great selectivity in the leachability of both zinc and iron; with iron being left in the solid residue.

Keywords: EAFD; Dielectric Properties, Microwave treatment; Leaching; zinc extraction; TBBPA

1. Introduction

Electric Arc Furnace Dust (EAFD) is a waste by-product generated by the secondary steelmaking industry. Treatment of EAFD is of prime importance for environmental and resource conservation

as it is considered as an environmentally hazardous waste according to the Environmental Protection Agency (EPA) as it contains easy leachable metals including Cd, Pb, and Cr [1, 2]. Due to the depletion of the primary resources of metals such as Zn and Pb, recycling of this dust has gained greater interest among researchers and investors in the metallurgical sector [3]. Both Pyrometallurgical and hydrometallurgical methods have been suggested to recover valuable metals from EAFD. Although pyrometallurgical treatment of EAFD is practiced now at the industrial scale utilizing Waelz Kiln technology [4] and rotary hearth furnaces [5] to recover zinc in the form of ZnO, these methods suffer from high energy requirements compared to hydrometallurgical methods.

Different leaching reagents including sulphuric acid [6, 7], hydrochloric acid [8], ammonia [9, 10], sodium hydroxide [11, 12], and some organic acids [13] have been used for extraction of zinc and other valuables from EAFD. According to Jha et al [14], the most effective lixiviants for zinc extraction from EAFD were found to be sulphuric acid and ammoniacal solutions. Sodium hydroxide, dissolves zinc selectively, however, this application needs further development for effective metal recovery from the sodium zincate solution by electrolysis.

There is a great interest nowadays to utilize waste halogenated plastic materials for the recovery of valuable materials from EAFD and to minimize its environmental impact as well as that of waste plastics. Among these waste plastic materials are flame retardant materials, with tetrabromobisphenol A (TBBPA) being the most widely used. Thermal treatment of these wastes results in release of large amounts of HBr and other brominated organic substances such as brominated phenols as well as wide array of other brominated organic compounds [15-19]. If TBBPA is pyrolysed in the presence of metal oxides, the later has high fixing ability toward HBr and subsequent reduction of brominated organic compounds released during the pyrolysis process [15, 20].

The largest volume brominated flame retardant in production today is TBBPA [21]; its annual production exceeded 170 kilotons in 2004 [22] and the estimated annual market demand from 2001 to 2003 was >200,000 ton/year [23]. The reports suggest that huge quantities of brominated plastic wastes are accumulated worldwide, which makes their disposal a real and current challenge.

Utilization of EAFD as a debromination catalyst for TBBPA based plastic materials offers numerous benefits such as HBr capture liberated during TBBPA pyrolytic incineration in the form

of metal bromides. These can be recovered in their vapor form ore leached from the pyrolysis residue using just water. Such a technique allows two waste materials to be treated concurrently ~~con-currently~~ to minimize their associated risks and at the same time recover valuable metals from EAFD by relatively simple means.

A major decomposition product from TBBPA degradation is HBr; which is an excellent brominating agent for ZnO present in EAFD and, it therefore, can be used as an agent to selectively separate zinc as a volatile bromide from the solid dust residues. These properties lead to the use of TBBPA as a source of (HBr) for zinc recovery from EAFD as zinc bromide $ZnBr_2$ [24, 25].

The de-bromination process is mainly the loss of bromination species from the backbone followed by an evaporation process. Hydrogen ~~bromide~~bromide (HBr) as the brominating agent is generated in relatively large amounts when the TBBPA decomposes during thermal processing (HBr accounts for ca. 59 wt.% of TBBP upon thermal decomposition). The HBr reacts with zinc minerals forming a bromide ($ZnBr_2$) that has a boiling point of 650^0C. Grabda et al [24] studied the effect of heating time and temperature on the vaporizing of $ZnBr_2$ under different conditions. They observed that the evaporation increases with heating time at constant heating rate and increasing temperature (due to an increase in the vapor pressure). A mixture of argon and oxygen were used to oxidize the high molecular weight compound ('char') that formed during thermal decomposition of the TBBPA and this affected the vaporization process; however this complex residue declined as heating time and temperature increased. The measured vaporization data show that at 950^o C the vaporization of $ZnBr_2$ was complete, with less than 11 wt% char. However, one-third of ZnO remained as un-reacted residue and required further treatment by carbothermic reduction by carbonaceous char where 4 wt% remained in solid residue. Grabda et al. [26] continued to investigate the possibility of EAFD treatment, using TBBPA and tetrabromobisphenol A diglycidyl ether (TBBPADGE) at 550°C for 80 min, under oxidizing and inert atmospheres; a maximum of 85wt.% of zinc and 81wt.% of lead recoveries were achieved using TBBPADGE. Oleszek-Kudlak et al. [27] also studied the reaction ~~of~~ between TBBPA ~~with~~ and EAFD and the effect of temperature on the ~~process~~ of bromination zinc oxide and the evaporation of ~~the metal oxides~~ its bromide ($ZnBr_2$) in the temperature range 250 - 950 °C.

This work aims at evaluating the possibility of heating EAFD-TBBPA mixtures by microwave irradiation under pyrolysis conditions. It also aims to study the possibility of extracting valuable

metals from the pyrolysis residue by a hybrid microwave pyrolysis-extraction method. Therefore, the dielectric properties of both materials (EAFD and TBBPA) and their mixtures were measured using cavity perturbation technique and reported herein. Additionally, the pyrolysis of EAFD-TBBPA mixtures, under microwaves, followed by leaching of microwave pyrolysis residue were also carried out.

2. Experimental work

2.1. Materials

The EAFD sample was collected from a Jordanian steel smelter. After homogenization by repeated cone and quartering, the sample was characterized for its chemical and mineralogical composition. A Perkin Elmer (Optima® 3300 DV) Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), was used to measure the content of elements in the EAFD following the procedure of sample preparation reported by Al-~~harahsheh~~ Harahsheh et al [28]. TBBPA was purchased from Sigma Aldrich. All other chemicals were reagent grade and used without further purification.

2.2. Microwave treatment procedure

The description of the experimental setup used for microwave treatment of the EAFD-TBBPA mixtures is reported elsewhere [29]. It consisted of a 3 kW microwave generator operated at 2.45 GHz a forward and reflected power measurement system connected to a PC, a WR340 standard rectangular waveguide operating in a dominate TE_{10} mode coupled to a cylindrical choke section (for sampling). The reaction system consisted of nitrogen cylinder fitted with a flow_meter, a vertical quartz tube fitted inside the vertical applicator, two 250 ml gas wash bottles connected in series and operated as gas extraction system, and vent connected to external extraction system.

EAFD was mixed with TBBPA in a tumbling mill with ceramic balls at a mass proportion of 1:1. The mixture was then made into cylindrical pellets of about 5g mass. A hydraulic oil press was then used to compress approximately 5 g of the mixture at 180 kg f/cm^2 for 60 s.

To perform the microwave pyrolysis experiments the pellets were placed in a quartz tube positioned vertically in the cylindrical microwave applicator. The sample was then irradiated with

microwave energy for a specified time and power level while nitrogen gas purged the reaction system. In order to collect any soluble vapors, the produced gases were vented through two gas wash bottles filled with water. Irradiation time was varied depending on the observations of the reaction systems and also based on the temperature reading obtained by an optical pyrometer. Microwave power was shut-off if arcing occurred.

At the end of the experiment, the solid residues were reweighed and removed from the quartz tube. Hot water was used to wash out the whole extraction system to collect any water soluble condensate. It was then analyzed for metal content using ICP.

2.3. Leaching of the microwave pyrolysis residues

The solid residue after microwave treatment was ground to a particle size of less than 1 mm and then subjected to leaching in boiling deionized water for 20 minutes. The mixture was then filtered and the leaching solution was then analyzed for the metal content. The remaining solid residues were also analyzed by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM).

2.4. Measurement of dielectric properties

Cavity perturbation method was employed to measure the dielectric properties of EAFD, TBBPA, and their mixture. The experimental setup details are reported elsewhere [30]. A representative mass of about 0.1-0.2 g of the material was packed in the quartz tube and heated to the desired temperature, then positioned in the microwave resonant cavity by means of an automated actuator. The frequency shift and quality factor were measured at 2470 and 912 MHz which are close to the most frequently used frequencies in domestic and industrial microwave processes. Extra care was taken to obtain similar packing density of samples, because powdered sample density has a great effect on the measured values of dielectric properties [31]. The variation in density of packing for 3 replicates was determined to be less than 3.5%. Additionally for each sample, a minimum of three replicates were measured. The dielectric constant (ε') and loss factor (ε'') were then calculated [30].

2.5.X-Ray diffraction and TGA analyses

Representative EAFD sample, taken after prolonged manual mixing, was analyzed for its mineral composition using X-ray diffraction analysis (XRD), furthermore, additional solid samples were analyzed by XRD after microwave pyrolysis and after leaching experiments. A Hiltonbrooks® generator with a Philips® PW 1050 diffractometer with an automatic divergence slit, and Cu-Kα anode producing X-rays of wavelength λ= 1.54056 Aº was used.

Thermogravemetric (TGA) and differential thermal analyses (DTA) of the dust (EAFD) and the plastic material (TBBPA) and their mixture containing 50wt % EAFD and 50wt% TBBPA were performed using a TA- Q600 thermal analyzer. About 10 mg of the sample was placed in fused alumina pan and heated at a heating rate of 10°C/ min under nitrogen with a flow rate of 50 ml/min.

3. Results and discussions

3.1.Physical and chemical characteristics of EAFD

Figure 1 shows the XRD pattern of EAFD. The dust contains zincite, magnetite, franklinite, halite, sylvite, lead hydroxyl chloride and hematite

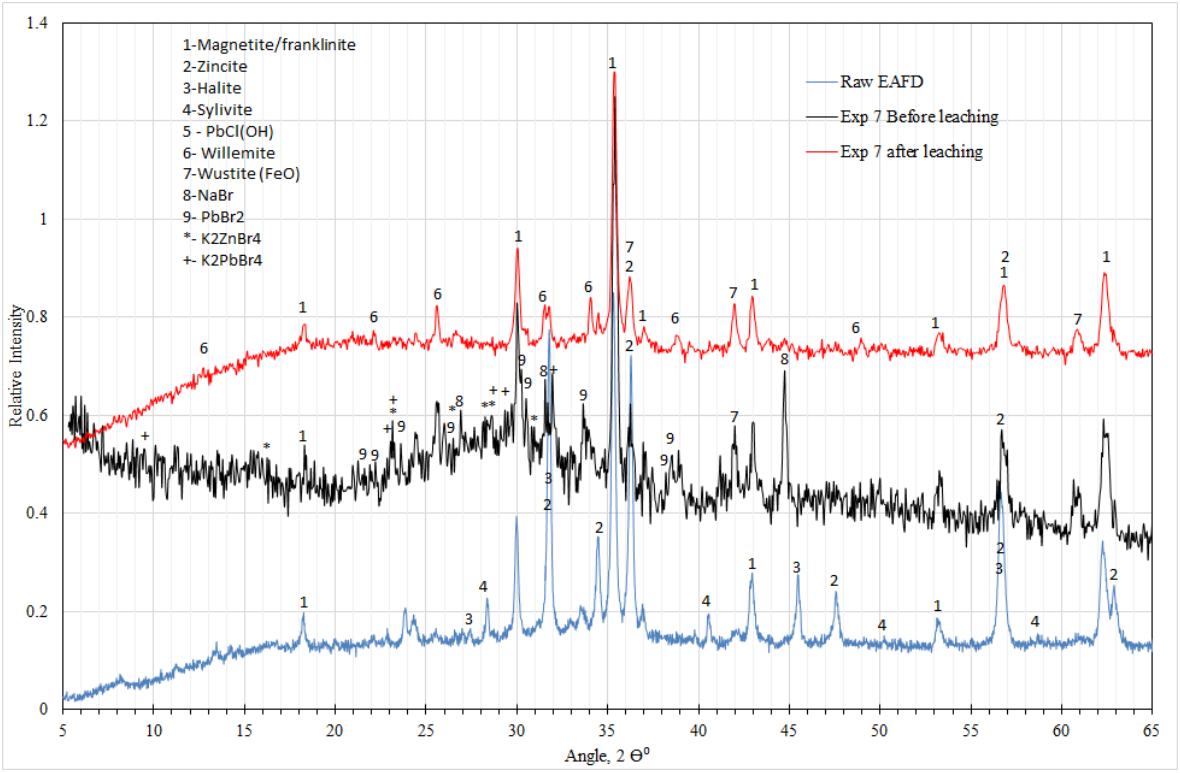


Figure 1 XRD pattern for EAFD, EAFD-TBBPA residue after pyrolysis and after leaching

The chemical composition of the EAFD sample used in this work was reported elsewhere [32]. The main elements present in the dust are~~:~~ (in wt%) 25.9~~%~~ Zn, 18~~%~~ Fe, 4~~%~~ Ca, 3.3~~%~~ Na, 3.2~~%~~ Pb, 2.8~~%~~ Si, 1.8~~%~~ K and 1.2~~%~~ Mn. Calorimetry showed that dust contains 2.63 ± 0.03wt% total carbon and 0.1wt% inorganic carbon suggesting that among mineral phases present in the dust are carbonates such as calcium carbonates.

3.2. Dielectric properties of the EAFD

The dielectric constant characterizes the capability of materials to absorb electromagnetic radiation, whereas, loss factor denote the ability of materials to dissipate the adsorbed radiation into heat. The dielectric constant and loss factor of EAFD were measured at two frequencies namely 911 MHz and 2.47 GHz across a temperature range from 25 to 600 °C [29]. Figure 2 shows the plot of dielectric constant (ε') and loss factor (ε") as a function of temperature. Both values increase with an increase of temperature and the rate of increase become greater when the temperature exceeded 300 °C.

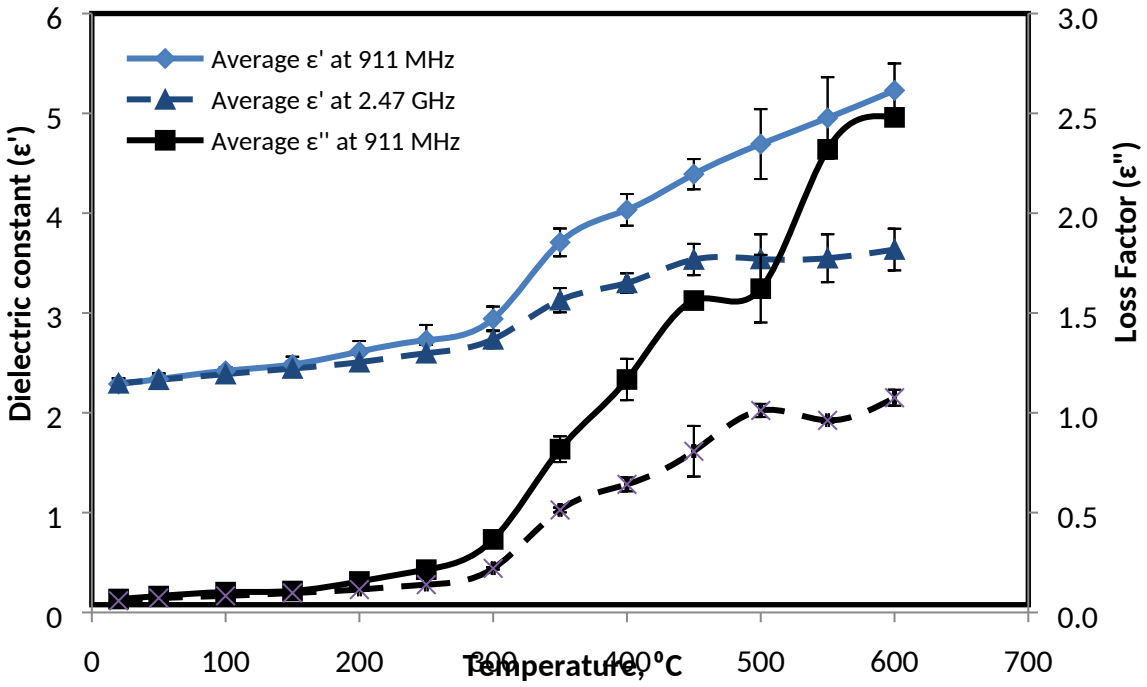


Figure 2 Dielectric properties of EAFD as a function of temperature) at frequencies of 911MHz and 2.47 GHz [4].

Additionally, the ratio of dielectric loss to the dielectric constant is called loss tangent (□”/□’). When the loss tangent is above 0.05, the material is considered to heat well under microwave irradiation. The loss tangent calculated for EAFD was found also to increase steadily with the increase of temperature up to 300°C, then it increases considerably with a further increase of temperature reaching a value of 0.3 at 600°C.

3.3. ~~Thermal and d~~Dielectric properties analysis of TBBPA

~~3.3.1. TGA of TBBPA~~

~~Figure 3 shows the TGA profile for TBBPA at a heating rate of 10°C/min under nitrogen flushing at a flowrate of 50mL/min. One major mass loss region is observed in the temperature region of 250-330°C, ascribed to the decomposition of TBBPA and the release of hydrogen bromide (HBr). The mass loss in this region was around 75% of the initial mass. The theoretical content of HBr in the TBBPA is 59.51%, which suggest that at least 15% of volatile hydrocarbons are evolved with the HBr such as brominated phenols [15].~~

Figure 4 shows the DTA profile of the pure TBBPA. It exhibits two endothermic events. The first event, occurring at a temperature of 178°C, indicated the smelting of TBBPA. The second event occurring across a broad temperature region (250-350°C), with a maximum peak derivative heat flow at 327°C, corresponds to TBBPA evaporation and decomposition and the evaporation of HBr and organic hydrocarbons.

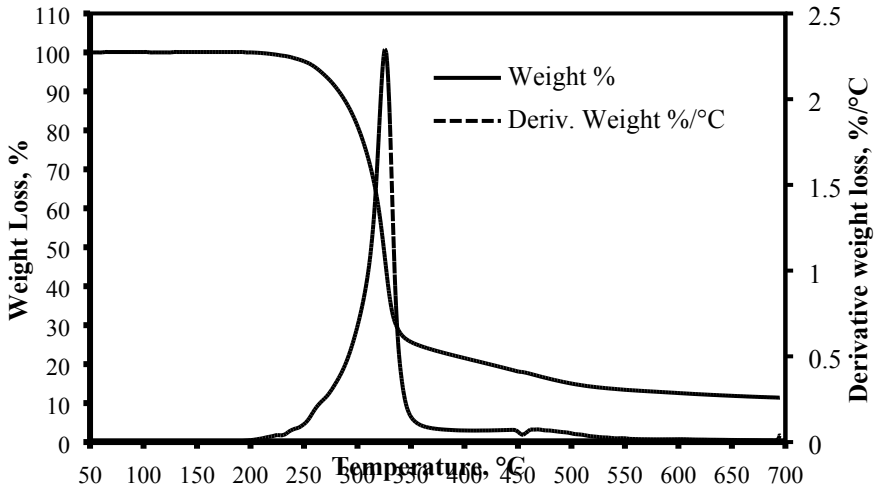


Figure 3 TGA profile of TBBPA (heating rate=10C/min, N_2 flowrate=50mL/min

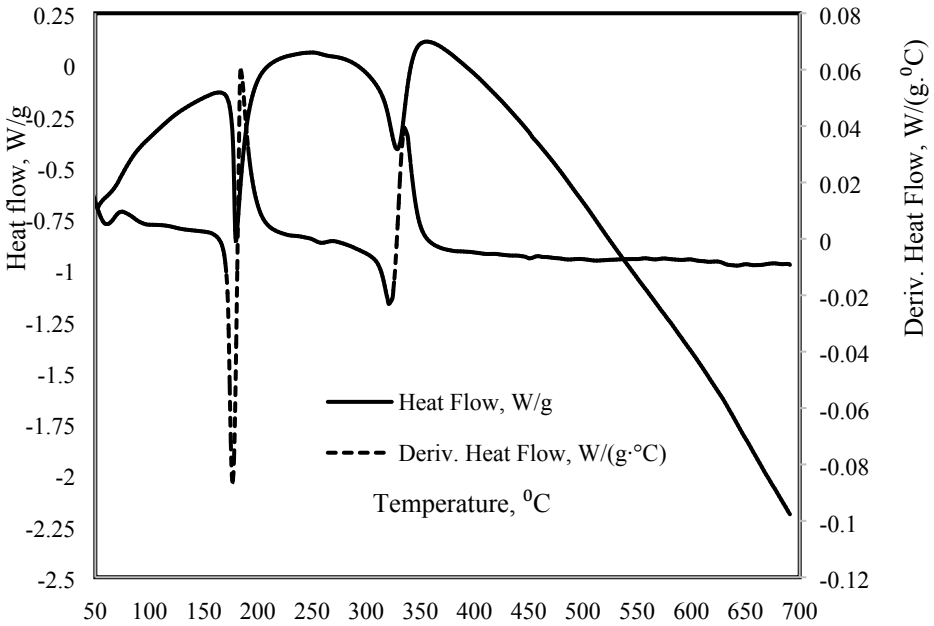


Figure 4 DTA profile of TBBPA (heating rate=10C/min, N2 flowrate=50mL/min

~~The thermal analysis of EAFD was reported by Al-Harahsheh et al~~ [29]~~. The main features of EAFD TGA profile include a mass loss appears at a temperature range of 160-200°C, assigned to the loss of associated moisture and possibly a level of bound water in metal chlorides present in the dust. A second mass loss was also observed in the temperature window 600-700 °C, assigned to the vaporization of metal chlorides, most likely $ZnCl_2$~~ [33]~~. The presence of ca. 2.6 % free carbon was thought to cause a reduction of some metal oxides such as ZnO to elemental zinc. The last mass loss region appearing at 770°C may be related to the energy intensive evaporation of zinc.~~

~~3.3.2. Dielectric Properties of TBBPA~~

~~Figure 5~~Figure 3 shows the dielectric properties of TBBPA as a function of temperature at frequencies of 911 and 2.47 GHz. The dielectric constant remains constant until a temperature of 150°C then increases suddenly at a temperature of 170°C followed by steady increase until a temperature of 270°C and then decreases sharply. The loss factor decreases with the increase in temperature up to a temperature of 150°C then increases sharply up to a temperature of 270°C and then drops sharply. The increase of both dielectric constant and loss factor after 170°C is related to the start of smelting of TBBPA (melting point of TBBPA=178°C). However the sharp decrease in both parameters after 270°C is an artifact related to the sharp reduction of sample volume due to the decomposition of TBBPA. To obtain more accurate dielectric properties values, a volume correction factor should be introduced; the weight loss at the decomposition temperature was measured to be around 75 wt% of the initial mass. The data reported in Figure 5 did not take into account the volume correction factor due to the difficulty in measuring the final volume at each temperature.

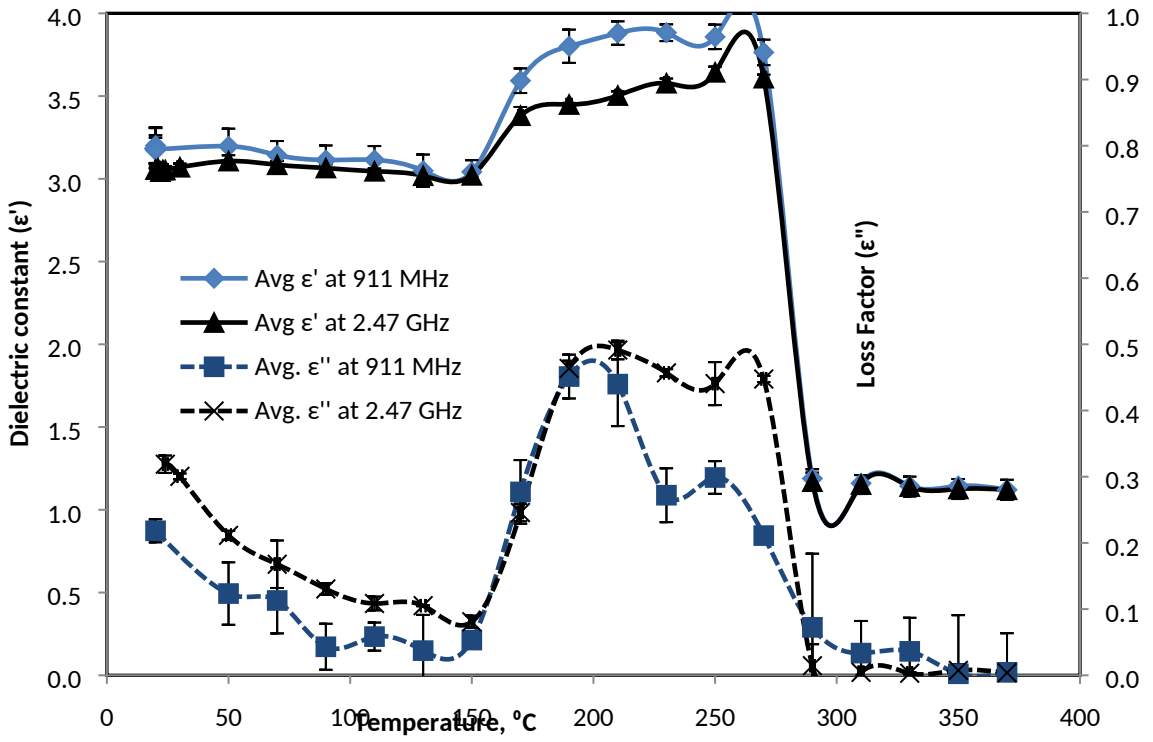


Figure 3 Dielectric Properties of TBBPA as a function of temperature at frequencies of 911 MHz and 2.47 GHz

3.4. Thermal and dielectric properties of TBBPA-EAFD mixture

To study the interaction of the TBBPA-EAFD mixture with microwaves it is essential to measure both dielectric constant and loss factor of the mixture. During thermal treatment of TBBPA-EAFD mixture several events are expected to occur, which will influence the dielectric properties of the mixture. Therefore, the change in mass loss, the heat flow, the dielectric constant and loss factor were measured at different temperatures for a mixture containing 50 wt. % TBBPA and 50 wt. % EAFD. The results of these measurements are plotted in ~~Figure 6 and Figure 7~~Figure 4 and Figure 5.

The presence of EAFD with TBBPA altered the TGA decomposition profile of TBBPA. Two main regions of mass loss can be seen in the TGA profile for the TBBPA-EAFD mixture, whereas, only one mass loss was seen for pure TBBPA. The later corresponds to the decomposition of TBBPA which ended at a temperature of 350^{o}C; the corresponding mass loss was 75wt% of the initial mass; the mass loss from EAFD alone at this temperature is only 2.5wt%. However, the mass loss for TBBPA-EAFD at the first decomposition stage, ending at a temperature of 310^{o}C, and was

21.5wt% although the decomposition event occurred at the same initial temperature. With the mixture containing 50wt% TBBPA and the remainder consisting of EAFD; the expected mass loss based on the losses of pure materials was determined to be 38.75wt% [29, 34]. The 17.25wt% increase in residual mass found from the experiment is believed to be due to the HBr released not leaving the sample, instead being fixed in the dust in the form of metal bromide ($ZnBr_2$, $PbBr_2$, $CdBr_2$, $FeBr_2$, $FeBr_3$, etc). The exothermic event seen in the heat flow of the TBBPA-EAFD mixture at a temperature of 310°C was evidence of the formation of metal bromides as seen in ~~Figure 7~~Figure 5, whereas, an endothermic event was seen in the case of the pure TBBPA as a result of decomposition.

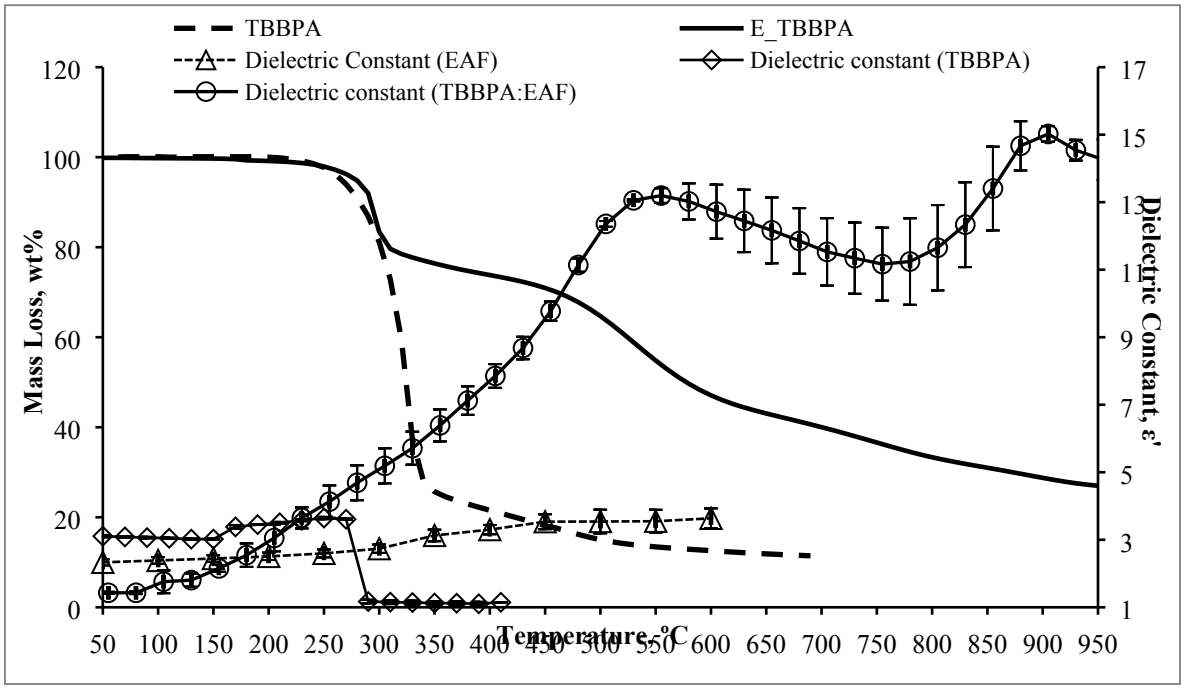


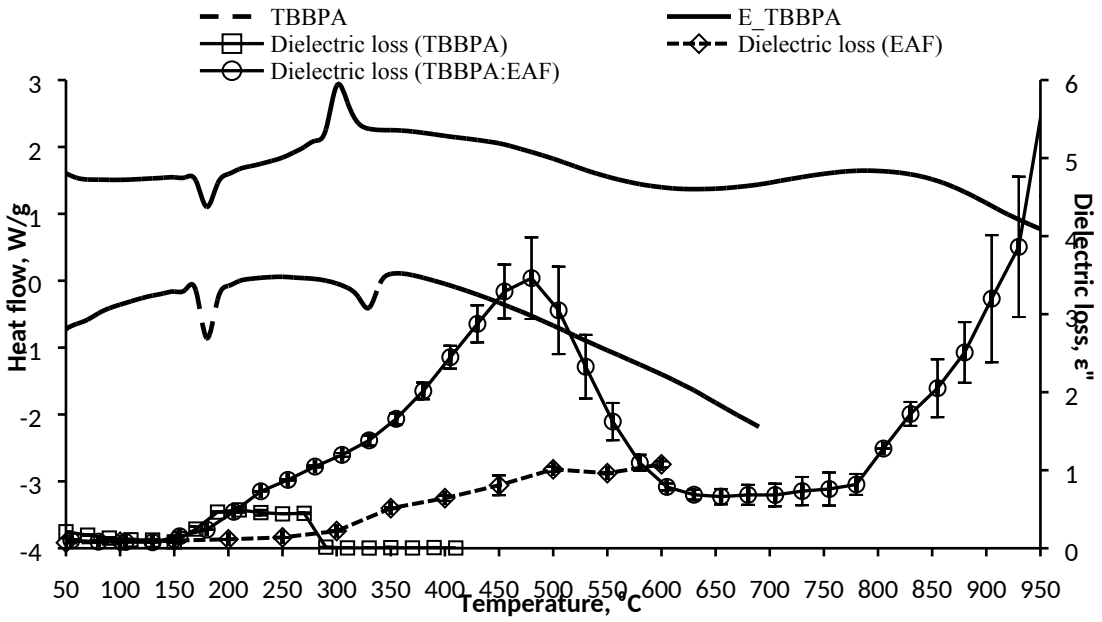
Figure 4 overlay of mass loss and dielectric constant measurement (2.47 GHz) of 1:1 mass ratio of TBBPA-EAFD mixture designated as E-TBBPA.

The second decomposition stage (470-600°C) seen in the TG profile of TBBPA-EAFD mixture could be related to evaporation of zinc bromide formed [35]. Further mass loss occurring above temperature 600°C could be related to evaporation of other metal bromides species like $PbBr_2$ and $FeBr_2$ as well as reduction of the remaining metal oxides present in the dust by the char/carbon (evidence of this will be demonstrated later) and also evaporation of metallic zinc produced by reduction reactions.

The dielectric constant of the mixture did not correlate with the mass loss occurring at the first decomposition stage as it increases with the increase in temperature up to a temperature of 550°C reaching the first maxima of 13.2. The different behavior of dielectric constant of TBBPA-EAFD mixture from that of pure TBBPA could be related to the formation ionic metal bromides which coincide with TBBPA decomposition and the release of HBr. These halide ionic species exhibit strong interaction with the electric field [29] due to ionic conduction and also the fusion of these halides (T_m ($ZnBr_2$)= 394°C [36]; T_m ($PbBr_2$=371°C) [37].

The steady drop in dielectric constant of the TBBPA-EAFD mixture beyond a temperature of 550°C until 760°C, reaching a minima of 11.16, could be related to the vaporization of the metal bromides which corresponds to the second thermal event described above. Beyond a temperature of 760°C, the dielectric constant starts to increase again reaching a second maxima (of 15.02) at a temperature of 905°C. In this temperature region reduction of the remaining metal oxides occurs by the char forming pure metal like Zn, Pb and Fe, as confirmed by SEM analysis shown below. Furthermore, zinc boils at a temperature of 907 °C [36].

The loss factor of TBBPA-EAFD mixtures, remained at very low values until the TBBPA smelts thereafter the values began to increase at a constant rate up to the decomposition temperature of TBBPA. Further increases occurred with a higher rate until reaching a maximum value (3.46) at a temperature of 480 °C~~.~~, which corresponds to ~~T~~the onset temperature of the second thermal event (zinc bromide vaporization). The loss factor then dropped to values as low as 0.68 at a temperature of 630°C then remained almost constant until the temperature reached 780 °C, where it was seen to increase rapidly. The loss of the ionic metal bromides beyond a temperature of 480 °C appeared to have contributed to the drop in the loss factor, however, the formation of the char at pyrolysis temperature is likely to the cause of the sharp increase of the loss factor.



271

272 **Figure 5 overlay of heat flow and dielectric constant measurement (2.47 GHz) of 1:1 mass ratio of TBBPA-EAFD mixture**

273 ## 3.5. Recovery of valuable metals

274 The recovery of valuable metals was performed for a TBBPA-EAFD mixture of mass ratio 1:1.
275 This was performed in two stages; metals evaporated during microwave pyrolysis and metals
276 leached from the pyrolysis residue using boiling water

277 The recovered metals from EAFD-TBBPA pellets after microwave pyrolysis in the extraction
278 system is shown in Table 1. The same experiment was repeated 6 times due to the great variations
279 in microwave coupling with the sample. Approximately 5wt% of zinc, 4wt% of lead and 6wt% of
280 cadmium were collected as metal bromide vapor. Other distinctive features observed (shown in
281 Table 1) was the absence of iron in the solution, implying that iron bromides were not evaporated
282 from the pellet.

283 **Table 1 Valuable metals (wt%) recovered as condensate in the extraction system after microwave treatment.**

Exp. #	Ca	Cd	Fe	K	Mg	Mn	Na	Pb	S	Zn
MH1	0.17	1.99	0.03	0.54	0.10	0.13	0.62	0.63	0.44	1.31
MH2	0.19	2.83	0.00	0.31	0.07	0.07	0.49	1.10	0.60	3.75
MH3	0.24	2.43	0.03	0.32	0.29	0.07	0.37	1.03	0.62	2.37
MH7	0.51	5.88	0.06	0.86	0.54	0.18	0.95	4.14	0.93	4.74
MH8	0.26	2.24	0.03	0.74	0.20	0.14	0.74	1.58	0.49	2.01
MH9	0.24	0.73	0.02	0.24	0.27	0.07	0.28	0.67	0.66	0.83

Table 2 shows the metal recovery from the TBBPA- dust mixtures after leaching of residues obtained in hot water for 20 minutes. Both K and Na show high recovery in the leaching solution, which is expected, as both K and Na are, initially, in the chloride form in the dust which are soluble in water. Cadmium recovery was as high as 87wt% in the leaching solution, while the highest lead and zinc recoveries were only 33wt% and 50wt%, respectively. These values were slightly lower than those obtained after conventional pyrolysis followed by leaching of the solid residues of E-TBBPA1 (1 Dust: 1 TBBPA) [12]. With regards to iron, no more 1wt% was recovered in the leaching solution and the remaining was mainly in the solid residue. This finding is of prime importance, which suggests that excellent selectivity of dissolution of lead and zinc with respect to iron, making further treatment of pregnant solution much simpler. Similar selectivity results were obtained under conventional pyrolysis conditions [34]. Additionally, both calcium and manganese showed good fixing capacity toward HBr.

Table 2 Valuable metals (wt%) recovered from TBBPA-EAFD mixtures by leaching of the pyrolysis residues in boiling water for 20 minutes

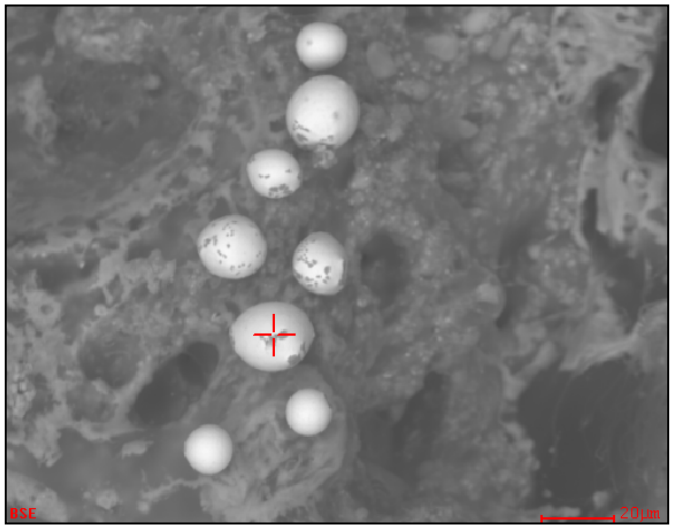
Exp. #	Ca	Cd	Fe	K	Mg	Mn	Na	Pb	S	Zn
ML1	29.83	67.52	0.00	76.69	12.13	7.93	74.21	3.14	17.05	12.63
ML2	46.19	58.80	0.00	87.09	7.01	23.55	86.72	7.58	8.71	27.36
ML3	49.04	79.45	1.30	93.87	8.41	28.98	92.36	20.48	17.82	46.69
ML7	50.74	80.66	0.47	97.15	4.14	33.10	95.72	31.00	16.59	45.57
ML8	52.48	81.74	0.08	95.24	5.60	30.64	93.35	24.16	32.67	50.38
ML9	48.32	87.13	0.19	96.92	3.67	34.26	95.05	14.92	10.98	42.04

For a better understanding of the reaction occurring between metal oxides present in the dust and the decomposition products of TBBPA (HBr and char), both SEM and XRD analyses of both pyrolysis and leaching residues were performed.

The XRD patterns of solid residues after microwave pyrolysis, and after leaching with hot water are shown in Figure 1. Table 3 shows the main mineral phases identified in the samples (EAFD, pyrolysis and leaching residue). After pyrolysis the peaks of zincite decreased considerably, however, still present in the sample after pyrolysis and leaching which explains the low zinc recovery which is also related to the presence of franklinite. This could be due to several reasons the principal one being that the HBr released from the TBBPA was stoichiometricallystochiometirically not sufficient to convert all of ZnO and $ZnFe_2O_4$ to zinc bromide. It is worth mentioning that part of HBr was reacted with NaCl and KCl to form both NaBr and KBr.

The presence of chloride salts also led to the formation of complex salts such as Na_2ZnBr_4, Na_2PbBr_4, K_2ZnBr_4 and K_2PBBr_4. Additionally, the presence of wustite in the pyrolysis residue is an evidence of the partial iron oxide (magnetite) reduction.

SEM analysis of samples of the TBBPA-dust mixture after microwave treatment showed the formation of lead-iron nodules as can be seen from ~~Figure 8~~Figure 6. These lead-iron nodules were not observed after conventional pyrolysis of the same mixture even at temperatures as high as 450 ^{o}C [34]. This suggests that the treatment temperature was high enough to carbonize the TBBPA and produce carbon that was able to reduce both iron and lead present in the dust. Such findings explain the lower recovery levels of iron, lead and zinc.



	Wt%	*At%*
CK	15.79	55.17
KK	00.40	00.43
CaK	00.44	00.46
FeK	42.65	32.05
ZnK	02.62	01.69
PbL	30.38	06.15
BrK	07.72	04.05

Figure 6 SEM micrograph and EDX analysis of TBBPA-dust residue (1:1) after microwave treatment showing iron nodules coated with lead.

The XRD pattern for residue after leaching showed also the presence of Pb(OH)Br in the solid residue, which explains the lower lead recovery than that of Zn. Ioannidis et al [38] reported that Pb(OH)Br can be precipitated in neutral water in the pH range between 4-8. This was confirmed by SEM and EDS analyses shown in ~~Figure 9~~Figure 7; the atomic ratio of Br and Pb is almost 1 suggesting that the analyzed spot is Pb(OH)Br. The presence of Pb(OH)Br was also detected in the conventional pyrolysis residue of the same mixture (50wt% EAFD+ 50wt% TBBPA) after leaching [34]. Additionally, the atomic ratio of Fe, Zn and O is consistent with the presence of an Fe-Zn alloy and iron and/or iron-zinc oxides; the atomic ratio of elements in franklinite is 1Zn:2Fe:4O, whereas, the ratio obtained in the area is 15Zn:19Fe:8O suggesting that almost

80wt% of Zn and Fe are in the form of Fe-Zn alloy. The latter was confirmed by XRD analysis (see Table 3). However, such alloy was not detected in the previous work by Al-Harahsheh et al [34] following conventional pyrolysis, which again confirms the high temperatures obtained by microwave heating. The formation of char coupled with the high temperatures led to reduction of Fe and Zn oxides into their metallic forms, while arcing during microwave pyrolysis have to their smelting and formation of such Fe-Zn alloys.

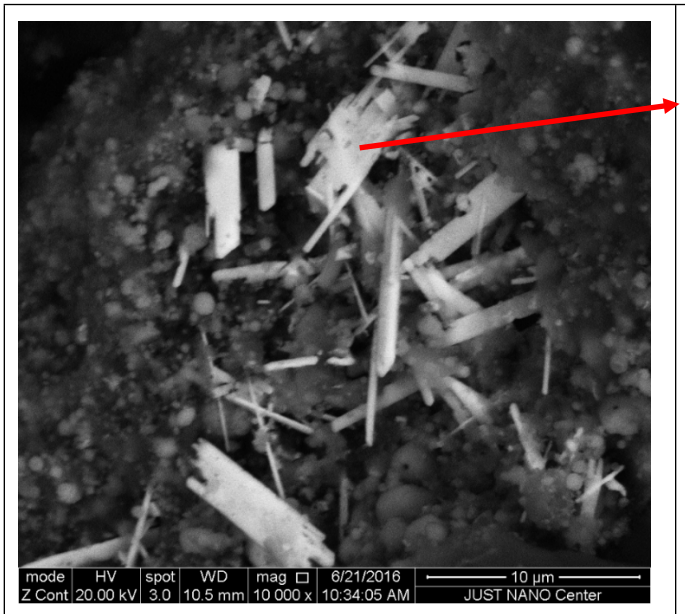
In summary, it was found that microwave heating was efficient for the pyrolysis of TBBPA-EAFD mixture in very short time (less than 2 minutes). An example of the power profile obtained during microwave treatment of the mixture is shown in Figure 8. The amount of microwave power absorbed increased rapidly reaching almost 80% of the incident power, and then dropped to almost 30%, followed by further increased to 60% after 1 minute then it remained constant. The absorbed power profile is consistent with the variations in both dielectric constant and loss factor observed shown in Figure 4 and Figure 5. ~~(less than 2 minutes)~~. After 115 seconds of microwave arcing was observed, therefore, the microwave power was shutoff. The maximum temperature detected by the optical pyrometer was about 650 °C. However, for the purpose to recover metal values by leaching of pyrolysis residue, it is required that the microwave pyrolysis temperature should not exceed 350°C to avoid evaporation of metal bromides and the reduction of these metals into their metallic form. Additionally, the ratio of TBBPA to EAFD should be increased to offer more HBr to convert both zinc and lead oxides into soluble metal bromides. The recent work by Al-Harahsheh et al [34] have shown that conventional pyrolysis TBBPA-EAFD mixture up to a temperature of 350°C followed by leaching of pyrolysis residue results in very high recoveries of both Zn and Pb leaving Fe in the pyrolysis residue.

Table 3 Mineral phases identified in the residue of EAFD-TBBPA (1:1) after microwave treatment and after water leaching.

Feed EAFD	Franklinite/Magnetite, Zincite, Halite, Sylvite, PbCl(OH), calcite, silicate
EAFD-TBBPA residue after microwave pyrolysis	Franklinite/Magnetite, Zincite, $PbBr_2$, Willemite, Wustite, NaBr, KBr, K_2ZnBr_4, K_2PbBr_4, Na_2ZnBr_4, Na_2PbBr_4, Iron, Lead, Iron-zinc

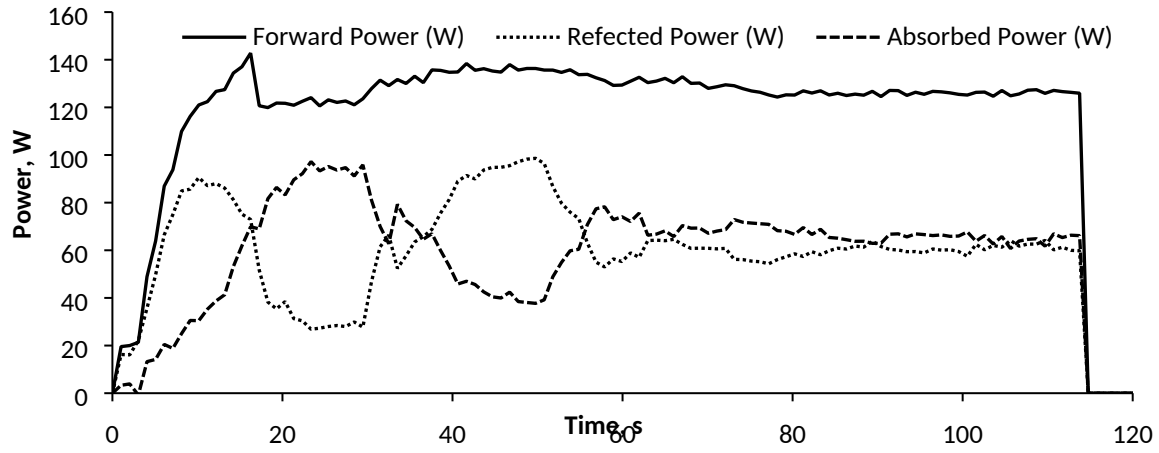
EAFD-TBBPA residue after microwave pyrolysis and leaching	Franklinite/Magnetite, Zincite, Willemite, Wustite, Hematite, Iron, Lead, iron-zinc, PbBr(OH)

354



element	Wt %	%At
CK	17.05	49.91
OK	3.61	7.93
AlK	1.5	1.95
SiK	0.6	0.75
CaK	1.25	1.1
FeK	29.75	18.73
ZnK	28.05	15.08
PbL	12.74	2.16
BrK	5.35	2.35

355 **Figure 7 SEM micrograph and EDX analysis of TBBPA-dust residue (1:1) after microwave treatment and leaching showing**
356 **PbBrOH precipitate**



357

358 **Figure 8 Example of microwave power log obtained for Exp. MH 3**

359

4. Conclusions

Comprehensive characterization of EAFD-TBBPA mixture (ratio 1:1) was carried out in terms of their dielectric and thermal behavior as well as chemical and mineralogical composition. The TBBPA-EAFD mixture exhibited good absorption of microwaves once the melting temperature of the TBBPA has been reached. The microwave treatment time was short (1-3 minutes) suggesting the high efficiency of microwave treatment. Microwave treatment of EAFD–TBBPA mixture followed by water leaching was found to be not very efficient for recovery of Zn, and Pb due to the reduction of these metals into their metallic form by the carbonaceous materials left after TBBPA decomposition and also due to the low proportion TBBPA used in the mixture. The SEM and XRD analyses confirmed that part of iron, lead and zinc oxides present in the dust were reduced to their metallic form. Additionally Pb was found to precipitate during the leaching process in the form of PbBrOH which implies that Zn and Pb can be separated during leaching of the residue.

The pyrolysis of TBBPA in presence of EAFD is showed to be good method of debromination of TBBPA to form a high value product. Although further work will be required to evaluate the possibility of the emission of hazardous brominated organic compounds

5. References

[1] T. Suetens, B. Klaasen, K. Van Acker, B. Blanpain, Comparison of electric arc furnace dust treatment technologies using exergy efficiency, Journal of Cleaner Production, 65 (2014) 152-167.

[2] EAP, European Waste Catalogue And Hazardous Waste List in, Environmental Protection Agency, 2002.

[3] E. Abkhoshk, E. Jorjani, M.S. Al-Harahsheh, F. Rashchi, M. Naazeri, Review of the hydrometallurgical processing of non-sulfide zinc ores, Hydrometallurgy, 149 (2014) 153-167.

[4] J. Rütten, C. Frias, G. Diaz, D. Martin, F. Sanchez, Processing EAF dust through Waelz Kiln and ZINCEXTM solvent extraction: the optimum solution, in: European Metallurgical Conference, SME, Düsseldorf/ Germany, 2011, pp. 1673-1688.

[5] H. Oda, T. Ibaraki, Y. Abe, Dust recycling system by the rotary hearth furnace, in: Nippon Steel Technical Report, 2006, pp. 147-152.

[6] T. Havlik, M. Turzakova, S. Stopic, B. Friedrich, Atmospheric leaching of EAF dust with diluted sulphuric acid, Hydrometallurgy, 77 (2005) 41-50.

[7] F. Kukurugya, T. Vindt, T. Havlík, Behavior of zinc, iron and calcium from electric arc furnace (EAF) dust in hydrometallurgical processing in sulfuric acid solutions: Thermodynamic and kinetic aspects, Hydrometallurgy, 154 (2015) 20-32.

[8] D.S. Baik, D.J. Fray, Recovery of zinc from electric-arc furnace dust by leaching with aqueous hydrochloric acid, plating of zinc and regeneration of electrolyte, Mineral Processing and Extractive Metallurgy, 109 (2000) 121-128.

[9] Z. Youcai, R. Stanforth, Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium, J. Hazard. Mater., 80 (2000) 223-240.

[10] K. Gargul, B. Boryczko, Removal of zinc from dusts and sludges from basic oxygen furnaces in the process of ammoniacal leaching, Archives of Civil and Mechanical Engineering, 15 (2015) 179-187.

[11] A.J.B. Dutra, P.R.P. Paiva, L.M. Tavares, Alkaline leaching of zinc from electric arc furnace steel dust, Miner Eng, 19 (2006) 478-485.

[12] C. Jarupisitthorn, T. Pimtong, G. Lothongkum, Investigation of kinetics of zinc leaching from electric arc furnace dust by sodium hydroxide, Materials Chemistry and Physics, 77 (2003) 531-535.

[13] J.M. Steer, A.J. Griffiths, Investigation of carboxylic acids and non-aqueous solvents for the selective leaching of zinc from blast furnace dust slurry, Hydrometallurgy, 140 (2013) 34-41.

[14] M.K. Jha, V. Kumar, R.J. Singh, Review of hydrometallurgical recovery of zinc from industrial wastes, Resources, Conservation and Recycling, 33 (2001) 1-22.

[15] O. Terakado, R. Ohhashi, M. Hirasawa, Thermal degradation study of tetrabromobisphenol A under the presence metal oxide: Comparison of bromine fixation ability, J Anal Appl Pyrol, 91 (2011) 303-309.

[16] O. Terakado, R. Ohhashi, M. Hirasawa, Bromine fixation by metal oxide in pyrolysis of printed circuit board containing brominated flame retardant, J Anal Appl Pyrol, 103 (2013) 216-221.

[17] S. Oleszek, M. Grabda, E. Shibata, T. Nakamura, Fate of lead oxide during thermal treatment with tetrabromobisphenol A, J. Hazard. Mater., 261 (2013) 163-171.

[18] M. Rzyman, M. Grabda, S. Oleszek-Kudlak, E. Shibata, T. Nakamura, Studies on bromination and evaporation of antimony oxide during thermal treatment of tetrabromobisphenol A (TBBPA), J Anal Appl Pyrol, 88 (2010) 14-21.

[19] M. Altarawneh, B.Z. Dlugogorski, Mechanism of Thermal Decomposition of Tetrabromobisphenol A (TBBA), J. Phys. Chem. A, 118 (2014) 9338-9346.

[20] G.-B. Liu, H.-Y. Zhao, T. Thiemann, Zn dust mediated reductive debromination of tetrabromobisphenol A (TBBPA), J. Hazard. Mater., 169 (2009) 1150-1153.

[21] EBFRIP-Europian-Brominated-Flame-Retardant-Industry-Panel, TBBPA, in, 2009.

[22] D.Y. Lai, S. Kacew, W. Dekant, Tetrabromobisphenol A (TBBPA): Possible modes of action of toxicity and carcinogenicity in rodents, Food and Chemical Toxicology, 80 (2015) 206-214.

[23] Q. He, X. Wang, P. Sun, Z. Wang, L. Wang, Acute and chronic toxicity of tetrabromobisphenol A to three aquatic species under different pH conditions, Aquatic Toxicology, 164 (2015) 145-154.

[24] M. Grabda, S. Oleszek, E. Shibata, T. Nakamura, Vaporization of zinc during thermal treatment of ZnO with tetrabromobisphenol A (TBBPA), J. Hazard. Mater., 187 (2011) 473-479.

[25] S. Oleszek, M. Grabda, E. Shibata, T. Nakamura, Study of the reactions between tetrabromobisphenol A and PbO and Fe2O3 in inert and oxidizing atmospheres by various thermal methods, Thermochim Acta, 566 (2013) 218-225.

[26] M. Grabda, S. Oleszek, E. Shibata, T. Nakamura, Study on simultaneous recycling of EAF dust and plastic waste containing TBBPA, J. Hazard. Mater., 278 (2014) 25-33.

[27] S. Oleszek-Kudlak, M. Grabda, T. Nakamura, Alternative Method for Pyrometallurgical Recycling of EAF Dust Using Plastic Waste Containing Tetrabromobisphenol A, High Temperature Materials and Processes, 30 (2011) 359-366.

[28] M. Al-Harahsheh, S. Kingman, C. Somerfield, F. Ababneh, Microwave-assisted total digestion of sulphide ores for multi-element analysis, Anal Chem Acta, 638 (2009) 101-105.

[29] M. Al-Harahsheh, S. Kingman, L. Al-Makhadmah, I.E. Hamilton, Microwave treatment of electric arc furnace dust with PVC: Dielectric characterization and pyrolysis-leaching, J. Hazard. Mater., 274 (2014) 87-97.

[30] M. Al-Harahsheh, S. Kingman, A. Saeid, J. Robinson, G. Dimitrakis, H. Alnawafleh, Dielectric properties of Jordanian oil shales, Fuel Process Technol, 90 (2009) 1259-1264.

[31] A.J. Cumbane, Microwave Processing of Minerals, in, University of Nottingham, Nottingham, UK, 2003.

[32] M. Al-Harahsheh, A. Al-Otoom, L. Al-Makhadmah, I.E. Hamilton, S. Kingman, S. Al-Asheh, M.A. Hararah, Pyrolysis of poly(vinyl chloride) and—electric arc furnacedust mixtures, J. Hazard. Mater., 299 (2015) 425-436.

[33] G.S. Lee, Y.J. Song, Recycling EAF dust by heat treatment with PVC, Miner Eng, 20 (2007) 739-746.

[34] M. Al-Harahsheh, M. Aljarrah, F. Rummanah, K. Abdellateef, S. Kingman, Leaching of valuable metals from electric arc furnace dust - Tetrabromobisphenol A Pyrolysis residues, J Anal Appl Pyrol, 125 (2017) 50-60.

[35] S. Oleszek, M. Grabda, E. Shibata, T. Nakamura, TG and TG-MS methods for studies of the reaction between metal oxide and brominated flame retardant in various atmospheres, Thermochim Acta, 527 (2012) 13-21.

[36] D.L. Perry, Handbook of Inorganic Compounds, 2nd ed., CRC Press, 2011.

[37] L.V. Gurvich, I.V. Veyts, C.B. Alcock, Thermodynamic properties of individual substances, in: Elements C, Si, Ge, Sn, Pb and thier compounds, Hemosphere Publishing Corporation, New York, 1991.

[38] T.A. Ioannidis, N. Kyriakis, A.I. Zouboulis, P. Akrivos, Lead and bromide precipitation from aqueous acidic solutions. Potential exploitation in industrial applications, Desalination, 211 (2007) 272-285.

468

469

Research highlights

- Thermal and dielectric characteristics of EAFD, TBBPA and their mixtures were evaluated.
- EAFD-TBBPA mixtures absorbed microwaves effectively resulting in fast heating
- Selective separation of Zn and Pb leaving most iron in the solid residue was achieved

Microwave treatment of electric arc furnace dust with Tetrabromobisphenol A: Dielectric characterization and pyrolysis-leaching

Mohammad Al-harahsheh*[1], Sam Kingman[2], Ian Hamilton

[1] Chemical Engineering Department, Jordan University of Science and Technology, Irbid, 22110, Jordan

* msalharahsheh@just.edu.jo

[2]Faculty of Engineering, University of Nottingham, Nottingham, NG7-2RD, UK

Abstract

In the present work microwave treatment of electric arc furnace dust (EAFD) mixed with tetrabromobisphenol A (TBBPA) was investigated. A range of characterization techniques were used to understand the thermal behaviour of TBBPA-EAFD mixtures under microwave pyrolysis conditions. Dielectric and thermal properties of EAFD, TBBPA and their mixtures were determined. Both the dielectric constant and loss factor of the mixture were found to vary considerably with temperature and subsequently it was found that the mixtures of these materials absorbed microwaves effectively, especially at temperatures above 170^0C. The high loss tangent of EAFD-TBBPA mixture above 170^0C resulted in fast heating and high temperatures (above 700^0C) resulting in reduction of Fe, Pb and Zn to their metallic form. This resulted in low recoveries of both Zn and Pb when the residue was leached in water. The recovery of Zn varied between 14 and 52 wt,%, while Pb recovery varied between 3 and 31 wt.% depending on microwave treatment efficiency. The low recovery of Zn and Pb could be ascribed by the reduction of metal oxides into their metallic form. More importantly this work has shown great selectivity in the leachability of both zinc and iron; with iron being left in the solid residue.

Keywords: EAFD; Dielectric Properties, Microwave treatment; Leaching; zinc extraction; TBBPA

1. Introduction

Electric Arc Furnace Dust (EAFD) is a waste by-product generated by the secondary steelmaking industry. Treatment of EAFD is of prime importance for environmental and resource conservation

as it is considered as an environmentally hazardous waste according to the Environmental Protection Agency (EPA) as it contains easy leachable metals including Cd, Pb, and Cr [1, 2]. Due to the depletion of the primary resources of metals such as Zn and Pb, recycling of this dust has gained greater interest among researchers and investors in the metallurgical sector [3]. Both Pyrometallurgical and hydrometallurgical methods have been suggested to recover valuable metals from EAFD. Although pyrometallurgical treatment of EAFD is practiced now at the industrial scale utilizing Waelz Kiln technology [4] and rotary hearth furnaces [5] to recover zinc in the form of ZnO, these methods suffer from high energy requirements compared to hydrometallurgical methods.

Different leaching reagents including sulphuric acid [6, 7], hydrochloric acid [8], ammonia [9, 10], sodium hydroxide [11, 12], and some organic acids [13] have been used for extraction of zinc and other valuables from EAFD. According to Jha et al [14], the most effective lixiviants for zinc extraction from EAFD were found to be sulphuric acid and ammoniacal solutions. Sodium hydroxide dissolves zinc selectively, however, this application needs further development for effective metal recovery from the sodium zincate solution by electrolysis.

There is a great interest nowadays to utilize waste halogenated plastic materials for the recovery of valuable materials from EAFD and to minimize its environmental impact as well as that of waste plastics. Among these waste plastic materials are flame retardant materials, with tetrabromobisphenol A (TBBPA) being the most widely used. Thermal treatment of these wastes results in release of large amounts of HBr and other brominated organic substances such as brominated phenols as well as wide array of other brominated organic compounds [15-19]. If TBBPA is pyrolysed in the presence of metal oxides, the later has high fixing ability toward HBr and subsequent reduction of brominated organic compounds released during the pyrolysis process [15, 20].

The largest volume brominated flame retardant in production today is TBBPA [21]; its annual production exceeded 170 kilotons in 2004 [22] and the estimated annual market demand from 2001 to 2003 was >200,000 ton/year [23]. The reports suggest that huge quantities of brominated plastic wastes are accumulated worldwide, which makes their disposal a real and current challenge.

Utilization of EAFD as a debromination catalyst for TBBPA based plastic materials offers numerous benefits such as HBr capture liberated during TBBPA pyrolytic incineration in the form

of metal bromides. These can be recovered in their vapor form ore leached from the pyrolysis residue using just water. Such a technique allows two waste materials to be treated concurrently to minimize their associated risks and at the same time recover valuable metals from EAFD by relatively simple means.

A major decomposition product from TBBPA degradation is HBr; which is an excellent brominating agent for ZnO present in EAFD and, it therefore, can be used as an agent to selectively separate zinc as a volatile bromide from the solid dust residues. These properties lead to the use of TBBPA as a source of (HBr) for zinc recovery from EAFD as zinc bromide $ZnBr_2$ [24, 25].

The de-bromination process is mainly the loss of bromination species from the backbone followed by an evaporation process. Hydrogen bromide (HBr) as the brominating agent is generated in relatively large amounts when the TBBPA decomposes during thermal processing (HBr accounts for ca. 59 wt.% of TBBP upon thermal decomposition). The HBr reacts with zinc minerals forming a bromide ($ZnBr_2$) that has a boiling point of 650^0C. Grabda et al [24] studied the effect of heating time and temperature on the vaporizing of $ZnBr_2$ under different conditions. They observed that the evaporation increases with heating time at constant heating rate and increasing temperature (due to an increase in the vapor pressure). A mixture of argon and oxygen were used to oxidize the high molecular weight compound ('char') that formed during thermal decomposition of the TBBPA and this affected the vaporization process; however this complex residue declined as heating time and temperature increased. The measured vaporization data show that at 950^o C the vaporization of $ZnBr_2$ was complete, with less than 11 wt% char. However, one-third of ZnO remained as un-reacted residue and required further treatment by carbothermic reduction by carbonaceous char where 4 wt% remained in solid residue. Grabda et al. [26] continued to investigate the possibility of EAFD treatment, using TBBPA and tetrabromobisphenol A diglycidyl ether (TBBPADGE) at 550°C for 80 min, under oxidizing and inert atmospheres; a maximum of 85wt.% of zinc and 81wt.% of lead recoveries were achieved using TBBPADGE. Oleszek-Kudlak et al. [27] also studied the reaction between TBBPA and EAFD and the effect of temperature on the of bromination zinc oxide and the evaporation of its bromide ($ZnBr_2$) in the temperature range 250 - 950 ^{o}C.

This work aims at evaluating the possibility of heating EAFD-TBBPA mixtures by microwave irradiation under pyrolysis conditions. It also aims to study the possibility of extracting valuable

metals from the pyrolysis residue by a hybrid microwave pyrolysis-extraction method. Therefore, the dielectric properties of both materials (EAFD and TBBPA) and their mixtures were measured using cavity perturbation technique and reported herein. Additionally, the pyrolysis of EAFD-TBBPA mixtures, under microwaves, followed by leaching of microwave pyrolysis residue were also carried out.

2. Experimental work

2.1. Materials

The EAFD sample was collected from a Jordanian steel smelter. After homogenization by repeated cone and quartering, the sample was characterized for its chemical and mineralogical composition. A Perkin Elmer (Optima® 3300 DV) Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), was used to measure the content of elements in the EAFD following the procedure of sample preparation reported by Al-Harahsheh et al [28]. TBBPA was purchased from Sigma Aldrich. All other chemicals were reagent grade and used without further purification.

2.2. Microwave treatment procedure

The description of the experimental setup used for microwave treatment of the EAFD-TBBPA mixtures is reported elsewhere [29]. It consisted of a 3 kW microwave generator operated at 2.45 GHz a forward and reflected power measurement system connected to a PC, a WR340 standard rectangular waveguide operating in a dominate TE_{10} mode coupled to a cylindrical choke section (for sampling). The reaction system consisted of nitrogen cylinder fitted with a flow meter, a vertical quartz tube fitted inside the vertical applicator, two 250 ml gas wash bottles connected in series and operated as gas extraction system, and vent connected to external extraction system.

EAFD was mixed with TBBPA in a tumbling mill with ceramic balls at a mass proportion of 1:1. The mixture was then made into cylindrical pellets of about 5g mass. A hydraulic oil press was then used to compress approximately 5 g of the mixture at 180 kg f/cm^2 for 60 s.

To perform the microwave pyrolysis experiments the pellets were placed in a quartz tube positioned vertically in the cylindrical microwave applicator. The sample was then irradiated with

microwave energy for a specified time and power level while nitrogen gas purged the reaction system. In order to collect any soluble vapors, the produced gases were vented through two gas wash bottles filled with water. Irradiation time was varied depending on the observations of the reaction systems and also based on the temperature reading obtained by an optical pyrometer. Microwave power was shut-off if arcing occurred.

At the end of the experiment, the solid residues were reweighed and removed from the quartz tube. Hot water was used to wash out the whole extraction system to collect any water soluble condensate. It was then analyzed for metal content using ICP.

2.3. Leaching of the microwave pyrolysis residues

The solid residue after microwave treatment was ground to a particle size of less than 1 mm and then subjected to leaching in boiling deionized water for 20 minutes. The mixture was then filtered and the leaching solution was then analyzed for the metal content. The remaining solid residues were also analyzed by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM).

2.4. Measurement of dielectric properties

Cavity perturbation method was employed to measure the dielectric properties of EAFD, TBBPA, and their mixture. The experimental setup details are reported elsewhere [30]. A representative mass of about 0.1-0.2 g of the material was packed in the quartz tube and heated to the desired temperature, then positioned in the microwave resonant cavity by means of an automated actuator. The frequency shift and quality factor were measured at 2470 and 912 MHz which are close to the most frequently used frequencies in domestic and industrial microwave processes. Extra care was taken to obtain similar packing density of samples, because powdered sample density has a great effect on the measured values of dielectric properties [31]. The variation in density of packing for 3 replicates was determined to be less than 3.5%. Additionally for each sample, a minimum of three replicates were measured. The dielectric constant (ε') and loss factor (ε'') were then calculated [30].

2.5.X-Ray diffraction and TGA analyses

Representative EAFD sample, taken after prolonged manual mixing, was analyzed for its mineral composition using X-ray diffraction analysis (XRD), furthermore, additional solid samples were analyzed by XRD after microwave pyrolysis and after leaching experiments. A Hiltonbrooks® generator with a Philips® PW 1050 diffractometer with an automatic divergence slit, and Cu-Kα anode producing X-rays of wavelength λ= 1.54056 Aº was used.

Thermogravemetric (TGA) and differential thermal analyses (DTA) of the dust (EAFD) and the plastic material (TBBPA) and their mixture containing 50wt % EAFD and 50wt% TBBPA were performed using a TA- Q600 thermal analyzer. About 10 mg of the sample was placed in fused alumina pan and heated at a heating rate of 10°C/ min under nitrogen with a flow rate of 50 ml/min.

3. Results and discussions

3.1.Physical and chemical characteristics of EAFD

Figure 1 shows the XRD pattern of EAFD. The dust contains zincite, magnetite, franklinite, halite, sylvite, lead hydroxyl chloride and hematite

Insert Figure 1

Figure 1 XRD pattern for EAFD, EAFD-TBBPA residue after pyrolysis and after leaching

The chemical composition of the EAFD sample used in this work was reported elsewhere [32]. The main elements present in the dust are(in wt%) 25.9 Zn, 18 Fe, 4 Ca, 3.3 Na, 3.2 Pb, 2.8Si, 1.8 K and 1.2 Mn. Calorimetry showed that dust contains 2.63 ± 0.03wt% total carbon and 0.1wt% inorganic carbon suggesting that among mineral phases present in the dust are carbonates such as calcium carbonates.

3.2. Dielectric properties of the EAFD

The dielectric constant characterizes the capability of materials to absorb electromagnetic radiation, whereas, loss factor denote the ability of materials to dissipate the adsorbed radiation

into heat. The dielectric constant and loss factor of EAFD were measured at two frequencies namely 911 MHz and 2.47 GHz across a temperature range from 25 to 600 °C [29]. Figure 2 shows the plot of dielectric constant (ε') and loss factor (ε") as a function of temperature. Both values increase with an increase of temperature and the rate of increase become greater when the temperature exceeded 300 °C.

Insert Figure 2

Figure 2 Dielectric properties of EAFD as a function of temperature) at frequencies of 911MHz and 2.47 GHz [4].

Additionally, the ratio of dielectric loss to the dielectric constant is called loss tangent (□"/□'). When the loss tangent is above 0.05, the material is considered to heat well under microwave irradiation. The loss tangent calculated for EAFD was found also to increase steadily with the increase of temperature up to 300°C, then it increases considerably with a further increase of temperature reaching a value of 0.3 at 600°C.

3.3. Dielectric properties analysis of TBBPA

Figure 3 shows the dielectric properties of TBBPA as a function of temperature at frequencies of 911 and 2.47 GHz. The dielectric constant remains constant until a temperature of 150°C then increases suddenly at a temperature of 170°C followed by steady increase until a temperature of 270°C and then decreases sharply. The loss factor decreases with the increase in temperature up to a temperature of 150°C then increases sharply up to a temperature of 270°C and then drops sharply. The increase of both dielectric constant and loss factor after 170°C is related to the start of smelting of TBBPA (melting point of TBBPA=178°C). However the sharp decrease in both parameters after 270°C is an artifact related to the sharp reduction of sample volume due to the decomposition of TBBPA. To obtain more accurate dielectric properties values, a volume correction factor should be introduced; the weight loss at the decomposition temperature was measured to be around 75 wt% of the initial mass. The data reported in Figure 5 did not take into account the volume correction factor due to the difficulty in measuring the final volume at each temperature.

Insert Figure 3

Figure 3 Dielectric Properties of TBBPA as a function of temperature at frequencies of 911 MHz and 2.47 GHz

3.4. Thermal and dielectric properties of TBBPA-EAFD mixture

To study the interaction of the TBBPA-EAFD mixture with microwaves it is essential to measure both dielectric constant and loss factor of the mixture. During thermal treatment of TBBPA-EAFD mixture several events are expected to occur, which will influence the dielectric properties of the mixture. Therefore, the change in mass loss, the heat flow, the dielectric constant and loss factor were measured at different temperatures for a mixture containing 50 wt. % TBBPA and 50 wt. % EAFD. The results of these measurements are plotted in Figure 4 and Figure 5.

The presence of EAFD with TBBPA altered the TGA decomposition profile of TBBPA. Two main regions of mass loss can be seen in the TGA profile for the TBBPA-EAFD mixture, whereas, only one mass loss was seen for pure TBBPA. The later corresponds to the decomposition of TBBPA which ended at a temperature of 350^{o}C; the corresponding mass loss was 75wt% of the initial mass; the mass loss from EAFD alone at this temperature is only 2.5wt%. However, the mass loss for TBBPA-EAFD at the first decomposition stage, ending at a temperature of 310^{o}C, and was 21.5wt% although the decomposition event occurred at the same initial temperature. With the mixture containing 50wt% TBBPA and the remainder consisting of EAFD; the expected mass loss based on the losses of pure materials was determined to be 38.75wt% [29, 33]. The 17.25wt% increase in residual mass found from the experiment is believed to be due to the HBr released not leaving the sample, instead being fixed in the dust in the form of metal bromide ($ZnBr_2$, $PbBr_2$, $CdBr_2$, $FeBr_2$, $FeBr_3$, etc). The exothermic event seen in the heat flow of the TBBPA-EAFD mixture at a temperature of 310^{o}C was evidence of the formation of metal bromides as seen in Figure 5, whereas, an endothermic event was seen in the case of the pure TBBPA as a result of decomposition.

Insert Figure 4

Figure 4 overlay of mass loss and dielectric constant measurement (2.47 GHz) of 1:1 mass ratio of TBBPA-EAFD mixture designated as E-TBBPA.

The second decomposition stage (470-600^{o}C) seen in the TG profile of TBBPA-EAFD mixture could be related to evaporation of zinc bromide formed [34]. Further mass loss occurring above temperature 600^{o}C could be related to evaporation of other metal bromides species like $PbBr_2$ and $FeBr_2$ as well as reduction of the remaining metal oxides present in the dust by the char/carbon

(evidence of this will be demonstrated later) and also evaporation of metallic zinc produced by reduction reactions.

The dielectric constant of the mixture did not correlate with the mass loss occurring at the first decomposition stage as it increases with the increase in temperature up to a temperature of 550°C reaching the first maxima of 13.2. The different behavior of dielectric constant of TBBPA-EAFD mixture from that of pure TBBPA could be related to the formation ionic metal bromides which coincide with TBBPA decomposition and the release of HBr. These halide ionic species exhibit strong interaction with the electric field [29] due to ionic conduction and also the fusion of these halides (T_m ($ZnBr_2$)= 394°C [35]; T_m ($PbBr_2$=371°C) [36].

The steady drop in dielectric constant of the TBBPA-EAFD mixture beyond a temperature of 550°C until 760°C, reaching a minima of 11.16, could be related to the vaporization of the metal bromides which corresponds to the second thermal event described above. Beyond a temperature of 760°C, the dielectric constant starts to increase again reaching a second maxima (of 15.02) at a temperature of 905°C. In this temperature region reduction of the remaining metal oxides occurs by the char forming pure metal like Zn, Pb and Fe, as confirmed by SEM analysis shown below. Furthermore, zinc boils at a temperature of 907 °C [35].

The loss factor of TBBPA-EAFD mixtures, remained at very low values until the TBBPA smelts thereafter the values began to increase at a constant rate up to the decomposition temperature of TBBPA. Further increases occurred with a higher rate until reaching a maximum value (3.46) at a temperature of 480 °C, which corresponds to the onset temperature of the second thermal event (zinc bromide vaporization). The loss factor then dropped to values as low as 0.68 at a temperature of 630°C then remained almost constant until the temperature reached 780 °C, where it was seen to increase rapidly. The loss of the ionic metal bromides beyond a temperature of 480 °C appeared to have contributed to the drop in the loss factor, however, the formation of the char at pyrolysis temperature is likely to the cause of the sharp increase of the loss factor.

Insert Figure 5

Figure 5 overlay of heat flow and dielectric constant measurement (2.47 GHz) of 1:1 mass ratio of TBBPA-EAFD mixture

3.5. Recovery of valuable metals

The recovery of valuable metals was performed for a TBBPA-EAFD mixture of mass ratio 1:1. This was performed in two stages; metals evaporated during microwave pyrolysis and metals leached from the pyrolysis residue using boiling water

The recovered metals from EAFD-TBBPA pellets after microwave pyrolysis in the extraction system is shown in Table 1. The same experiment was repeated 6 times due to the great variations in microwave coupling with the sample. Approximately 5wt% of zinc, 4wt% of lead and 6wt% of cadmium were collected as metal bromide vapor. Other distinctive features observed (shown in Table 1) was the absence of iron in the solution, implying that iron bromides were not evaporated from the pellet.

Table 1 Valuable metals (wt%) recovered as condensate in the extraction system after microwave treatment.

Exp. #	Ca	Cd	Fe	K	Mg	Mn	Na	Pb	S	Zn
MH1	0.17	1.99	0.03	0.54	0.10	0.13	0.62	0.63	0.44	1.31
MH2	0.19	2.83	0.00	0.31	0.07	0.07	0.49	1.10	0.60	3.75
MH3	0.24	2.43	0.03	0.32	0.29	0.07	0.37	1.03	0.62	2.37
MH7	0.51	5.88	0.06	0.86	0.54	0.18	0.95	4.14	0.93	4.74
MH8	0.26	2.24	0.03	0.74	0.20	0.14	0.74	1.58	0.49	2.01
MH9	0.24	0.73	0.02	0.24	0.27	0.07	0.28	0.67	0.66	0.83

Table 2 shows the metal recovery from the TBBPA- dust mixtures after leaching of residues obtained in hot water for 20 minutes. Both K and Na show high recovery in the leaching solution, which is expected, as both K and Na are, initially, in the chloride form in the dust which are soluble in water. Cadmium recovery was as high as 87wt% in the leaching solution, while the highest lead and zinc recoveries were only 33wt% and 50wt%, respectively. These values were slightly lower than those obtained after conventional pyrolysis followed by leaching of the solid residues of E-TBBPA1 (1 Dust: 1 TBBPA) [12]. With regards to iron, no more 1wt% was recovered in the leaching solution and the remaining was mainly in the solid residue. This finding is of prime importance, which suggests that excellent selectivity of dissolution of lead and zinc with respect to iron, making further treatment of pregnant solution much simpler. Similar selectivity results were obtained under conventional pyrolysis conditions [33]. Additionally, both calcium and manganese showed good fixing capacity toward HBr.

Table 2 Valuable metals (wt%) recovered from TBBPA-EAFD mixtures by leaching of the pyrolysis residues in boiling water for 20 minutes

Exp. #	Ca	Cd	Fe	K	Mg	Mn	Na	Pb	S	Zn
ML1	29.83	67.52	0.00	76.69	12.13	7.93	74.21	3.14	17.05	12.63
ML2	46.19	58.80	0.00	87.09	7.01	23.55	86.72	7.58	8.71	27.36
ML3	49.04	79.45	1.30	93.87	8.41	28.98	92.36	20.48	17.82	46.69
ML7	50.74	80.66	0.47	97.15	4.14	33.10	95.72	31.00	16.59	45.57
ML8	52.48	81.74	0.08	95.24	5.60	30.64	93.35	24.16	32.67	50.38
ML9	48.32	87.13	0.19	96.92	3.67	34.26	95.05	14.92	10.98	42.04

For a better understanding of the reaction occurring between metal oxides present in the dust and the decomposition products of TBBPA (HBr and char), both SEM and XRD analyses of both pyrolysis and leaching residues were performed.

The XRD patterns of solid residues after microwave pyrolysis, and after leaching with hot water are shown in Figure 1. Table 3 shows the main mineral phases identified in the samples (EAFD, pyrolysis and leaching residue). After pyrolysis the peaks of zincite decreased considerably, however, still present in the sample after pyrolysis and leaching which explains the low zinc recovery which is also related to the presence of franklinite. This could be due to several reasons the principal one being that the HBr released from the TBBPA was stoichiometrically not sufficient to convert all of ZnO and $ZnFe_2O_4$ to zinc bromide. It is worth mentioning that part of HBr was reacted with NaCl and KCl to form both NaBr and KBr.

The presence of chloride salts also led to the formation of complex salts such as Na_2ZnBr_4, Na_2PbBr_4, K_2ZnBr_4 and K_2PBBr_4. Additionally, the presence of wustite in the pyrolysis residue is an evidence of the partial iron oxide (magnetite) reduction.

SEM analysis of samples of the TBBPA-dust mixture after microwave treatment showed the formation of lead-iron nodules as can be seen from Figure 6. These lead-iron nodules were not observed after conventional pyrolysis of the same mixture even at temperatures as high as 450 ^{o}C . This suggests that the treatment temperature was high enough to carbonize the TBBPA and produce carbon that was able to reduce both iron and lead present in the dust. Such findings explain the lower recovery levels of iron, lead and zinc.

Insert Figure 6

Figure 6 SEM micrograph and EDX analysis of TBBPA-dust residue (1:1) after microwave treatment showing iron nodules coated with lead.

The XRD pattern for residue after leaching showed also the presence of Pb(OH)Br in the solid residue, which explains the lower lead recovery than that of Zn. Ioannidis et al [37] reported that Pb(OH)Br can be precipitated in neutral water in the pH range between 4-8. This was confirmed by SEM and EDS analyses shown in Figure 7; the atomic ratio of Br and Pb is almost 1 suggesting that the analyzed spot is Pb(OH)Br. The presence of Pb(OH)Br was also detected in the conventional pyrolysis residue of the same mixture (50wt% EAFD+ 50wt% TBBPA) after leaching [33]. Additionally, the atomic ratio of Fe, Zn and O is consistent with the presence of an Fe-Zn alloy and iron and/or iron-zinc oxides; the atomic ratio of elements in franklinite is 1Zn:2Fe:4O, whereas, the ratio obtained in the area is 15Zn:19Fe:8O suggesting that almost 80wt% of Zn and Fe are in the form of Fe-Zn alloy. The latter was confirmed by XRD analysis (see Table 3). However, such alloy was not detected in the previous work by Al-Harahsheh et al [33] following conventional pyrolysis, which again confirms the high temperatures obtained by microwave heating. The formation of char coupled with the high temperatures led to reduction of Fe and Zn oxides into their metallic forms, while arcing during microwave pyrolysis have to their smelting and formation of such Fe-Zn alloys.

In summary, it was found that microwave heating was efficient for the pyrolysis of TBBPA-EAFD mixture in very short time (less than 2 minutes). An example of the power profile obtained during microwave treatment of the mixture is shown in Figure 8. The amount of microwave power absorbed increased rapidly reaching almost 80% of the incident power, and then dropped to almost 30%, followed by further increased to 60% after 1 minute then it remained constant. The absorbed power profile is consistent with the variations in both dielectric constant and loss factor observed shown in Figure 4 and Figure 5. . After 115 seconds of microwave arcing was observed, therefore, the microwave power was shutoff. The maximum temperature detected by the optical pyrometer was about 650 ^{o}C. However, for the purpose to recover metal values by leaching of pyrolysis residue, it is required that the microwave pyrolysis temperature should not exceed 350^{o}C to avoid evaporation of metal bromides and the reduction of these metals into their metallic form. Additionally, the ratio of TBBPA to EAFD should be increased to offer more HBr to convert both zinc and lead oxides into soluble metal bromides. The recent work by Al-Harahsheh et al have shown that conventional pyrolysis TBBPA-EAFD mixture up to a temperature of 350^{o}C followed by leaching of pyrolysis residue results in very high recoveries of both Zn and Pb leaving Fe in the pyrolysis residue.

Table 3 Mineral phases identified in the residue of EAFD-TBBPA (1:1) after microwave treatment and after water leaching.

Feed EAFD	Franklinite/Magnetite, Zincite, Halite, Sylvite, PbCl(OH), calcite, silicate
EAFD-TBBPA residue after microwave pyrolysis	Franklinite/Magnetite, Zincite, $PbBr_2$, Willemite, Wustite, NaBr, KBr, K_2ZnBr_4, K_2PbBr_4, Na_2ZnBr_4, Na_2PbBr_4, Iron, Lead, Iron-zinc
EAFD-TBBPA residue after microwave pyrolysis and leaching	Franklinite/Magnetite, Zincite, Willemite, Wustite, Hematite, Iron, Lead, iron-zinc, PbBr(OH)

Insert Figure 7

Figure 7 SEM micrograph and EDX analysis of TBBPA-dust residue (1:1) after microwave treatment and leaching showing PbBrOH precipitate

Insert Figure 8

Figure 8 Example of microwave power log obtained for Exp. MH 3

4. Conclusions

Comprehensive characterization of EAFD-TBBPA mixture (ratio 1:1) was carried out in terms of their dielectric and thermal behavior as well as chemical and mineralogical composition. The TBBPA-EAFD mixture exhibited good absorption of microwaves once the melting temperature of the TBBPA has been reached. The microwave treatment time was short (1-3 minutes) suggesting the high efficiency of microwave treatment. Microwave treatment of EAFD–TBBPA mixture followed by water leaching was found to be not very efficient for recovery of Zn, and Pb due to the reduction of these metals into their metallic form by the carbonaceous materials left after TBBPA decomposition and also due to the low proportion TBBPA used in the mixture. The SEM and XRD analyses confirmed that part of iron, lead and zinc oxides present in the dust were reduced to their metallic form. Additionally Pb was found to precipitate during the leaching process in the form of PbBrOH which implies that Zn and Pb can be separated during leaching of the residue.

The pyrolysis of TBBPA in presence of EAFD is showed to be good method of debromination of TBBPA to form a high value product. Although further work will be required to evaluate the possibility of the emission of hazardous brominated organic compounds

5. References

[1] T. Suetens, B. Klaasen, K. Van Acker, B. Blanpain, Comparison of electric arc furnace dust treatment technologies using exergy efficiency, Journal of Cleaner Production, 65 (2014) 152-167.

[2] EAP, European Waste Catalogue And Hazardous Waste List in, Environmental Protection Agency, 2002.

[3] E. Abkhoshk, E. Jorjani, M.S. Al-Harahsheh, F. Rashchi, M. Naazeri, Review of the hydrometallurgical processing of non-sulfide zinc ores, Hydrometallurgy, 149 (2014) 153-167.

[4] J. Rütten, C. Frias, G. Diaz, D. Martin, F. Sanchez, Processing EAF dust through Waelz Kiln and ZINCEXTM solvent extraction: the optimum solution, in: European Metallurgical Conference, SME, Düsseldorf/ Germany, 2011, pp. 1673-1688.

[5] H. Oda, T. Ibaraki, Y. Abe, Dust recycling system by the rotary hearth furnace, in: Nippon Steel Technical Report, 2006, pp. 147-152.

[6] T. Havlik, M. Turzakova, S. Stopic, B. Friedrich, Atmospheric leaching of EAF dust with diluted sulphuric acid, Hydrometallurgy, 77 (2005) 41-50.

[7] F. Kukurugya, T. Vindt, T. Havlík, Behavior of zinc, iron and calcium from electric arc furnace (EAF) dust in hydrometallurgical processing in sulfuric acid solutions: Thermodynamic and kinetic aspects, Hydrometallurgy, 154 (2015) 20-32.

[8] D.S. Baik, D.J. Fray, Recovery of zinc from electric-arc furnace dust by leaching with aqueous hydrochloric acid, plating of zinc and regeneration of electrolyte, Mineral Processing and Extractive Metallurgy, 109 (2000) 121-128.

[9] Z. Youcai, R. Stanforth, Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium, J. Hazard. Mater., 80 (2000) 223-240.

[10] K. Gargul, B. Boryczko, Removal of zinc from dusts and sludges from basic oxygen furnaces in the process of ammoniacal leaching, Archives of Civil and Mechanical Engineering, 15 (2015) 179-187.

[11] A.J.B. Dutra, P.R.P. Paiva, L.M. Tavares, Alkaline leaching of zinc from electric arc furnace steel dust, Miner Eng, 19 (2006) 478-485.

[12] C. Jarupisitthorn, T. Pimtong, G. Lothongkum, Investigation of kinetics of zinc leaching from electric arc furnace dust by sodium hydroxide, Materials Chemistry and Physics, 77 (2003) 531-535.

[13] J.M. Steer, A.J. Griffiths, Investigation of carboxylic acids and non-aqueous solvents for the selective leaching of zinc from blast furnace dust slurry, Hydrometallurgy, 140 (2013) 34-41.

[14] M.K. Jha, V. Kumar, R.J. Singh, Review of hydrometallurgical recovery of zinc from industrial wastes, Resources, Conservation and Recycling, 33 (2001) 1-22.

[15] O. Terakado, R. Ohhashi, M. Hirasawa, Thermal degradation study of tetrabromobisphenol A under the presence metal oxide: Comparison of bromine fixation ability, J Anal Appl Pyrol, 91 (2011) 303-309.

[16] O. Terakado, R. Ohhashi, M. Hirasawa, Bromine fixation by metal oxide in pyrolysis of printed circuit board containing brominated flame retardant, J Anal Appl Pyrol, 103 (2013) 216-221.

[17] S. Oleszek, M. Grabda, E. Shibata, T. Nakamura, Fate of lead oxide during thermal treatment with tetrabromobisphenol A, J. Hazard. Mater., 261 (2013) 163-171.

[18] M. Rzyman, M. Grabda, S. Oleszek-Kudlak, E. Shibata, T. Nakamura, Studies on bromination and evaporation of antimony oxide during thermal treatment of tetrabromobisphenol A (TBBPA), J Anal Appl Pyrol, 88 (2010) 14-21.

[19] M. Altarawneh, B.Z. Dlugogorski, Mechanism of Thermal Decomposition of Tetrabromobisphenol A (TBBA), J. Phys. Chem. A, 118 (2014) 9338-9346.

[20] G.-B. Liu, H.-Y. Zhao, T. Thiemann, Zn dust mediated reductive debromination of tetrabromobisphenol A (TBBPA), J. Hazard. Mater., 169 (2009) 1150-1153.

[21] EBFRIP-Europian-Brominated-Flame-Retardant-Industry-Panel, TBBPA, in, 2009.

[22] D.Y. Lai, S. Kacew, W. Dekant, Tetrabromobisphenol A (TBBPA): Possible modes of action of toxicity and carcinogenicity in rodents, Food and Chemical Toxicology, 80 (2015) 206-214.

[23] Q. He, X. Wang, P. Sun, Z. Wang, L. Wang, Acute and chronic toxicity of tetrabromobisphenol A to three aquatic species under different pH conditions, Aquatic Toxicology, 164 (2015) 145-154.

[24] M. Grabda, S. Oleszek, E. Shibata, T. Nakamura, Vaporization of zinc during thermal treatment of ZnO with tetrabromobisphenol A (TBBPA), J. Hazard. Mater., 187 (2011) 473-479.

[25] S. Oleszek, M. Grabda, E. Shibata, T. Nakamura, Study of the reactions between tetrabromobisphenol A and PbO and Fe2O3 in inert and oxidizing atmospheres by various thermal methods, Thermochim Acta, 566 (2013) 218-225.

[26] M. Grabda, S. Oleszek, E. Shibata, T. Nakamura, Study on simultaneous recycling of EAF dust and plastic waste containing TBBPA, J. Hazard. Mater., 278 (2014) 25-33.

[27] S. Oleszek-Kudlak, M. Grabda, T. Nakamura, Alternative Method for Pyrometallurgical Recycling of EAF Dust Using Plastic Waste Containing Tetrabromobisphenol A, High Temperature Materials and Processes, 30 (2011) 359-366.

[28] M. Al-Harahsheh, S. Kingman, C. Somerfield, F. Ababneh, Microwave-assisted total digestion of sulphide ores for multi-element analysis, Anal Chem Acta, 638 (2009) 101-105.

[29] M. Al-Harahsheh, S. Kingman, L. Al-Makhadmah, I.E. Hamilton, Microwave treatment of electric arc furnace dust with PVC: Dielectric characterization and pyrolysis-leaching, J. Hazard. Mater., 274 (2014) 87-97.

[30] M. Al-Harahsheh, S. Kingman, A. Saeid, J. Robinson, G. Dimitrakis, H. Alnawafleh, Dielectric properties of Jordanian oil shales, Fuel Process Technol, 90 (2009) 1259-1264.

[31] A.J. Cumbane, Microwave Processing of Minerals, in, University of Nottingham, Nottingham, UK, 2003.

[32] M. Al-Harahsheh, A. Al-Otoom, L. Al-Makhadmah, I.E. Hamilton, S. Kingman, S. Al-Asheh, M.A. Hararah, Pyrolysis of poly(vinyl chloride) and—electric arc furnacedust mixtures, J. Hazard. Mater., 299 (2015) 425-436.

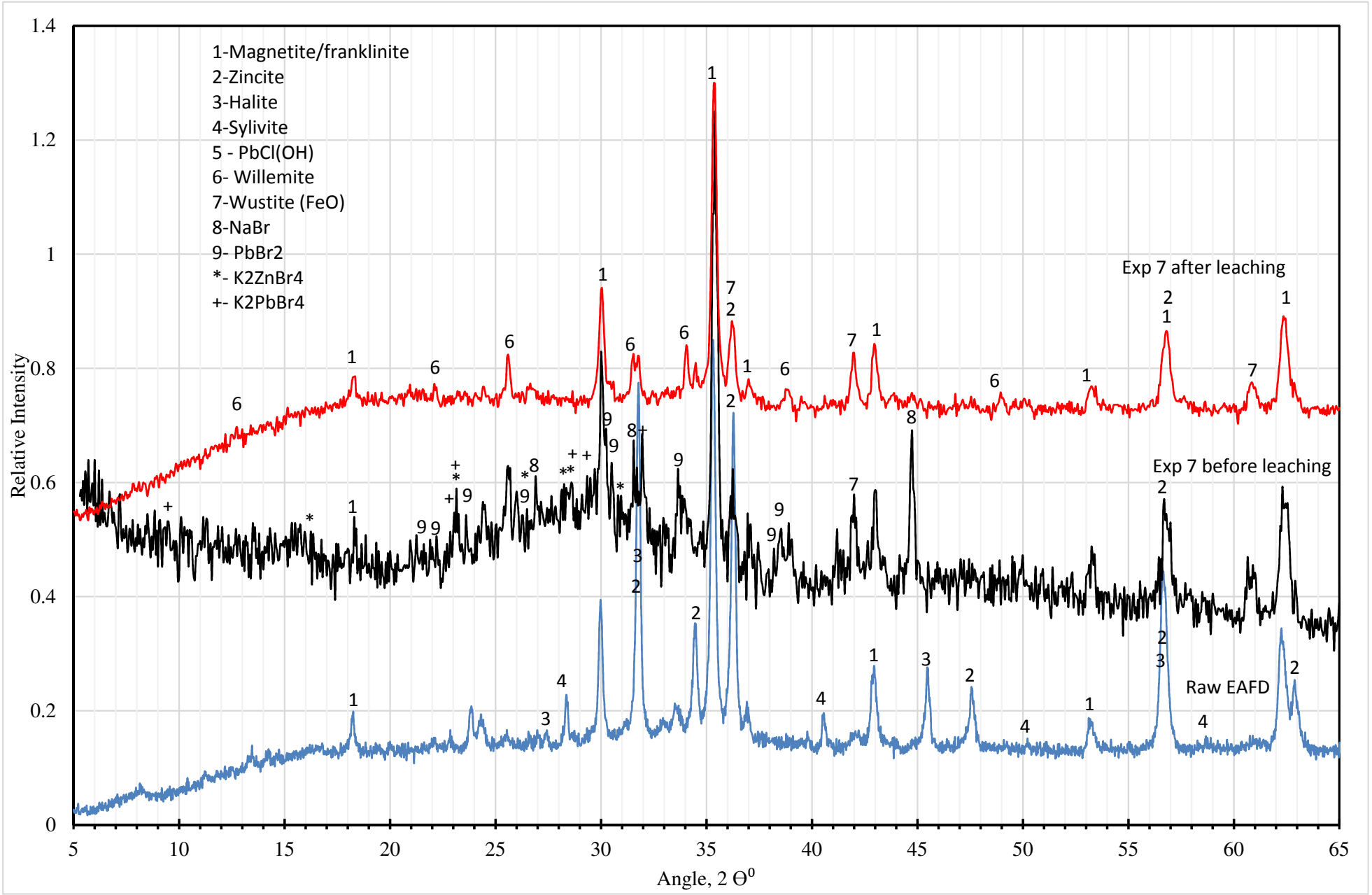
[33] M. Al-Harahsheh, M. Aljarrah, F. Rummanah, K. Abdellateef, S. Kingman, Leaching of valuable metals from electric arc furnace dust - Tetrabromobisphenol A Pyrolysis residues, J Anal Appl Pyrol, 125 (2017) 50-60.

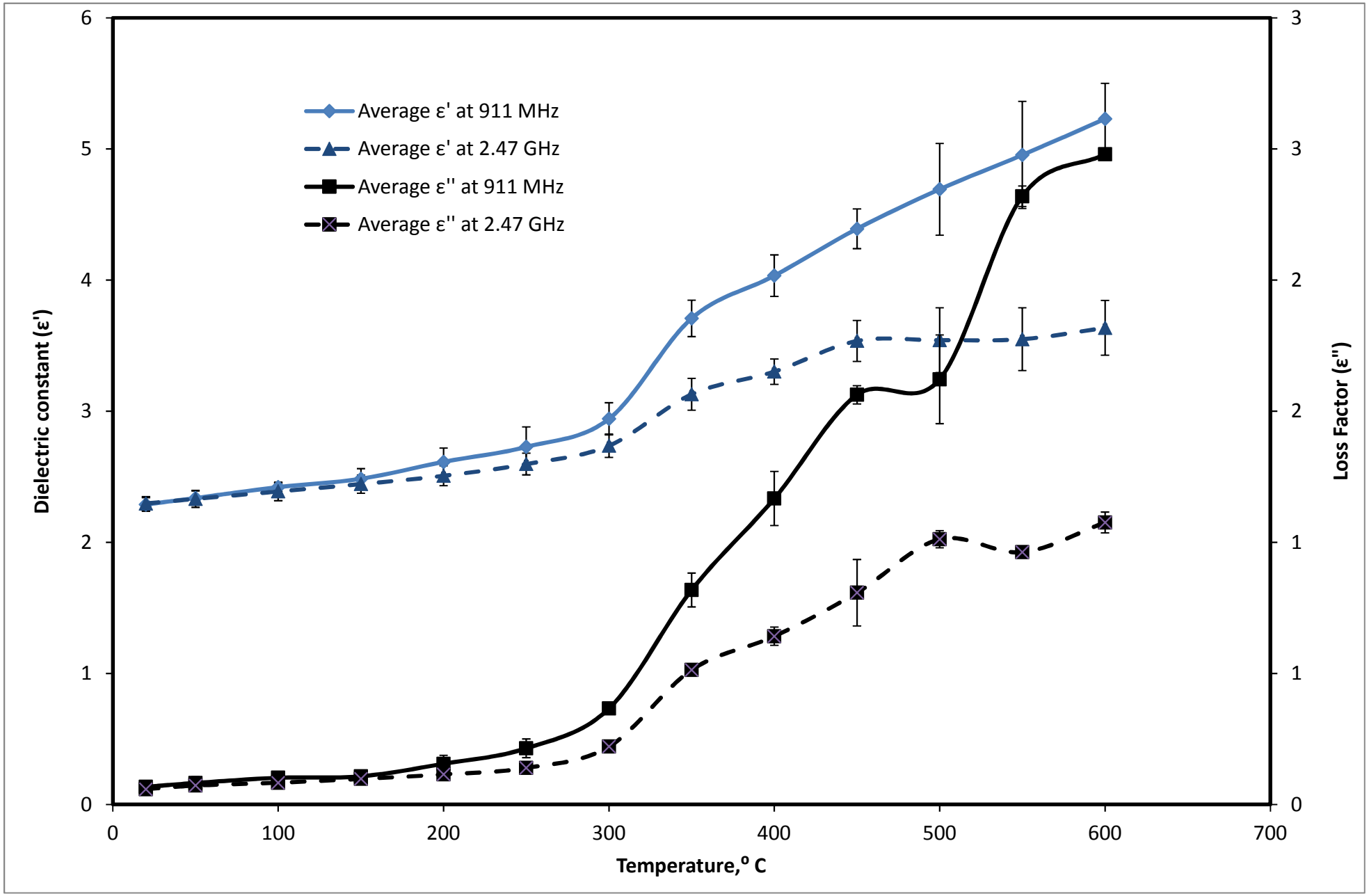
[34] S. Oleszek, M. Grabda, E. Shibata, T. Nakamura, TG and TG-MS methods for studies of the reaction between metal oxide and brominated flame retardant in various atmospheres, Thermochim Acta, 527 (2012) 13-21.

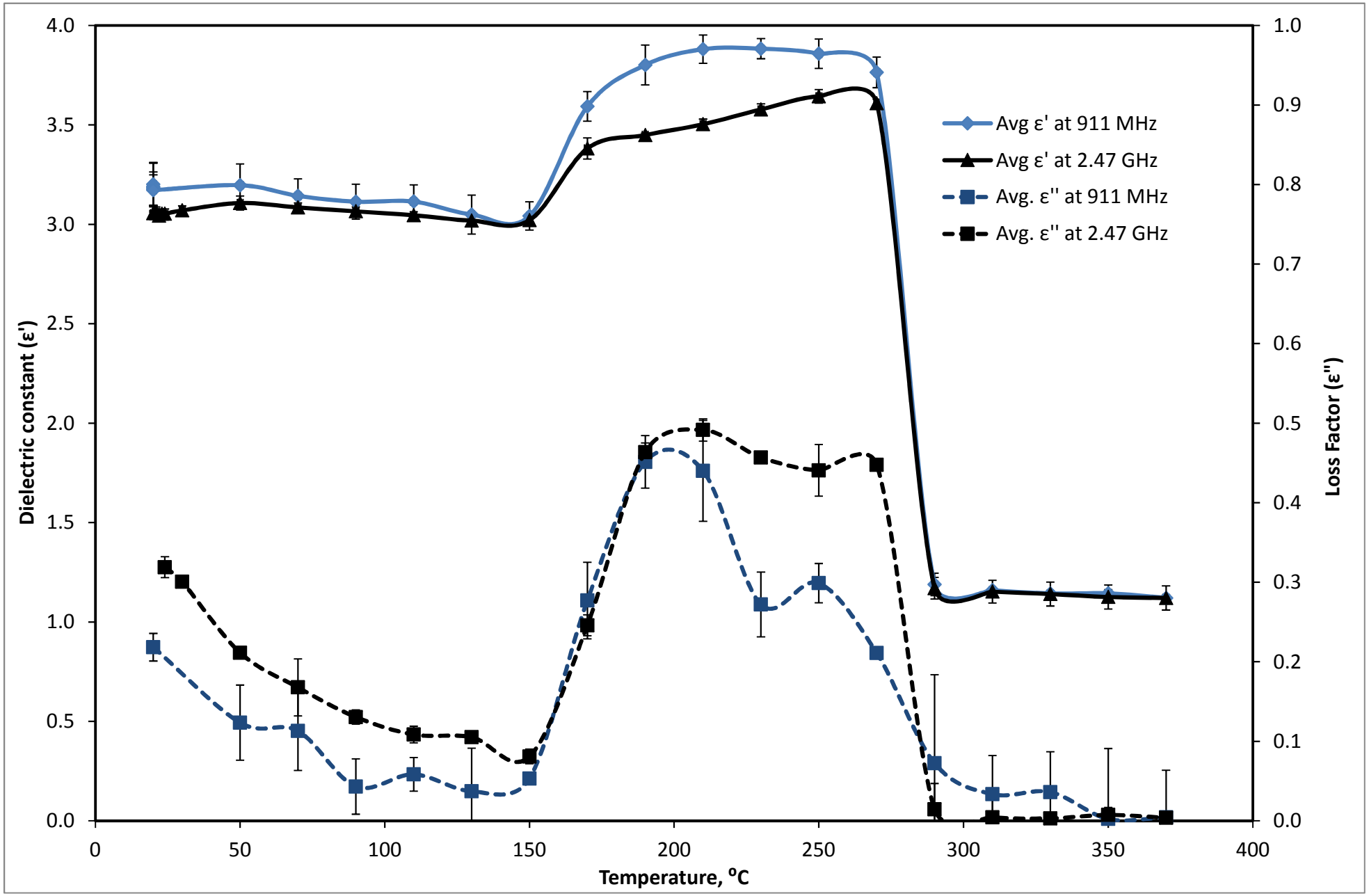
[35] D.L. Perry, Handbook of Inorganic Compounds, 2nd ed., CRC Press, 2011.

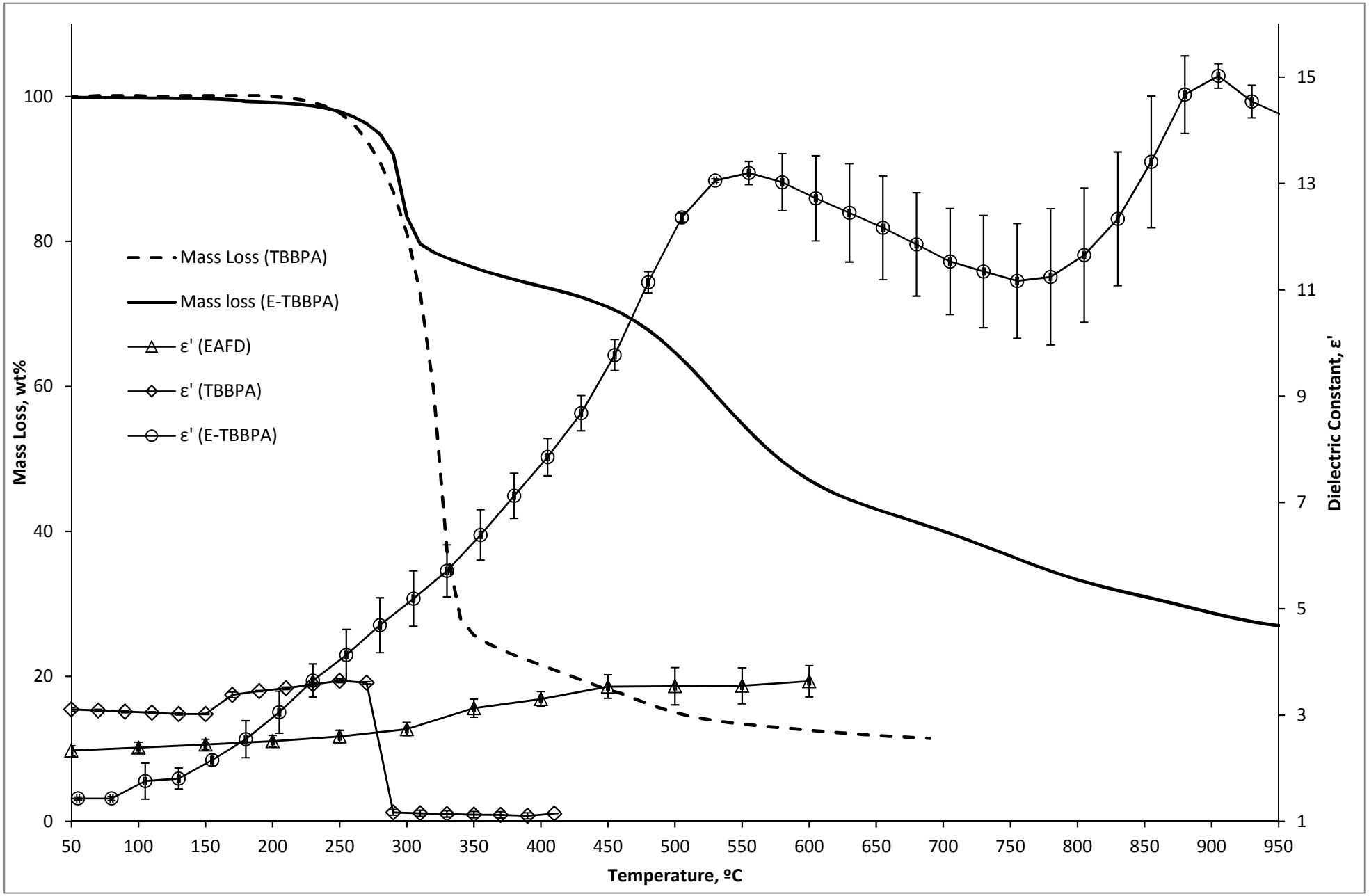
[36] L.V. Gurvich, I.V. Veyts, C.B. Alcock, Thermodynamic properties of individual substances, in: Elements C, Si, Ge, Sn, Pb and thier compounds, Hemosphere Publishing Corporation, New York, 1991.

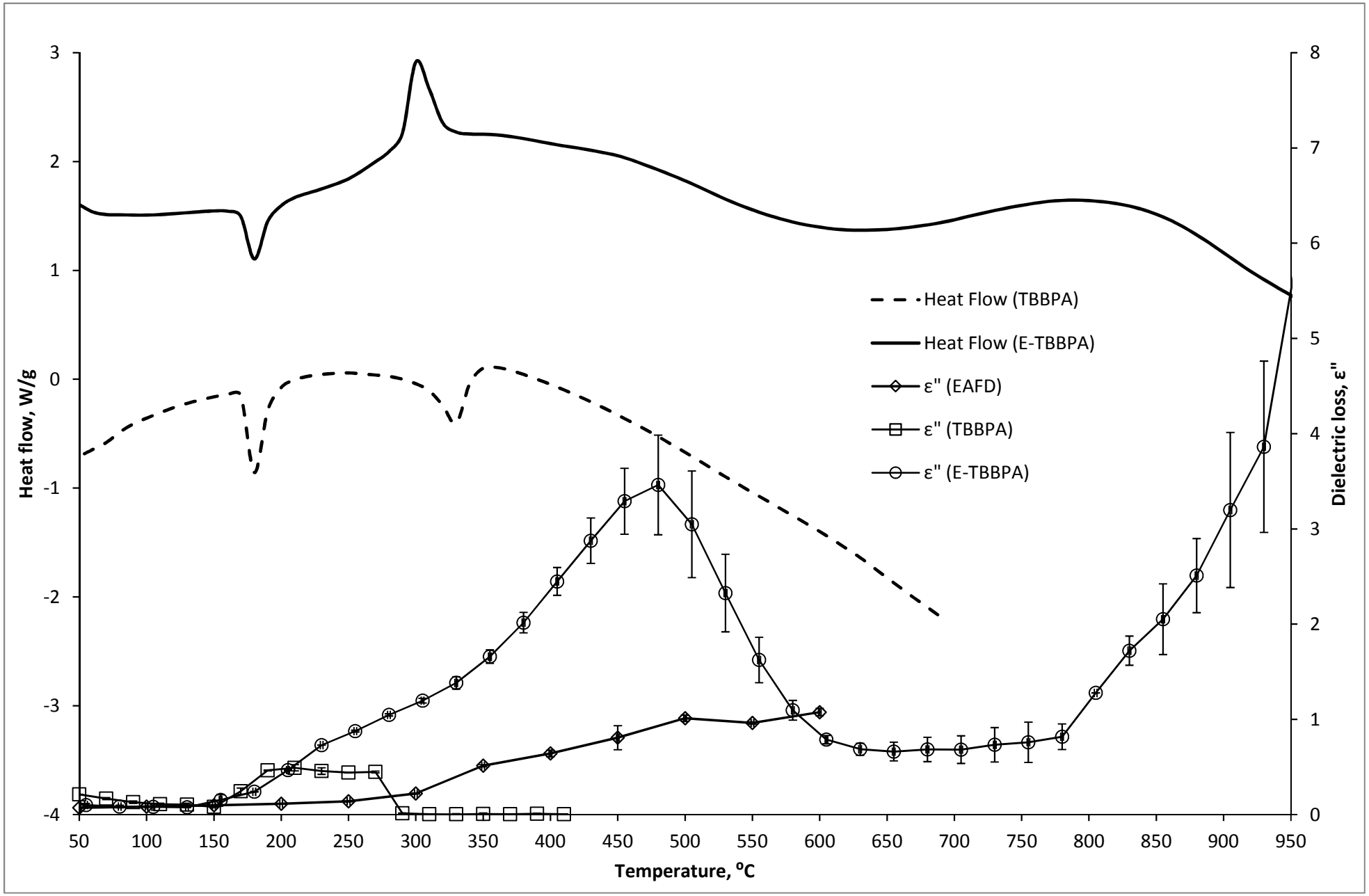
[37] T.A. Ioannidis, N. Kyriakis, A.I. Zouboulis, P. Akrivos, Lead and bromide precipitation from aqueous acidic solutions. Potential exploitation in industrial applications, Desalination, 211 (2007) 272-285.

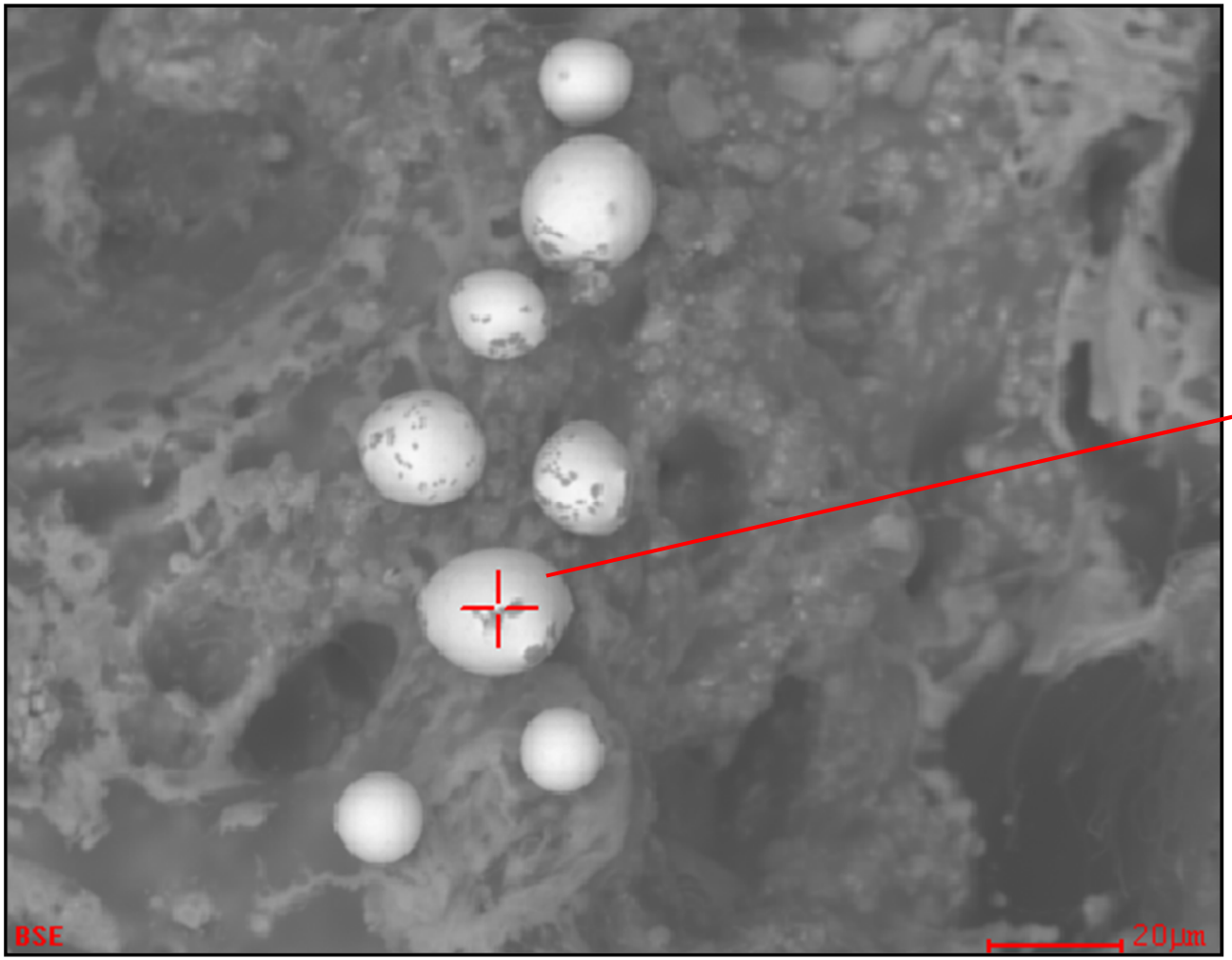

1-Magnetite/franklinite
2-Zincite
3-Halite
4-Sylivite
5 - PbCl(OH)
6- Willemite
7-Wustite (FeO)
8-NaBr
9- PbBr2
*- K2ZnBr4
+- K2PbBr4
Exp 7 after leaching
Exp 7 before leaching
Raw EAFD
Relative Intensity
Angle, 2 Θ⁰
0
0.2
0.4
0.6
0.8
1
1.2
1.4
5
10
15
20
25
30
35
40
45
50
55
60
65


Average ε' at 911 MHz
Average ε' at 2.47 GHz
Average ε'' at 911 MHz
Average ε'' at 2.47 GHz
Dielectric constant (ε')
Loss Factor (ε'')
Temperature,° C
0
100
200
300
400
500
600
700
1
2
3
4
5
6

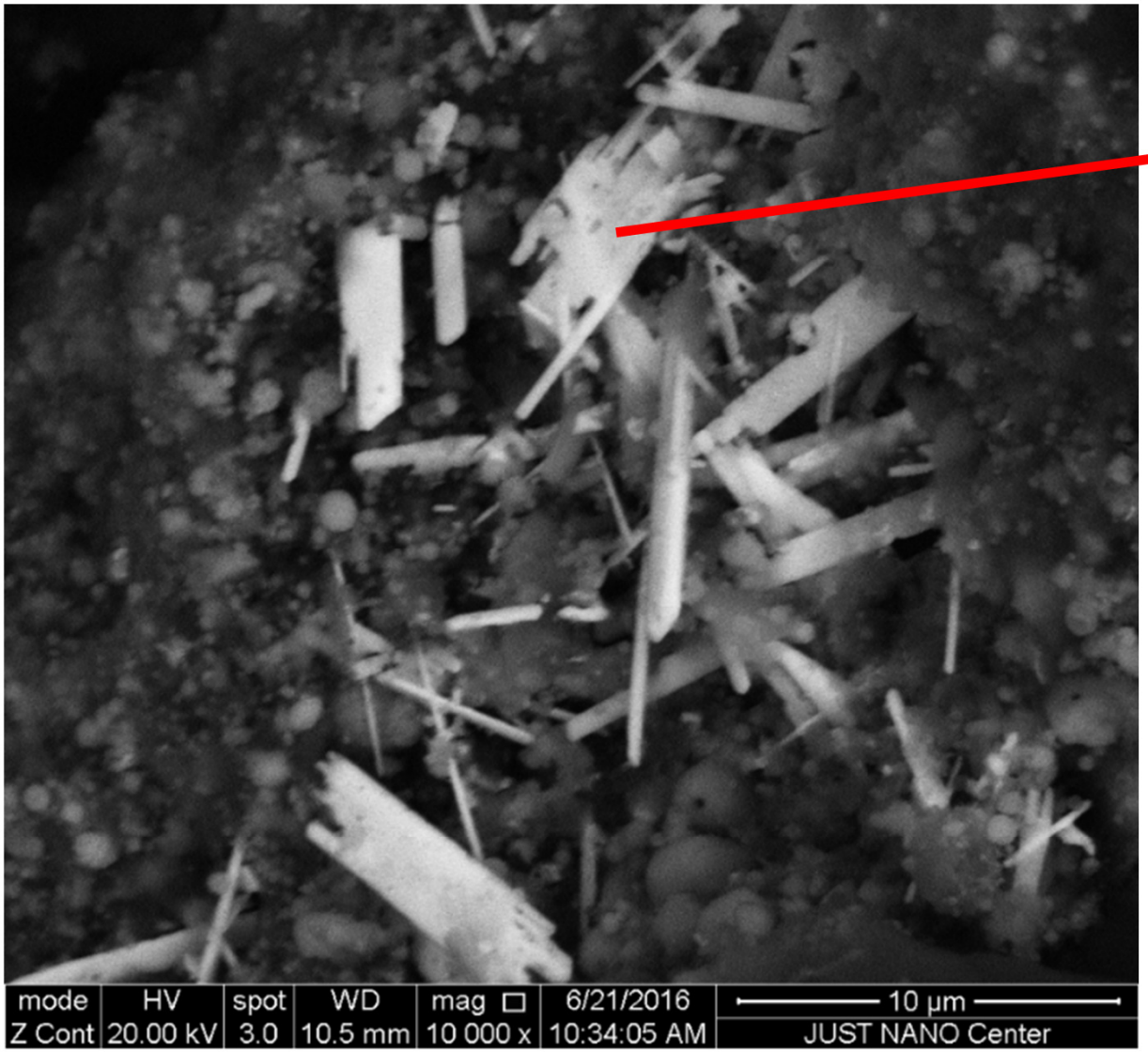

Avg ε' at 911 MHz
Avg ε' at 2.47 GHz
Avg. ε'' at 911 MHz
Avg. ε'' at 2.47 GHz
Dielectric constant (ε')
Loss Factor (ε'')
Temperature, °C
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
50
100
150
200
250
300
350
400


Mass Loss (TBBPA)
Mass loss (E-TBBPA)
ε' (EAFD)
ε' (TBBPA)
ε' (E-TBBPA)
Mass Loss, wt%
Dielectric Constant, ε'
Temperature, ºC
0
20
40
60
80
100
1
3
5
7
9
11
13
15
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950

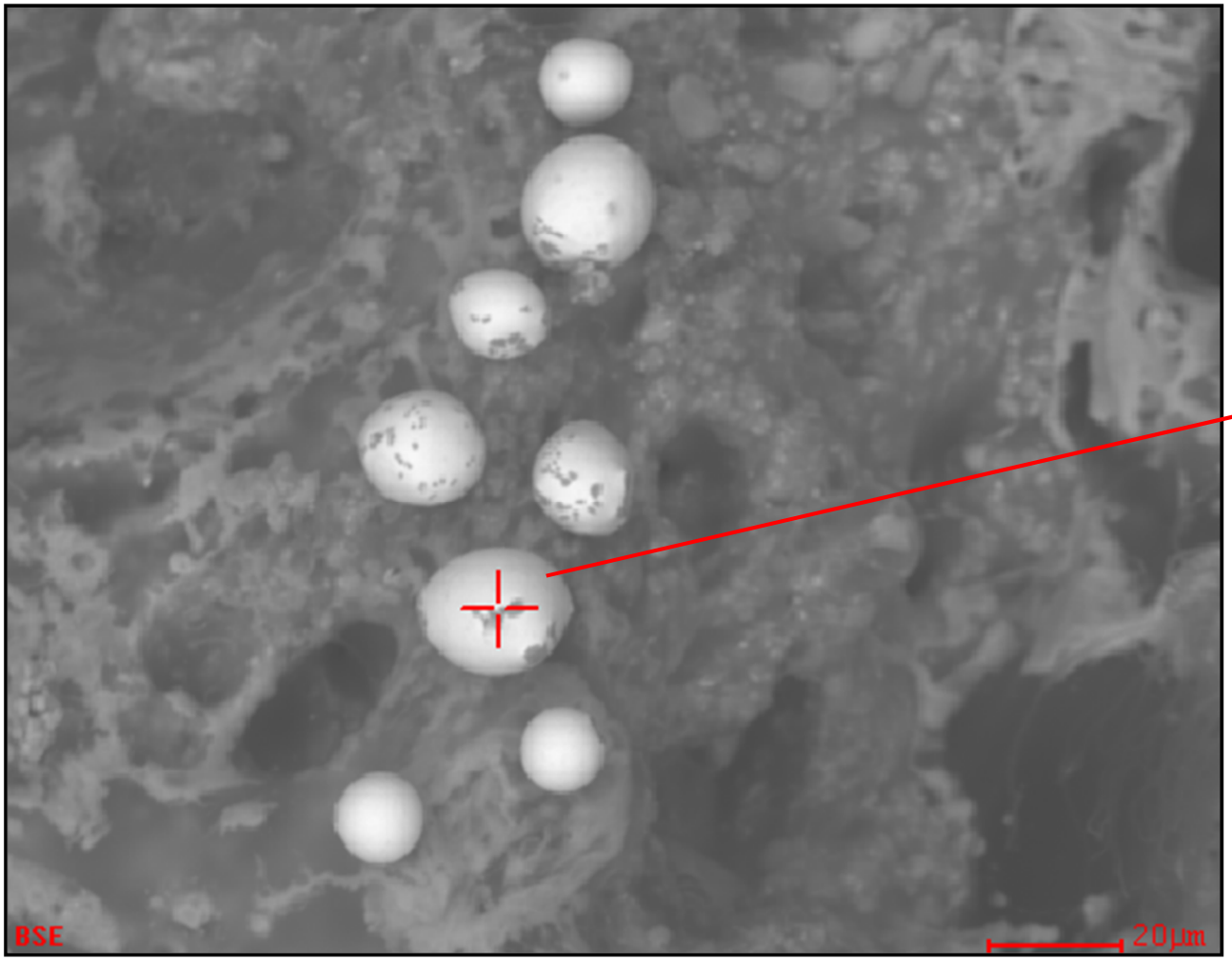

Heat Flow (TBBPA)
Heat Flow (E-TBBPA)
ε" (EAFD)
ε" (TBBPA)
ε" (E-TBBPA)
Heat flow, W/g
Dielectric loss, ε"
Temperature, °C
3
2
1
0
-1
-2
-3
-4
8
7
6
5
4
3
2
1
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950



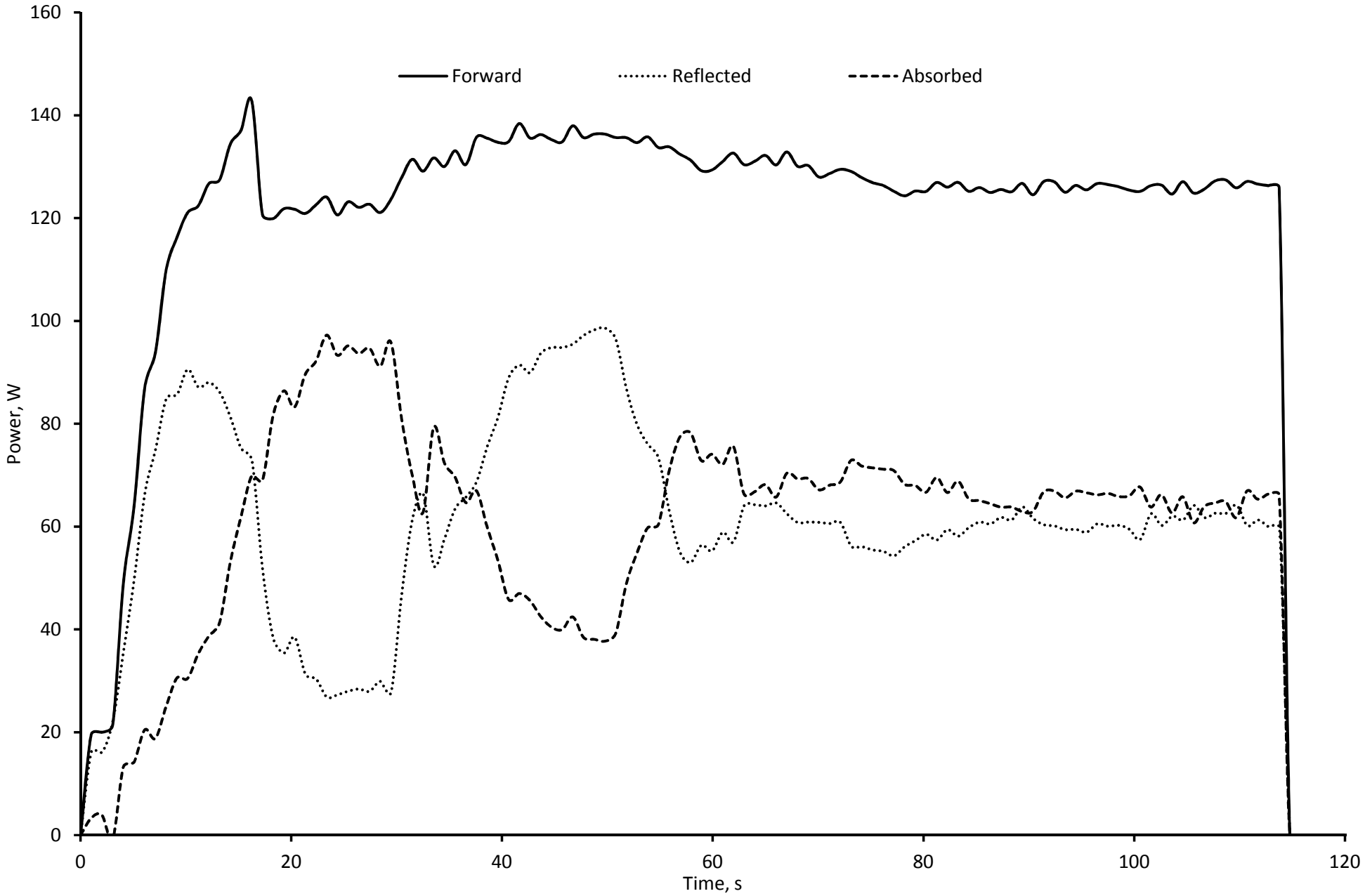
	Wt%	*At%*
C_K	15.79	55.17
K_K	0.40	0.43
Ca_K	0.44	0.46
Fe_K	42.65	32.05
Zn_K	2.62	1.69
Pb_L	30.38	6.15
Br_K	7.72	4.05



element	Wt %	%At
C_K	17.05	49.91
O_K	3.61	7.93
Al_K	1.5	1.95
Si_K	0.6	0.75
Ca_K	1.25	1.1
Fe_K	29.75	18.73
Zn_K	28.05	15.08
Pb_L	12.74	2.16
Br_K	5.35	2.35



	Wt%	*At%*
C_K	15.79	55.17
K_K	0.40	0.43
Ca_K	0.44	0.46
Fe_K	42.65	32.05
Zn_K	2.62	1.69
Pb_L	30.38	6.15
Br_K	7.72	4.05


Forward
Reflected
Absorbed
Power, W
Time, s
0
20
40
60
80
100
120
140
160