PRINTED CIRCUIT BOARD LEACH RESIDUE AS A REDUCTANT FOR PYROMETALLURGICAL OPERATION

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ABSTRACT

In recent years, there has been an increase in the generation of Waste electrical and electronic equipment (WEEE) due to the advancement of technology. Printed circuit board (PCB) is the main focus of electronic waste because of the inherently high value of contained metals such as copper and gold. Hydrometallurgical processes, consisting of several leaching stages, are the most feasible option for the recovery of metals from PCB waste. However, hydrometallurgy does not address the issue of non-metallic PCB fractions that may end up being dumped at land fill sites or incinerated. When the nonmetallic fractions are dumped, the heavy metals and the brominated flame retardants leach into groundwater leading to secondary pollution. Several options for treatment of the non-metallic fraction including material recycling, where the residue may be used as inclusions in concrete or asphalt materials with minimal processing or chemical recycling, where chemicals and fuels are produced from the residue using techniques such as pyrolysis exist.

Due to the complex composition of PCB leach residue, recovery by thermal treatment is likely to be the most feasible process route from technical and economical perspectives. In this study, the utilisation of the non-metallic leached PCB waste fraction as reductant in primary metal smelting operations and solid state pre-reduction is investigated. Analysis of the leached residue revealed that PCB is highly amorphous and has a carbon content of 28.5%, oxygen content of 23.1%, with the ash and volatile matter contents being 40.1% and 44.8% respectively.

Thermodynamic modelling and laboratory-scale experiments that simulate chromite smelting and solid state pre-reduction operations were performed using various blends of PCB and carbonaceous reducing agents. The models showed that PCB residue might be used to partially replace the conventional reductants. Preliminary investigations revealed that in chromite smelting the optimal blend contains up to 20 wt% PCB residue, with energy savings of 200 kWh/t of ore to achieve the same metal recovery.

KEYWORDS

Printed circuit board (PCB), Hydrometallurgy, Reductant, Pyrometallurgy, Polymer, Recycling, Thermodynamic modelling, Hematite, Chromite, Solid Pre-reduction

INTRODUCTION

One of the fastest growing sectors of the manufacturing industry in the world is the production of electrical and electronic equipment (EEE). Any product that relies on electricity to function is categorized EEE. The proliferation of technology and remarkable market growth of EEE has shortened the lifespan resulting in the increase of e-waste. Eng, Cui, & Anderson, (2016) define e-waste as the end-of-life electric and electronic equipment without the intent of reuse. According to Anderson, (2016), there were approximately 41.8 million tonnes of electronic waste generated through the world in 2014 and it is expected that the amount of electronic waste will reach 49.8 million tonnes in 2018, with an annual growth rate of four to five percent. As a result of the high content of heavy metals and brominated flame retardants (BFR), disposal of electronic waste via landfilling is destructive to the environment.

Printed circuit boards (PCBs) are the principal and essential part of electronics because they contain more base and precious metals than their respective ore. They contain many electronic components such as resistors, capacitors and integrated circuits. Eng et al. (2016) reported that the gold content in PCBs is 35-50 times higher than gold ore. As a result of its high concentration, e-waste recycling, and metal recovery is an appealing prospect from economic, technical and environmental points of view**.**

Zheng, Shen, Cai, Ma, & Xing, (2009) classified PCB recycling into three branches according to the different material recovering processes; physical, thermal and chemical processing. In physical processing, the PCB is crushed and the metallic components are separated from the non-metallic based on their densities, magnetic properties, and electric conductivities. Thermal processing involves the use of incineration to in order to recover the metals (pyrometallurgical treatment) or as part of the combustion of municipal solid waste (MSW). This method is available and very simple. However, gases produced from combustion contain brominated and mixed halogenated dibenzo-p-dioxins and dibenzofurans which are known to be extremely toxic to human and environmental health. In the chemical recycling process, PCB is treated using hydrometallurgical techniques. It consists mainly of leaching, purification, and recovery of metals. The constituents of PCB is dissolved to form a pregnant solution using a suitable lixiviant such as sulphuric cyanide, thiosulphate, halides. The metallic fraction is leached from the PCB.

Hydrometallurgical treatment of e-waste has been found to be more efficient and environmentally friendly than other recovery processes, such as physical separation and pyrometallurgical processes (Anderson, 2016; Diaz, Lister, Parkman, & Clark, 2016; Sohaili, Muniyandi, & Mohamad, 2012).The drawback of this process is that it does not take into account the non-metallic fractions. When the nonmetallic fractions are dumped at land fill sites, the heavy metals and the brominated flame retardants leach into groundwater leading to secondary pollution.From an environmental management perspective, a zero-waste approach of recycling should be developed to gain value from and reduce the environmental impact of both the metallic and non-metallic fractions of the PCB waste.

Bazargan, Bwegendaho, Barford, & McKay, (2014) investigated recovery of high purity silica from non-metallic component of PCB using thermal treatment. The results revealed the possibility of getting 99% pure SiO_2 of specific surface area (BET) as high as $300 m^2/g$. Recycling of polymeric compounds are generally classified as material recycling, chemicals recycling, or energy recycling (i.e. combustion) (Fink, 1999; Fisher et al., 2005). Material recycling approaches refer to applications where the non-metallic fractions of the PCBs are used as inclusions or fillers in concrete, asphalt materials, or thermoplastic, resin, or similar matrix composites with minimal processing. Chemical recycling, on the other hand, refers to processes in which chemicals and fuels are produced from PCB leach residue using techniques such as pyrolysis, supercritical fluids depolymerisation or hydrogenolytic degradation. While material recycling is promising, it has found only limited industrial applications due to the diverse composition of circuit boards, poor compatibility between the non-metallic fractions and matrix materials, potential leaching of residual hazardous metals, and generally low public acceptance of products containing recycled PCBs. The high costs associated with chemical recycling methods, on the other hand, often deter the adoption of these processes even though it is the most effective method to manage hazardous components and to fully utilise all elements (Guo, Guo, & Xu, 2009).

Due to the complex composition of PCB, recovery by thermal treatment is likely to be the most feasible process route from a technical and economic standpoint. In this study, the feasibility of using the non-metallic PCB fractions as a reductant in pyrometallurgical unit operations was investigated. Several authors have investigated the recycling of plastics as feedstock for reductive smelting operations. One of the major application in this field involves the use of polymer waste in blast furnaces for steelmaking, where plastics are substituted for coke, coal, or oil used for ore reduction and heating. NKK Keihnn Works in Japan first implemented this technology after it was developed by Bremen Steelworks in Germany (Zie & Stanek, 2001).

Some factors that influence the amount of polymer waste that can be added to blast furnace feeds include the carbon to hydrogen ratio, the energy content, supply rates required to sustain continuous operation, as well as the chloride and the residual non-ferrous metal content of the waste (Fink, 1999; Nourreddine, 2007).Fink (1999), Nourreddine (2007) and Zie & Stanek (2001) reported that the formation of dioxins is not problematic in these processing routes, but the formation of chlorine-containing gases such as HCl might result in corrosion of equipment.

The use of polymer waste to replace conventional reducing agents provide a number of advantages. The coal resources are conserved since there is a lower consumption of both coke and pulverized coal as well as a reduction in polymer waste being landfilled or incinerated.

MATERIALS AND METHOD USED

Pre-treatment and Leaching of PCB

The waste printed circuit boards (PCB) was obtained from Cape E-waste Recyclers. Waste PCB were partially dismantled by manually removing the toxic components like batteries and the large components such as stainless steel heat sinks which are difficult to crush. The partially dismantled PCB were desoldered by submerging in 2mol/dm^3 Nitric acid for 24hours. The desoldered PCB was then cut into pieces of approximately 3cm×3cm using a band saw. The pieces were crushed using a cutting mill with the largest size passing a sieve of aperture 2mm.

Leaching was performed using sulphuric acid and subsequently aqua regia. 5litres of the acid was placed in a vessel and 500 g of the crushed PCB was added. Further leaching was performed using aqua regia as lixiviant to ensure that the metals are completely dissolved in the acid. The residue was washed and air dried.

(a) **(b)** **(c)**

Figure 1: (a) printed circuit board (PCB); (b) Desoldered PCB; (c) crushed PCB

Characterisation of the PCB

Proximate and ultimate analysis together with the ash content analysis were performed on the PCB leach residue using LECO CS 230 and induced couple plasma optical emission spectrometer respectively (ICP-OES).The morphology of the PCB leached residue were observed by Scanning Electron Microscopy (SEM) and also characterised by X-ray powder diffraction (XRD).

For XRD analyses a PANalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-Kα radiation was used. The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weight %) were estimated using the Rietveld method. The quantitative XRD results showed that the different particles in the residues contained 99% amorphous phase and trace amounts of silica and titanium oxide.

FEG-SEM results revealed that the residue contained carbon which ranged from 15 wt% to 67 wt% among different particles. Oxygen content among the particles was varying from 15 wt% to 67 wt%. Silicon content ranged from 0.65 wt% to 30 wt%. Aluminium also fluctuated from particle to particle from 0.69 wt% to 4.74 wt%. Chlorine was found changing from 0.65 wt% to 18 wt%. Some particles contained iron up to 1.65 wt%. Copper and Ti were also present in relatively small amounts around 0.46 wt% and 0.3% respectively in some PCB residue grains.

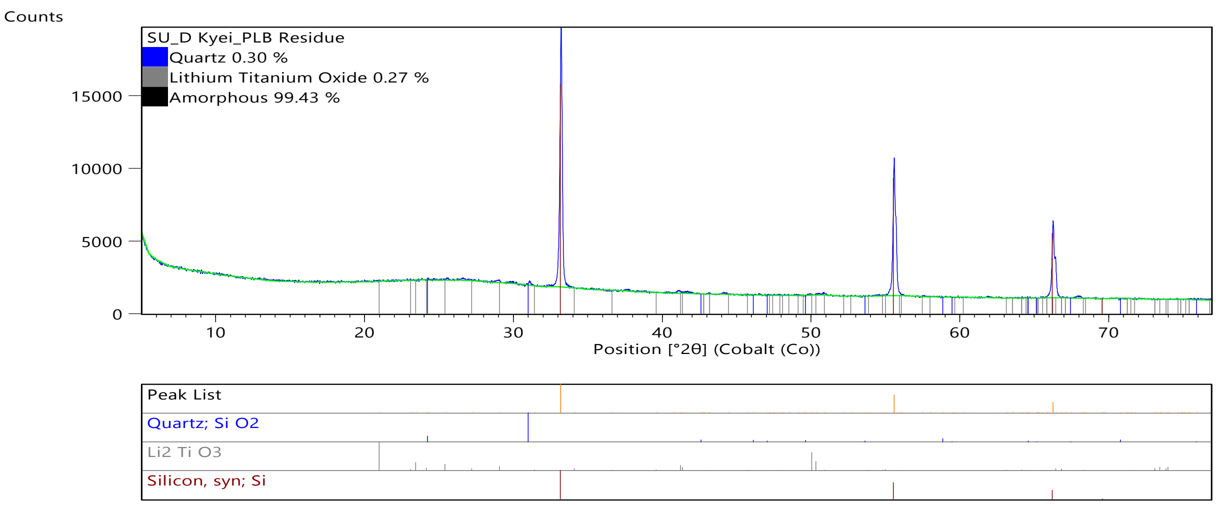

Figure 2: X-Ray Diffraction Pattern

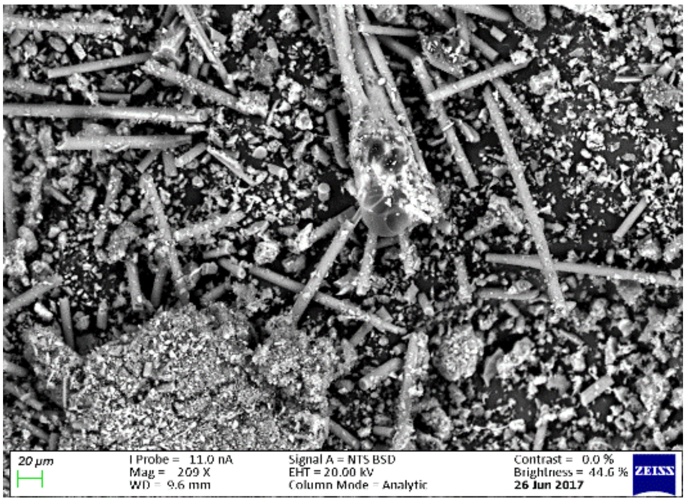

Figure 3: Scanning Electron Microscope Image of PCB residue

Table 1: Proximate Analysis and Halide determination of the PCB

C	H	N	S	O	Ash	Moisture	F	Cl
28.5%	3.06%	1.10%	0.54%	23.1%	40.1%	3.06%	0.25%	0.42%

Table 2: Ultimate Analysis and Calorific value

Inherent Moisture	Ash	Volatiles	Fixed Carbon	Calorific Value
3.6%	40.1%	44.8%	11.5%	12.08MJ/kg

Table 3: Ash Analysis

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P	Ba	Cu
84.0%	6.28%	0.73%	0.73%	6.00%	0.70%	0.001%	0.072%	0.009%	0.49%	0.105%

Thermodynamic Simulation and Reduction Experiments

EMSIM (Ex Mente Technologies, 2018) simulator for modelling industrial chromite ore smelting was used to understand the feasibility of adding PCB in smelting operation. EMSIM (Ex Mente Technologies, 2018) is a web-based modelling and simulation application that users interact with through a web browser. When feed rates and ratios for the input streams are specified, the model would calculate the flow rates and compositions of the output streams, as well as parameters such as yields, recoveries, specific raw material consumptions, and specific energy consumption at equilibrium. EMSIM (Ex Mente Technologies, 2018) uses FactSage thermochemical data (Zietsman, Steyn, & Pretorius, 2018). The properties of the leach residue were used as inputs in the thermodynamic modelling using EMSIM simulator. Smelting of Chromite was studied at 1700℃ using blends of PCB with coal as reductants. The off gas composition, degree of metallization as well as the energy required using the various blends were compared with those of conventional metallurgical coke under the same conditions.

Reduction Tests Using Differential Scanning Calorimetry and Thermogravimetry

Samples were prepared by mixing 1g of hematite of high purity (>99) and 0.532g of reducing agents. The reducing agents were blends of high purity graphite (99.99%) and leached residue of PCB. In order to understand the reduction process, thermo-gravimetric test were carried out in Linseis STA PT1600 with a balance of resolution 0.5µg and B-type thermocouple. About 15mg of sample was weighed and placed in a crucible and transferred to the DSC-TGA afterwards. The samples were heated from ambient temperature to 1250℃ at a heating rate of 5℃/min. A constant flowrate of 8 standard litres per hour Ar with purity (99.99%) was used to purge the system. Reduction tests were carried out on the mixture of hematite and PCB-graphite blend.

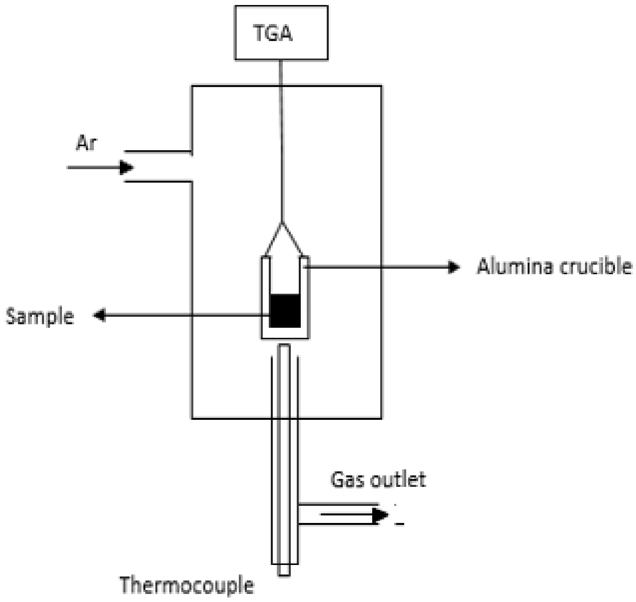

Figure 4: Experimental setup for the reduction of hematite

RESULTS AND DISCUSSION

The mass and energy balance in all the reduction cases show that (Figure 5), increasing the mass percent of PCB in the blend decreases the metal recovery as well as the energy required for the reduction. The alloy content in the product also decreases as PCB increases in the blend as shown in Figure 6. The decrease in metal recovery and the alloy content may be due to PCB having very low carbon unit in PCB compared to the coal. However, since PCB contains more volatiles, it tends to reduce the amount of energy required for the reduction.

Dankwah, Koshy, O'Kane, & Sahajwalla (2012) stated that coke and plastics blends could be effectively used to increase slag foaming in steel making. The simulations confirmed this with an increase in the slag content of the product as the amount of PCB in the blend increased (Figure 6). This increase in the slag content is attributed to the high amount of silica in the PCB.

Since the PCB contained more volatiles, it was expected that the total gas released would be higher during reduction with blends containing higher mass percent of PCB. However, this is not the observation. It can be seen in Figure 6 the total gas released decreases as the mass percent of PCB increases in the blend. This is because the volatiles in the PCB contains hydrocarbons which take part in the reduction process.

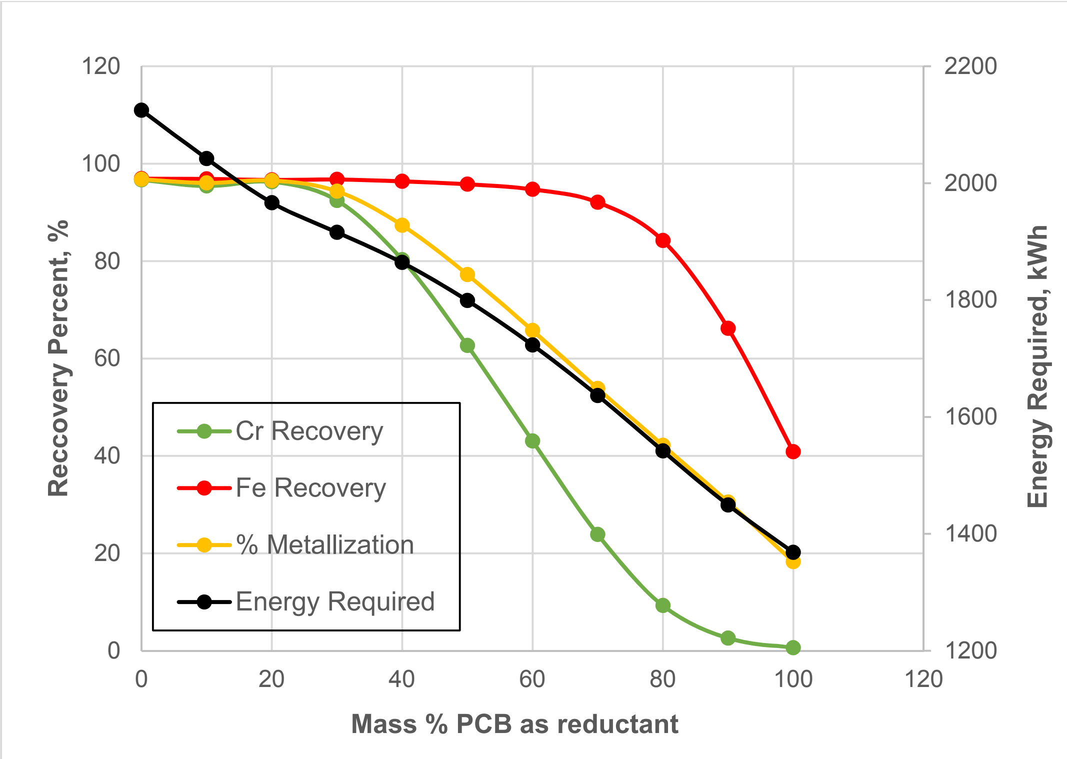

Figure 5: Energy required and percentage recovery during chromite smelting at 1700□

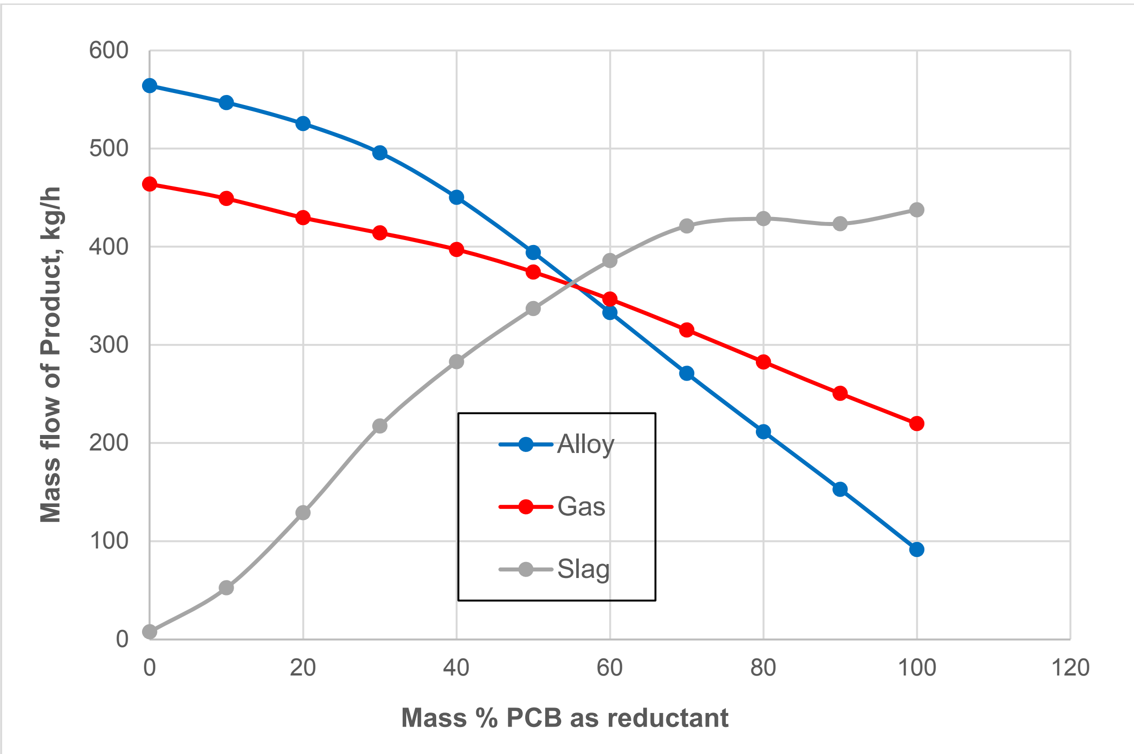

Figure 6: Products obtained during chromite smelting at 1700℃

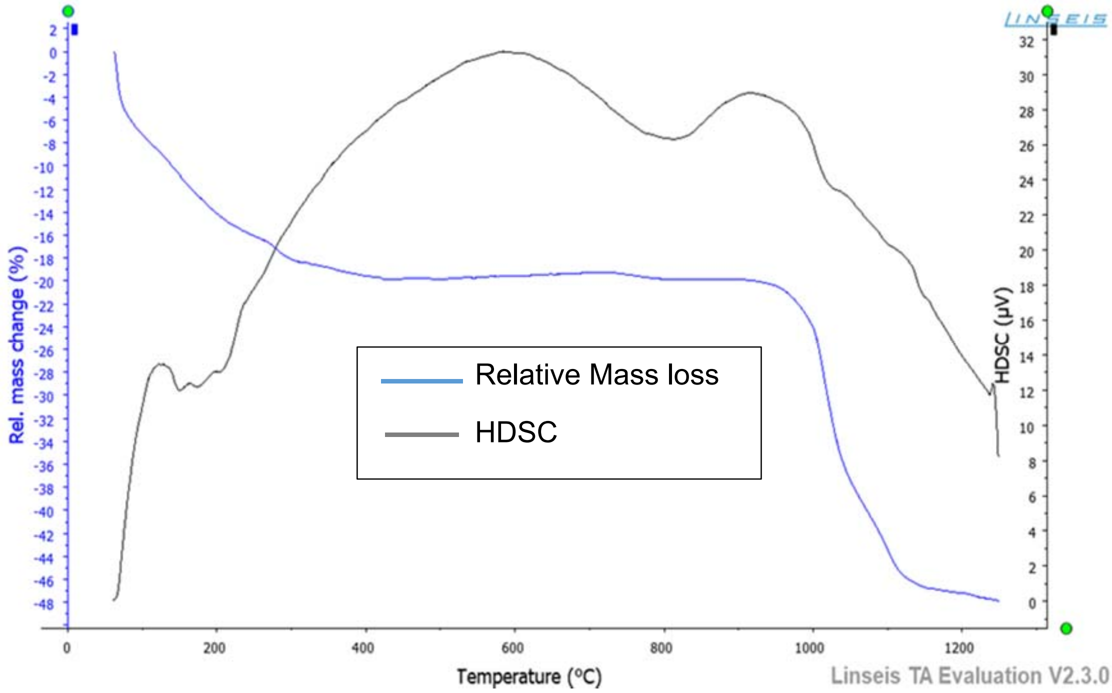

Figure 7: DSC-TGA curves from hematite-20%PCB reduction test

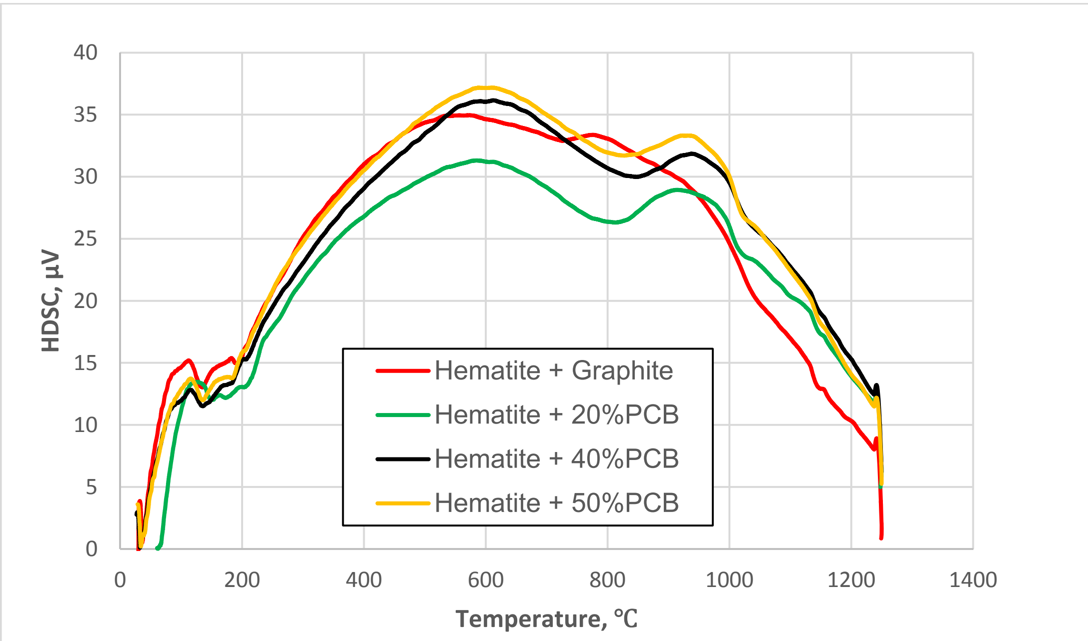

Figure 8: DSC Curves obtained during hematite reduction

The DSC plots showed three peaks for all the reduction experiments (Figure 8). The first occurring at about 120℃ may be as a result of vaporization of moisture present in the sample. Another peak occurred at 600℃. This may be the temperature at which reduction of hematite begins. The peak at about 950 ℃ may be regarded as the temperature at which iron begins to form

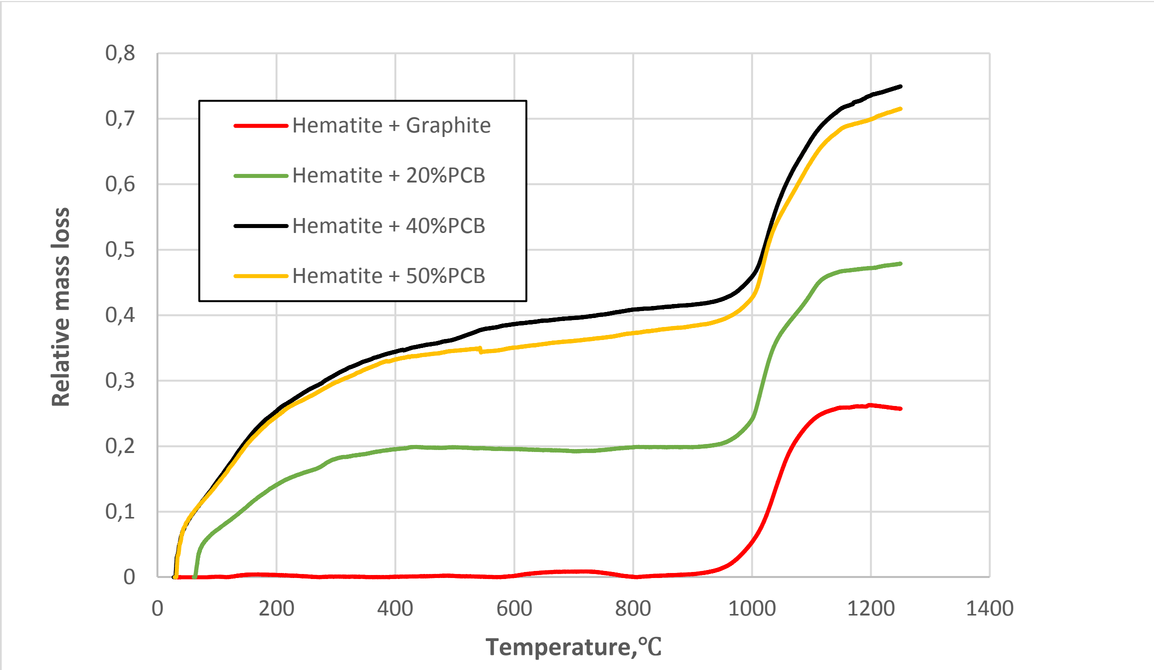

Figure 9: Relative mass lost during hematite reduction

It can be seen from Figure 9 that between 50℃ and 350℃ there is a significant mass loss when PCB blends are used as reductants. This can be ascribed to the pyrolysis of the PCB. The plastic component as well as the brominated flame reductants are believed to decompose at these temperatures. At 950℃, about 25% of the initial sample mass is lost. This loss may be attributed to the gasification of graphite or the formation of iron. The mass loss increased as the mass percentage of PCB in the blend increases. This is because PCB contains a higher amount of volatiles compared to the graphite. During the reduction of hematite using graphite, there was a slight change in mass observed around 700℃ which is probably due to the formation of Fe_3O_4.

The overall reduction may be expressed by the reaction:

$$Fe_2O_3 (s) + 3C = 2Fe + 3CO \qquad \text{Equation 1}$$

The reduction degree was calculated based on the mass lost during the reduction in the DSC-TGA testwork.

The reduction degree (Figure 10) shows that at lower temperatures between 600 and 1000℃, using PCB or the PCB blends acts as better reductant in converting Fe_2O_3 to Fe_3O_4, FeO or Fe. At higher temperatures, however, the advantage shifts towards pure carbon.

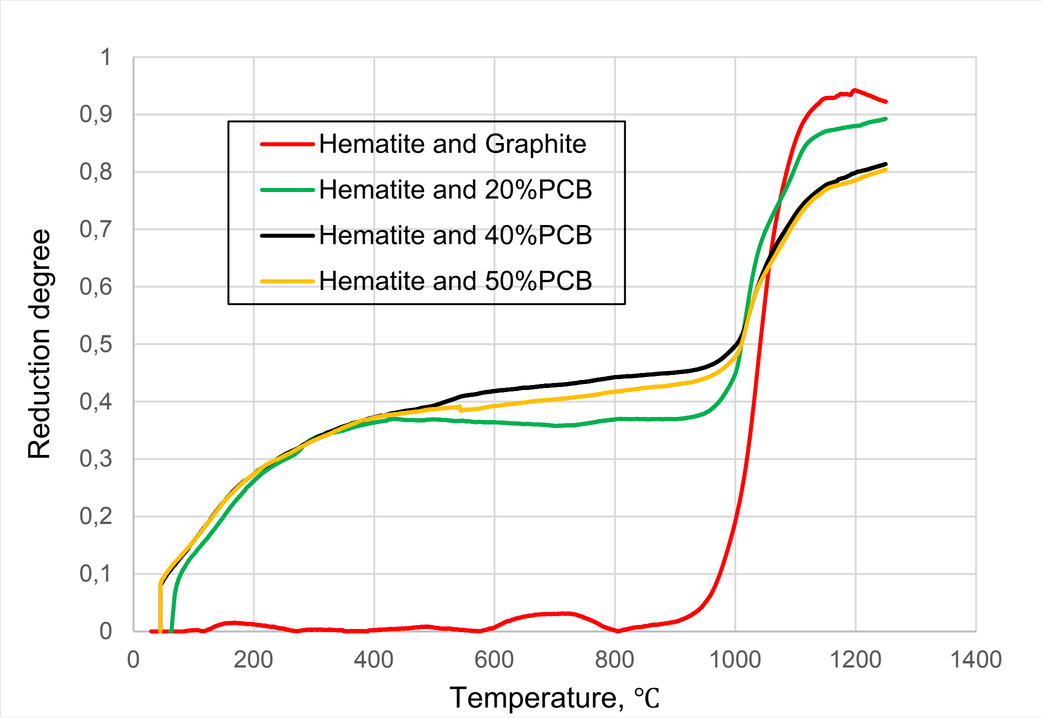

Figure 10: Degree of Reduction

CONCLUSION

The use of printed circuit board as a reductant in pyrometallurgy has been investigated using thermodynamic simulations of chromite smelting and solid state pre-reduction of hematite. The study revealed that PCB can be partially be used to replace conventional reducing agents. During the solid state pre-reduction of hematite, blends of PCB-carbon acts as better reductants that pure carbon due to the presence of hydrocarbons in the PCB. In chromite smelting, there is a decrease in the energy required for reduction as the weight percent in the PCB in the blend increases. In light of overall results, the optimum mass percent of PCB in the blend appears to be around 20% with 200 kWh/t_{ore} energy saving.

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