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# Novel Approach for Processing Hazardous Electronic Waste

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**Abstract**

Rapid urbanization, a general improvement in living standards and increased consumption has resulted in the generation of unprecedented amounts of waste in recent years. Among different wastes, electronic wastes (e-waste) volumes are growing three times faster than any other forms of urban waste. It is estimated that 20 to 50 million tonnes of e-waste are generated worldwide every year. E-waste contains over 1000 different substances; some are toxic and hazardous, which cause serious problems to environment and on human health. Generation of waste residues during recovery of precious metals from e-waste, the presence of hazardous lead, waste plastics, secondary pollution caused by landfilling non-metallic residues are some of the problems associated with recycling e-waste.

We report a novel approach to recover valuable materials from waste printed circuit boards; controlled pyrolysis of e-waste was carried out at high temperatures (750-1550°C) in an argon atmosphere. Segregation of lead and other metals was investigated as a function of temperature and reaction products were analyzed using Inductively Coupled Plasma spectroscopy and Scanning Electron Microscopy. Temperatures above 1350°C were required to completely remove lead and other metals from e-waste; waste residue that was left behind was predominantly composed of carbon. Further research was carried out on the utilization of lead free non-metallic residue as a carbon source in ironmaking application. Non-metallic residual waste from recycling PCB was found to be a promising reductant in ironmaking applications. This research has laid the foundations of a 'Zero Waste' approach for managing and recycling electronic waste.


Selection and peer review under the responsibility and editorial leadership of Guest Editor Dr. Luke Beesley

*Keywords:* Electronic waste; Printed circuit boards; Lead free residue; Reductant; Ironmaking application

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## 1. Introduction

In the 1980's the tendency to export hazardous waste from developed countries to less developed countries increased tremendously causing severe environmental pollution burdens. The main motive for the export of hazardous waste is due to strict regulations by developed countries to recycle, and that the export of waste was more economic than to recycle hazardous waste [1].The Basel Convention (the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal) came into effect in 1992 to solve waste export problem; as of 14 August 2013 there are 180 countries as parties to the Convention. The main three stated objectives of the Convention are (a) to minimize the generation of hazardous waste, (b) to encourage countries and manufacturers to treat and dispose of hazardous waste locally and (c) to minimize the export of hazardous waste from developed to developing countries [2]. As a consequence of the Basel Convention, the trading of waste for 'final disposal' has been replaced by the trading of waste for 'reuse and recycling'. In the last decades the world has also experienced an unprecedented level of urban growth with more than 50 percent of the population now living in urban cities [3]. Due to rapid urbanization and a rise in standards of living, the amount of waste generated is increasing significantly. The accumulation of vast amount of waste in landfills due to urbanization has led to concerns about the environment and the potential negative impact to human health.

According to the United States Environmental Protection Agency (US EPA), electronic waste (e-waste) typically consists of a broad range of electrical and electronic products which have finished their useful life including televisions, monitors, computers, computer peripherals, audio and stereo equipment, video cameras, printers, scanners, fax machines, cellular phones and telephones [4]. Due to advances in technology, demand for newer products and a decrease in the life span of existing electronic products during the last decade have resulted the generation of significant amount of e-waste worldwide. According to the European Directive on Waste Electrical and Electronics Equipment, e-waste is the fastest-growing waste stream in all the countries around the world [5]. E-waste is growing three times faster than normal municipal solid waste at the rate of 3-5% per annum [6]. Annually, it is estimated that 20-50 million tons of e-waste are generated around the world, mainly in developed countries [7]. By the next decade, the developing countries like China and India are expected to grow the usage of electronic products by up to 500%, which results in the generation of vast amounts of e-waste [8]. E-waste is very different compared with other municipal waste, as e-waste contains over thousands of toxic ingredients, which includes heavy metals such as lead, cadmium, mercury, arsenic etc., and harmful chemicals such as polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs). About 50-80% of e-waste generated around the world end up in recycling sites of China, India, Pakistan, Vietnam and increase in domestic demand has led to serious environmental and health challenges due to high toxicity and huge volume [7]. According to report published by Basel Action network and Silicon Valley Toxics Coalition, the import of hazardous e-waste has caused a serious environmental pollution in China and India due to improper recycling methods [8].

The techniques used for recycling of e-waste in underdeveloped countries like Africa, India and China are often primitive and, lack the technical capabilities necessary to handle and recycling the hazardous materials within the e-waste [9]. The e-waste recycling sector in underdeveloped countries is largely unregulated and often it takes place in small workshops. The techniques includes to recover valuable materials or recycling in underdeveloped countries are 1) Use of mixtures of concentrated nitric acid and hydrochloric acid to extract gold and copper, during these process a volatile compound of nitrogen and chlorine are known to be emitted [10]. 2) The primitive mechanical method followed during disassembly of electrical components may lead to accidental spillage of hazardous substances and generation of toxic and other material dusts may contaminate the surroundings [10]. 3) Open air burning of electrical wires or other components to recover copper from plastics may lead to the formation of dioxin and furan compounds, which are considered as carcinogenic agents [11]. 4) Heating of printed circuit boards (PCBs) to get valuable materials; during this method the workers might get expose to fumes of metals, particularly those form solder (lead and tin) and also other hazardous substance might release potentially [12]. 5) The increase of pollutants release by heating e-waste at low temperature in comparison with incinerators have concerned countries like India, Brazil, Mexico and increase in health problem and environmental damage have been identified and reported [13]. 6) Disposing of the residual materials after recovery of valuable materials in landfill and riverbanks. The following rudimentary techniques involved in recycling e-waste release a large range of toxins in high concentrations, exposing e-waste workers and communities.

Printed Circuit Boards (PCB) are a key component of all electrical and electronic components. The components in PCB can be divided broadly into Metallic fractions (MFs) and Non-metallic fractions (NMFs). The PCB is always an interesting component for recyclers in terms of the MFs as it contains more than 28-30% metal. The typical composition of PCB is non-metals (plastics, epoxy resins, glass) >70%, copper ~16%, solder ~4%, iron ~3%, lead ~2%, nickel ~2%, silver ~0.05%, gold ~0.03%, palladium ~0.01%, others (antimony, bismuth etc) <0.01% [14]. Per ton of typical PCB waste therein are contained 20% copper and 250g of gold. PCB can be considered as important secondary resource of base (Cu) and precious metals (Au, Ag, Pd) [15]. The NMFs mostly includes polymer, glass fibers and other additives, and constitutes upto 70% weight of PCBs. Traditionally, after metal recovery process the NMFs are landfilled, thus forming a secondary pollutant. The processed NMFs possibly contain heavy metals/hazardous substance, which get integrated during recycling process and in turn pollutes the environment after discarding to landfills.

More attention has been given to recover valuable metals from PCBs than research on recycling NMFs. Physical recycling and chemical recycling techniques have been reported to recycle NMFs from waste PCBs. Physical recycling techniques releases dust and toxic substances during crushing, and also both toxic and valuable metals usually adhere with NMFs. In chemical recycling, pyrolysis techniques look more promising than combustion processes as the low volatile heavy metals are not released to the atmosphere and valuable metals are not oxidized. Hall and William separated organic and glass fiber from metals by pyrolysis [16]. A few applications of NMFs have been reported such as in manufacturing compound boards and also as fillers [17-19] but none of the recycled NMFs were evaluated for their heavy metal content before using it for application. During recycling process, the study of flow of heavy metal is very crucial to save the environment from damage. In this paper we have attempted to recycle lead free NMFs from waste PCBs by a simple pyrolysis technique and also investigated the leaching of lead from NMFs at various temperatures. This work greatly enriches the understanding of the flow of lead during pyrolysis process and provides information of achieving NMFs which is environmentally benign. The obtained recycled NMFs have been successfully used in reduction of iron oxide.

## 2. Materials and Methods

### *2.1. Materials*

In this research, we have used single/double sided PCBs which was provided by Steinert Company, Melbourne, Australia. The PCBs were crushed in a hammer before using it. To determine the elemental composition of waste PCBs, Laser induced - Inductive Coupled Plasma Mass Spectrometry (ICP-MS) spectrometry analysis was carried out and the Pb concentration was found to be 20206 µg/g. The detailed ICP results are illustrated in figure 1 of the supporting information.

### *2.2. Pyrolysis process*

The pyrolysis experiments of waste PCBs were carried out in argon atmosphere in horizontal tubular furnace (Figure 2). The crushed PCBs were pyrolyzed at different temperatures for the period of 20 minutes to recycle NMFs and also to study the leaching of lead with temperature. The weight of the sample used in each pyrolysis experiment was around 2 gm. The samples were placed into ceramic boat and fed into hot zone of a reactor. After the thermal treatment, the metallic part could be easily separated from the non-metallic residue/fractions. The NMFs were collected for further analytical investigation to analyse the lead and other toxic metals content. All experiments were repeated at different temperature to enhance the reproducibility of the results.

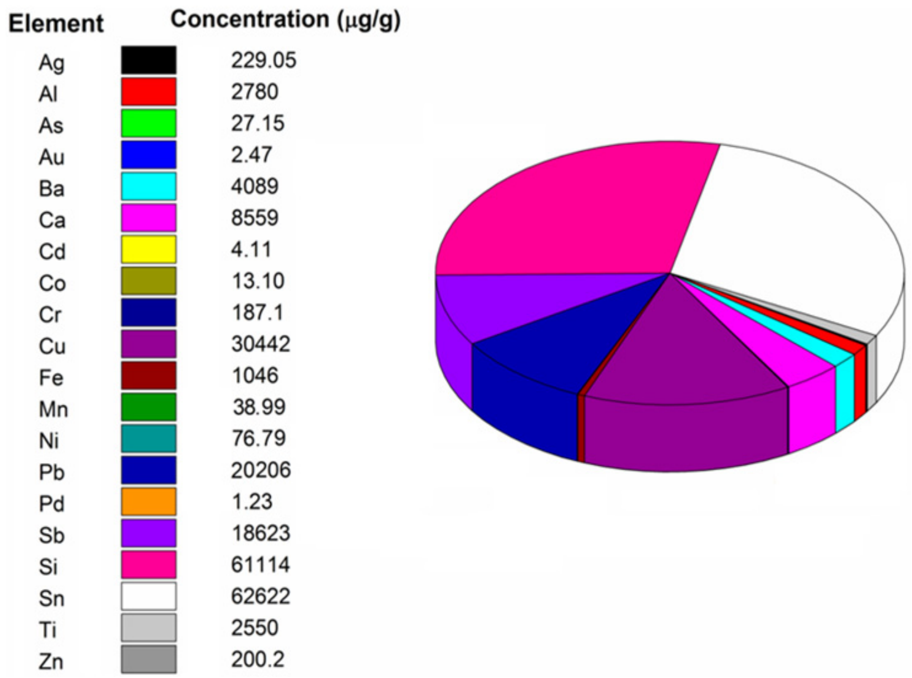


Fig. 1. Elemental composition of PCB by ICP analysis

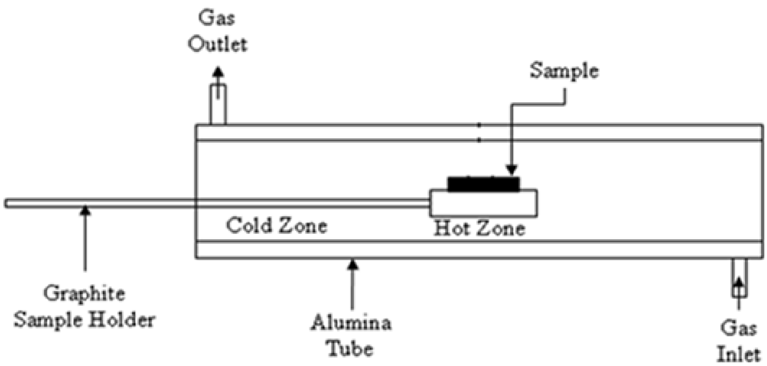


Fig. 2. A schematic representation of pyrolysis set up

*2.3 Reduction of Iron Oxide.*

NMF residue obtained at 1350 °C for 20 min by pyrolysis of PCBs was used for reduction of iron oxide studies. The NMF residue was grounded to an upper size limit of 150µm using a ring mill and hematite (99% pure) with a particle diameter of 5µmwas used as iron oxide for reduction studies. The iron oxide and NMF residue were thoroughly mixed using rolling mill for 2 hr. The mole ratio of carbon to oxygen in the mixture was mixed in stoichiometric ratio. The reduction experiments were performed in horizontal tubular furnace at 1350 ºC temperatures in an argon atmosphere at flow rate of 1.0 L/min for 20 min residence time. The reduced mixtures were analyzed by Scanning Electron Microscope and X-ray Diffraction techniques.

*2.4 Analytical Methods.*

**-Elemental analysis.** The percentage of elemental carbon in NMFs obtained at various pyrolytic conditions was analyzed by LECO carbon analyzer.

**-Scanning Electron Microscope (SEM).** The surface elemental composition of NMFs was analyzed with HITACHI S3400 scanning electron microscope equipped with Energy Dispersive X-ray Spectrometer (EDS).

**-Laser induced - Inductive Coupled Plasma Mass Spectrometry (ICPMS).** LA-ICPMS is capable of analyzing solid residues. Approximately 2g of NMFs residue was put in a die and compacted under a load of 10 KN using a hydraulic press to form pellet. The pulsed 213nm laser was used, and depth profiling of surface and ultra trace elemental analysis was performed on the NMFs obtained at different pyrolytic conditions.

**-X-ray diffraction (XRD).** The iron oxide reduced mixture by NMF residue was analyzed by PANalytical X'Pert Pro multipurpose X-ray diffractometer, operating at 40 kV and 40 mA and measurements were recorded from a start angle $2\theta = 10°$ to an end angle of 80°, with total accumulation time of around 30 min

## 3. Results and Discussion

PCBs are broadly divided into two types i.e. (a) Single/double sided PCBs (b) Multilayer PCBs. The dynamic range of interconnects and complex methodology design is allowed in multilayer PCBs, and hence is used in computers, satellite systems, space probe equipment and medical devices etc. Multilayer PCBs uses a range of materials for its construction, extensively from basic epoxy glass to exotic ceramic fills. Whereas, single/double sided PCBs uses range of polymers as base materials with certain oxides. So during recycling PCBs, both the types of PCBs should be considered as different waste materials in order to enhance the recovery of all valuable materials. In this research work, we have used waste single/double sided PCBs, and ICP results shows the presence of valuable elements such as copper, tin in larger extent along with other toxic elements such as lead, cadmium and chromium as shown in figure 1. The lead concentration in waste PCBs was found to be 20206 μg/g.

Initially thermo gravimetric analysis (TGA) was performed on waste PCBs in order to determine the weight loss with temperature. The TGA result indicates that the pyrolysis of waste PCBs includes only one stage of major weight loss. The main weight loss started at ~320 °C and finished at ~400 °C (Figure 3). The maximum weight loss was ~40% which indicates that majority of polymers of PCBs have undergone complete decomposition at ~400 °C. After ~400 °C, there was a gradual decrease in weight loss as seen in Figure 3. As reported in literature, the temperature between 350 to 400 °C is highly favorable condition for the formation of dioxins and furans during pyrolysis of PCBs. Hence, in this research work, the rapid pyrolysis experiments were carried out in argon atmosphere at different high temperatures i.e. 750, 950, 1150 and 1350 °C.

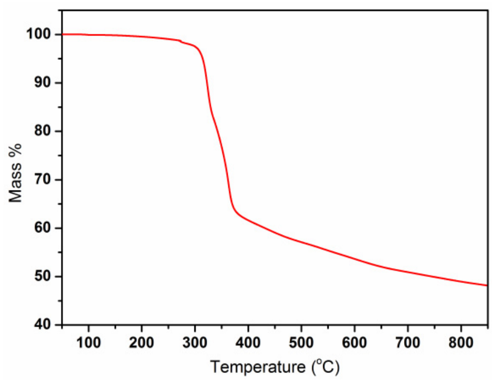


Fig. 3. TGA curve of waste PCBs

The rapid pyrolysis of waste PCBs yields two major components: gas and solid residue. During rapid pyrolysis the gas generation appears during initial 3 minutes and weight of solid residue was ~50%. The metals and non-metallic residue were easily separated from solid residue (Figure 4). The non-metallic fraction residue obtained was further examined by ICP and LECO carbon analyser in order to determine the elemental composition.

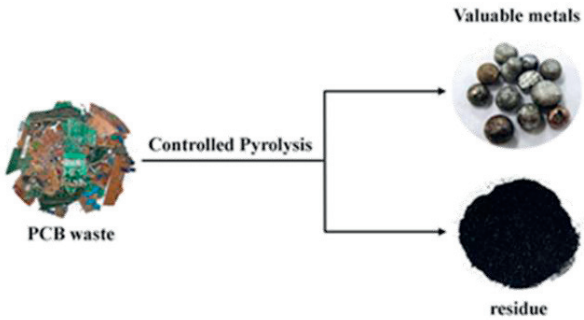


Fig. 4. Solid residue obtained during rapid pyrolysis of PCBs

The LECO carbon analysis on NMFs obtained at different temperatures (750-1350 °C) shows 85-90 % carbon. The high carbon content in NMFs clearly indicates that pyrolysis of single/double sided PCBs yields carbon rich residue. The lead content analysis performed on NMFs obtained at different temperature is shown in figure 5. The lead content in NMFs obtained at 750 °C shows 3059 μg/g and decreases significantly with pyrolysis temperature which is clearly noticeable from figure 5. At 1350 °C pyrolysis temperature residue the lead content was 72 μg/g. The gradual decrease in the lead content in residue at higher pyrolysis temperature is due to increase in vaporisation of lead. The main advantages of controlled pyrolysis technique are (a) lead free NMF residue can be obtained and (b) Lead from PCB can also be easily separated and collected in gas phase using condenser/trapper. So this technique doesn't allow lead to reach the environment to cause pollution. The other elements present in NMF residue is shown in table 1. The valuable metals such as copper, gold, silver and tin were present in very negligible quantity and were separated in the form of metal balls. The silicon, calcium and aluminium were present in the form of oxides and were associated in non-metallic residue.

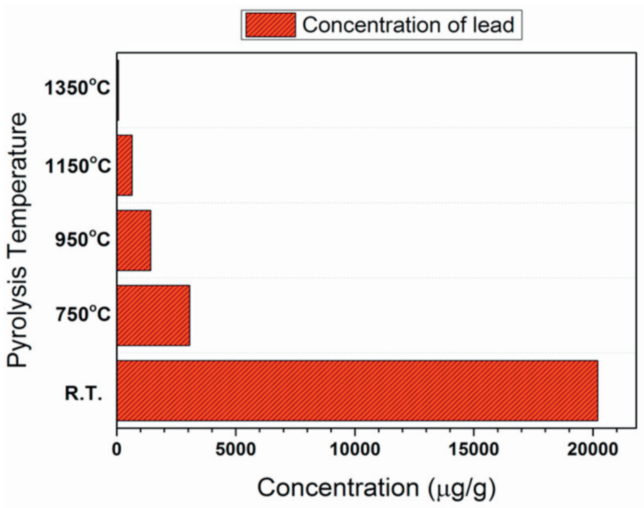


Fig. 5. Lead content in NMF residues obtained at different rapid pyrolytic temperatures

Table 1: Different elemental contents in NMF residue obtained at 1350 °C pyrolysis temperature

| Elements | Concentration (μg/g) | Elements | Concentration (μg/g) |
|---|---|---|---|
| Ag | 1.46 | Cu | 645.0 |
| Al | 692.9 | Fe | 500.7 |
| As | 17.77 | Mn | 119.0 |
| Au | 0.83 | Ni | 9.50 |
| Ba | 84.18 | Pb | 72.89 |
| Ca | 3681 | Pd | 0.10 |
| Cd | 0.88 | Sb | 1522 |
| Co | 3.38 | Si | 21928 |
| Cr | 60.36 | Sn | 185.5 |
| Zn | 176.5 | Ti | 252.0 |

Figure 6 shows the SEM image and carbon mapping of NMF residue obtained at 1350 °C. The SEM image shows that residue consists of close network of fibrous structures (Figure 6a). Carbon mapping on NMF residue clearly indicates that fibrous structures are made up of carbon and signifies a lower ash content (Figure 6b).The EDS scan and line mapping studies was also performed on NMF residue to determine the elemental composition and distribution (Figure 7). The EDS graph clearly shows the high carbon content in NMF residue with small percentage of other elements such as calcium, silicon, copper and phosphorous. EDS line mapping also clearly indicates that carbon is distributed uniformly with small ash content. The ash was, in the majority, composed of silicon, phosphorous and copper.

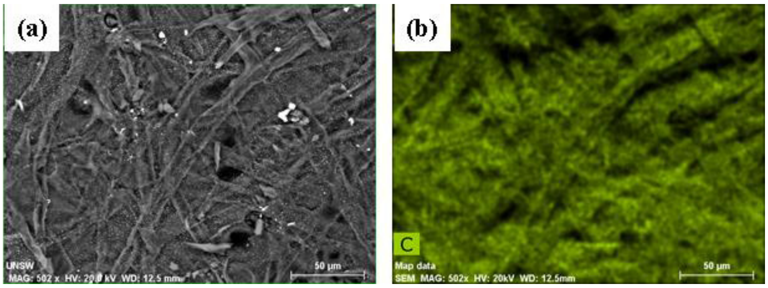


Fig. 6. (a) SEM image and (b) carbon mapping of non-metallic residue obtained at 1350 °C

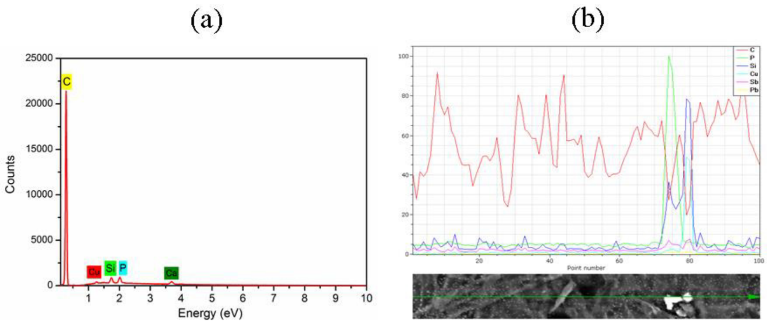


Fig. 7. (a) EDS and (b) Elemental line mapping of non-metallic residue obtained at 1350 °C

Figure 8a shows the XRD pattern of haematite used for reduction of iron oxide studies. XRD pattern of reduced iron oxide at 1350 ºC by using NMF residue as a reductant is shown in Figure 8b. The appearances of peaks corresponding to Iron (Fe) phases were observed in XRD pattern of reduced haematite sample. The Fe phase peak appeared to be dominant and absence of haematite phase clearly indicates complete reduction. This study evidently confirms that PCB NMF residue can be used as a promising supplementary carbon source or reductant in ironmaking industries.

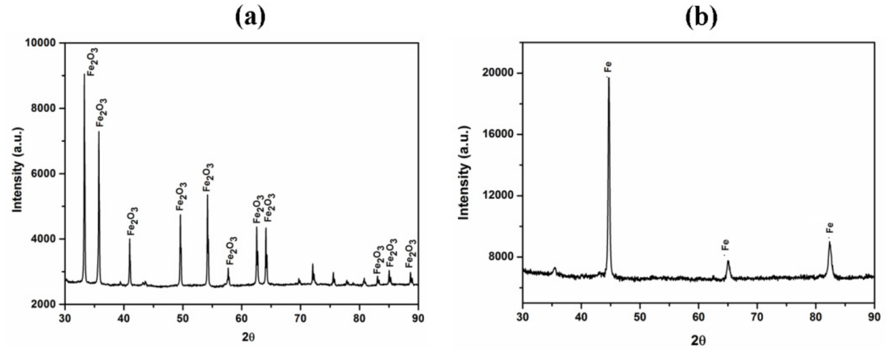


Fig. 8. XRD spectra of (a) haematite and (b) reduced sample at 1350 °C using NMF residue

## Conclusions

In this study, recycling of waste PCBs by simple pyrolysis technique to obtain lead free non metallic residue has been investigated. The main conclusions are summarized below.

(a) The NMF residue obtained at higher pyrolysis temperatures contains less lead content and decreased from 3059 to 72 μg/g when pyrolysis temperature increased from 750 to 1350 °C.

(b) The valuable metals such as copper, gold, silver and tin were present in negligible quantity and LECO analysis clearly indicate that NMF residue is rich in carbon (85-90%). SEM studies clearly indicate that NMFs are made up of carbon fibrous structures.

(c) The XRD result of reduced haematite sample indicates that NMF residue of PCBs can be used as a promising supplementary carbon source in ironmaking industries as reductant.

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