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INVESTIGATING THE USE OF PRINTED CIRCUIT BOARD LEACH RESIDUE AS REDUCTANT IN PYROMETALLURGICAL OPERATIONS

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KEY FINDINGS

This project aimed to determine the technical feasibility of using the non-metallic fraction of PCB residue recovered after leaching of valuable metals as a supplementary reducing agent in ferrous and ferroalloy industries and quantify the potential advantages and disadvantages associated with its potential use in smelting operations. Thermodynamic simulations of chromite smelting and solid state pre-reduction of hematite revealed that PCB can be used partially to replace conventional reducing agents. From chromite smelting simulations, there was a decrease in the energy required for reduction as the weight percent of the PCB in the blend increased. In light of overall results, the optimum mass percent of PCB in the blend appeared to be around 20% with an energy savings of 200 kWh/t of ore. Furthermore, solid state pre-reduction tests with hematite showed that blends of PCB-carbon acted as better reductant than pure carbon due to the presence of hydrocarbons in the PCB.

INTRODUCTION

Electrical and electronic equipment (EEE) manufacturing is one of the fastest growing global sectors. The proliferation of technology and remarkable market growth of EEE has shortened the lifespan resulting in the increase of e-waste. Electronic waste without the intent of reuse reached 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 toxic flame retardants, disposal of electronic waste via landfilling is deleterious to the environment.

In this study, the utilisation of the non-metallic PCB waste fraction as reductant in primary metal smelting operations and solid state reduction was investigated. The organic components as well as the ash composition of the PCB were characterised using Fourier transform infrared spectroscopy (FTIR) and X-ray fluorescence spectroscopy (XRF) respectively. Proximate analysis on the PCB revealed the ash and volatile matter content to be 40.1% and 44.8%, which is higher than coal used in reductive smelting operations. The elemental analysis showed carbon and oxygen content of 30.43% and 20.72% respectively.

Thermodynamic modelling of chromite and iron smelting were performed using various blends of PCB and coal. The models showed that PCB residue might be used to partially replace the conventional reductants. The study revealed that in chromite smelting the optimal blend contains around 20 wt% PCB residue, with energy savings of 200 kWh/t of ore to achieve the same metal recovery. Laboratory-scale experiments simulating solid state reduction of hematite (Fe_2O_3) were also performed using various blends of PCB and graphitic carbon. The tests were carried out in a Differential Scanning Calorimeter (DSC) from ambient temperature to 1200℃ as well as in Single particle reactor (SPR) at 900℃ and 1000℃. The product of each test was analysed using scanning electron microscope (SEM) and X-ray powder diffraction (XRD). The degree of reduction calculated from the mass loss during the test showed that PCB acts as better reductant at lower temperatures. However, at higher temperatures the preference shifts towards carbon.

APPROACH

Pre-treatment and Leaching of PCB

The waste printed circuit boards (PCB) was obtained from Cape E-waste Recyclers. Waste PCB were dismantled and desoldered with nitric acid before crushed to -2mm. Leaching was performed using sulphuric acid and subsequently aqua regia to ensure that the metals were completely dissolved in the acid. The residue was then washed and air dried.

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) shown in Tables 1-3. The morphology of the PCB leached residue were examined by Scanning Electron Microscopy (Fig.1) and contents were also characterized by X-ray powder diffraction (XRD) with a PANalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-Kα radiation. 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%. Aluminum 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.

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

EMSIM (Ex Mente Technologies, 2018) simulator for modelling industrial chromite ore smelting was used to understand the feasibility of adding PCB in smelting operation. Smelting of Chromite was studied at 1700°C 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

Samples were prepared by mixing 1 g of hematite of high purity (>99%) and 0.532 g of reducing agents. The reducing agents were blends of high purity graphite (99.99%) and leached residue of PCB. Differential scanning calorimeter and thermogravimetric (DSC-TGA) was used to investigate the reduction potential of PCB under non-isothermal conditions. The set up used for this study was a Netzsch STA 449 F1 Jupiter DSC-TGA instrument with a sensitivity of ±1µg. The DSC-TGA was coupled with a Pfeiffer Vacuum ThermoStar GSD 301 T3 quadruple mass spectrometer (QMS) to simultaneously analyze the evolved gas to further confirm the reactions occurring. The tests were carried out from ambient temperature to 1200°C using high purity argon. The results showed the pyrolysis of PCB occurred at temperatures between 275°C and 325°C. About 30% of the initial mass of the PCB was lost. QMS show the release of CO, CO_2, CH_4, HBr and other gases during the pyrolysis stage. Further reduction tests were carried out in a single particle reactor (SPR) to study reduction tests occurring under isothermal conditions.

CONCLUDING REMARKS

It was revealed that the reduction of hematite with PCB has faster kinetics than reduction with graphite due to the presence of hydrocarbons in PCB. The hydrocarbons were found to be reducing hematite at lower temperatures than pure carbon.

Smelting of chromite ore and iron ore were simulated using EMSIM. Mass and energy balance models showed that the energy required for smelting decreases when PCB or PCB blends are used as reducing agent.

The optimum mass percent of PCB used in the blend is about 20% since about 200 kWh of energy is saved per ton of ore to achieve the same metal recovery. The decrease in the amount of energy required for the operation is also attributed to the higher volatile content of the PCB which also takes part in the reduction process.

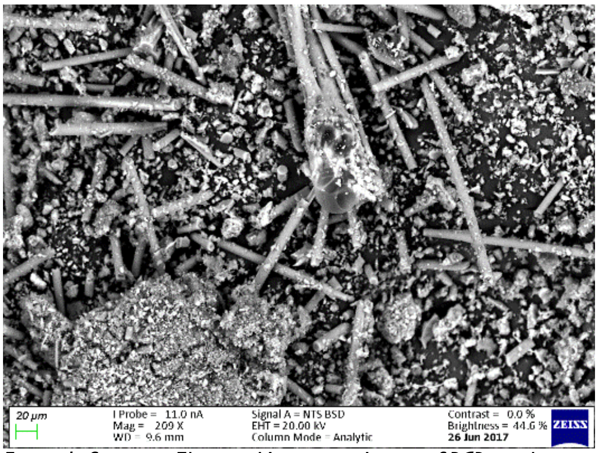

Figure 1. Scanning Electron Microscope Image of PCB residue

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