Plastic-containing materials as alternative reductants for base metal production

Samira Lotfian, Tommy Vikström, Andreas Lennartsson, Bo Björkman, Hesham Ahmed & Caisa Samuelsson

To cite this article: Samira Lotfian, Tommy Vikström, Andreas Lennartsson, Bo Björkman, Hesham Ahmed & Caisa Samuelsson (2019): Plastic-containing materials as alternative reductants for base metal production, Canadian Metallurgical Quarterly, DOI: 10.1080/00084433.2018.1532951

To link to this article: https://doi.org/10.1080/00084433.2018.1532951

© 2019 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group

Published online: 15 Feb 2019.

Submit your article to this journal

Article views: 154

View Crossmark data

Citing articles: 1 View citing articles
Plastic-containing materials as alternative reductants for base metal production

Samira Lotfiā, Tommy Vikströmb, Andreas Lennartsson a, Bo Björkmana, Hesham Ahmedc and Caisa Samuelsson a

aDepartment of Civil, Environmental and Natural Resource Engineering, Process Metallurgy, Minerals and Metallurgical Engineering, Luleå University of Technology, Luleå, Sweden; bBoliden Mineral AB, Skelleftehamn, Sweden; cCentral Metallurgical Research and Development Institute (CMRDI), Cairo, Egypt

ABSTRACT
Shredder residue materials are produced after the removal of ferrous and non-ferrous fractions from end-of-life electronic equipment. Despite the high plastic content and metal value in the ash, high percentages of these materials are currently sent to landfills. In this study, the potential of utilising shredder residue material and other plastic-containing materials as reducing agents was studied. Plastic-containing materials were co-injected with coal into a zinc-fuming furnace in Boliden-Rönnskär smelter. The data obtained from the trial, such as the data from the chemical analysis of the slag and the steam production, are discussed. The observations indicate that plastic-containing material can replace up to 1 ton h−1 of coal without a significant decrease in the zinc reduction rate.

RÉSUMÉ
Les résidus de broyeur sont produits après l’élimination des fractions ferreuses et non ferreuses de l’équipement électronique en fin de vie. En dépit de la haute teneur en plastique et de la valeur du métal dans la cendre, des pourcentages élevés de ces matériaux sont présentement envoyés dans les décharges. Dans cette étude, on a examiné le potentiel d’utilisation de résidus de broyeur et autres matériaux contenant du plastique comme agents réducteurs. On a co-injecté avec du charbon des matériaux contenant du plastique, dans un four de volatilisation du zinc, à la fonderie de Boliden-Rönnskär. On discute les données obtenues à partir de cet essai, comme les données de l’analyse chimique de la scorie et de la production de vapeur. Les observations indiquent que le matériau contenant du plastique peut remplacer jusqu’à 1 tonne/heure de charbon, sans diminution importante du taux de réduction du zinc.

1. Introduction
Waste electric and electronic equipment (WEEE) and end-of-life vehicles (ELV) are increasingly important secondary sources of ferrous and non-ferrous metals. WEEE comprises a wide spectrum of electrical equipment ranging from household appliances and electric and electronic tools to telecommunications equipment [1]. Table 1 presents the WEEE statistics for Sweden from 2012 to 2015. The non-recyclable fraction is the material that was sent to landfills, including slag from incineration [2].

The most problematic streams from WEEE and ELV recycling, which have been primarily sent to landfills in the past, is shredding residue material (SRM). SRM is composed of organic (plastic, rubber and textile), glass, ceramic and metal fractions. This material is estimated to make up 20 to 25% of the total ELV in Europe each year. The value of the energy and metals in SRM is increasingly being recognised; therefore, the options for recycling are becoming more attractive. One option is using its energy through incineration while the metal becomes ash and is then sent to a smelter [1]. Another more attractive option is to use this material directly in base metal production, in which the plastic content can be used as a source of reduction while the metal content can be recovered.

The utilisation of plastic-containing materials in iron and steel making has been studied previously [3,4]. However, the application of SRM during these processes is limited due to the presence of elements such as copper and zinc. One possible use of these materials is for base metal production processes such as bath smelting. Because plastic-containing materials primarily decompose by release of volatiles, bath-smelting processes provide an opportunity for volatiles to participate in
reactions with the slag bath. One example of these types of processes is the zinc-fuming process, which vaporises zinc from zinc-containing slags. During this process, the reduction is achieved using pulverised coal, lump coal or natural gas [5]. Several researchers have studied zinc-fuming from lead blast furnace slag, which contains 11–18 wt-% Zn [6]. Within the slag bath, the coal/air mixture reduces the zinc oxide from the slag to metallic zinc vapour. Above the bath, the metallic zinc vapour and off-gases are oxidised by air [7].

Richards et al. [7] performed a comprehensive industrial study of the zinc-fuming furnace. Using a mathematical model, these researchers described the furnace as consisting of two zones within the slag bath. The first is, a reduction zone, in which the reduction of zinc oxide and ferric iron occurs, and the second is, an oxidation zone, in which the oxidation of coal and ferrous iron occurs. The coal particles entrained in the slag bath are subjected to devolatilisation. Coal devolatilisation produces an initial gas bubble (consisting primarily of H2 and CO) surrounding the coal particle. The presence of hydrogen also indicates that reactions involving H2–H2O will occur in the bubble. Oxides in the slag are reduced by CO and H2, producing CO2 and H2O. The resulting gases react with the fixed carbon in char through the Boudouard reaction.

Previous work regarding the thermal characterisation of SRM, and researchers have observed that the decomposition of SRM results in the release of volatiles. These findings indicate that for SRM to be an appropriate reductant, it is crucial that the evolved volatiles participate in the reduction reactions [8]. Several researchers have emphasised the importance of the fixed carbon content of the reductant in the fuming process [9]. However, the volatile content is also known to play a role during the process. Bell et al. [10] reported that coal with a high volatile content is more efficient than coal with less volatile content. Waladan and Nilmani [11] studied the effect of various carbonaceous reductants on the rate of zinc-fuming from lead blast furnace slag. These researchers reported that volatiles contribute to the reduction reaction. These studies suggest that SRM could be a suitable candidate for replacing coal in zinc-fuming furnaces. However, notably few studies are available regarding the utilisation of plastic-containing materials in general or for SRM specifically as alternatives to coal in zinc-fuming furnaces.

It is complicated to simulate several phenomena involved in the zinc-fuming process, such as the injection and combustion of reducing agents, at a laboratory scale. Therefore, in this study, an industrial scale trial was performed at the Boliden-Rönnskär smelter zinc-fuming plant. Two pure plastic materials, polyethylene (PE) and polyurethane (PUR) (which were selected due to their different thermal decomposition characteristics) and shredder residue material were injected. The objective of this study was to evaluate the possibility of partially substituting plastic-containing residue materials for coal.

2. Materials and methods

2.1. Description of selected materials

The plastic-containing materials selected in this study were PE, PUR in extruded form, and SRM obtained by shredding end-of-life electrical and electronic equipment after the removal of the ferrous and non-ferrous parts. For the industrial trials, the plastic-containing materials were injected alongside coal. Reference trials were also conducted with coal injection only. Proximate and ultimate analyses based on standard methods [12] were performed for all the samples by a certified laboratory, ALS Scandinavia AB, Sweden, and the results are presented in Table 2. Ultimate analyses were performed to determine the elemental compositions of the samples, namely C, H, N, O and S. Proximate analyses were used to determine the moisture, volatile matter, ash and fixed carbon contents.

The primary differences between the coal and the plastic-containing materials were the presence of high fixed carbon in the coal, the high volatile content and ash content of the plastic materials. Among the plastic-containing materials, PE had the highest content of reducing elements (C and H); however, it decomposed primarily into volatiles, as shown in the proximate analysis. PUR had a slightly higher fixed carbon content of up to 7 wt%- The difference in the proximate analyses of these two pure plastic-containing materials was the primary reason why they were selected for the tests. Furthermore, the materials were tested for gross caloric value (IKA calorimeter, C200) and true density (Helium pycnometer, Accupyc II 1340), which are presented in Table 2.

2.2. Description of the furnace

At the Boliden- Rönnskär smelter, copper matte is produced in an electrical smelting furnace (ESF). The slag
generated in the ESF is charged to the zinc-fuming furnace. There, fayalite slag is treated to recover zinc and lead [13]. The fuming furnace is rectangular in shape, with water-cooled walls and a water-cooled base. The dimensions are 25 × 8 m, and the height is approximately 9 m. Pulverised coal is blown into the fuming furnace through 52 oppositely positioned submerged tuyeres by primary air along with secondary air. The process operates in batches at a temperature of 1150–1250°C. The zinc and lead oxide contents of the bath are reduced, and the resulting metal vapour is fumed off the bath by the process gas. The process gas, which contains Zn and Pb vapour goes to the combustion shaft, where it reacts with tertiary air. These reactions generate heat and the Zn and Pb are oxidised. Subsequently, the process gas goes to the waste heat boiler, where its energy is recovered by producing steam and pre-heating air. The gas is further cooled in the cooling tower and ultimately it goes to the electrostatic precipitators to recover the ZnO and PbO as dust.

The process is shown schematically in Figure 1. The capacity of the boiler is 55 tons of steam per hour at a pressure of 40 bar and a superheated temperature of 370°C. The total fuming time is approximately 120 min, with the zinc concentration being reduced from approximately 10 wt-% to less than 2 wt-%. Throughout the batch, the water flow in the water cooling panel is constant, while the temperature of the water may vary. The heat loss through the water cooling panel is calculated from the change in the water temperature and the flow rate. Before tapping, the coal injection rate is reduced, increasing the extent of combustion, which raises the bath temperature, resulting in higher fluidity. After the fuming cycle is finished, the slag is transferred to a settling furnace to separate the matte, slag and speiss [14].

### 2.3. Description of the injection system for plastic-containing materials

Coal is milled, wind-sieved and transported by primary air to the coal distribution system. The fuming furnace has three coal mills, with each supplying two distributors. Each of these distributors supplies eight or nine tuyeres, dividing the whole furnace into six zones, as shown in Figure 2. The plastic-containing material is injected through a separate handling system that is connected to only one of the injection zones, which is marked in Figure 2. Plastic-containing materials are charged from a storage silo to a vessel with a certain volume. Once the vessel is filled, it pressurises, and

#### Table 2. Characterisation of materials, including ultimate and proximate analyses, densities and gross calorific values.

<table>
<thead>
<tr>
<th></th>
<th>Ultimate analyses</th>
<th>Proximate analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H (wt-%)</td>
<td>O (wt-%)</td>
</tr>
<tr>
<td>Coal</td>
<td>4.8</td>
<td>5.2</td>
</tr>
<tr>
<td>SRM</td>
<td>6.1</td>
<td>12.9</td>
</tr>
<tr>
<td>PE</td>
<td>11.6</td>
<td>1.6</td>
</tr>
<tr>
<td>PUR</td>
<td>6.2</td>
<td>15.3</td>
</tr>
</tbody>
</table>

![Figure 1](https://example.com/figure1.png)  
**Figure 1.** Schematic of the zinc-fuming process in the Boliden-Rönnskär smelter [14].
material is injected by air through a rotary feeder at the bottom of the vessel (Figure 3). Therefore, the charging of plastic material occurs periodically, as shown in Figure 4. The total amount of plastic material charged and the amount charged at each interval are dependent on the shape and density of the material and how it is carried by air. As a result, PUR packs better into the vessel due to its uniform cylindrical shape. PUR also passes more easily through the rotary feeder with air and, thus is charged in more compared with SRM, which is an inhomogeneous material.

2.4. Experimental design and sampling

Before the industrial trials, 50 tons of selected plastic-containing materials with particle sizes smaller than...
10 mm were prepared. The coal had particle sizes smaller than 38 μm. The charge to the fuming furnace primarily consisted of molten slag from the ESF and was charged to the fuming furnace with ladle (80–100 ton/batch). Additionally, cold charges, such as electric arc furnace (EAF) dust and revert slag, were charged in some of the trials. Table 3 shows the typical composition of the slag and the cold charges used in the trials. For the industrial trials, 11 batches with coal injection only, 2 trials with co-injection of coal and PE, 4 trials with coal and PUR and 6 trials with coal and SRM were conducted. The important operational parameters during each batch are as follows: the amount of slag (cold and hot), the batch process time, the coal injection rate and the amount of injected air. These parameters for all the trials have been summarised in Table 4. For the trials involving the injection of plastic materials, the amount of plastic injected per batch is also reported. The amount of injected plastic was dictated by the injection system. The primary air flow rate during all the trials was 19 kNm³ h⁻¹ while the secondary air flow changed. For trials with only coal injection, the coal injection rate varied, while the amount remained the same during the trial with plastic injection. The most important data acquired from the batches during the zinc-fuming process were the changes in slag compositions, especially the change in zinc concentration. A sample was taken immediately after the last ladle of slag was charged and thereafter at 10-min intervals until the start of the tapping period. Sample collection was conducted by inserting a steel rod through a tuyere. The steel rod was subsequently withdrawn and cooled in water, and the slag was separated from the rod. Slag samples were collected from the side opposite to the plastic injection zone. As chemical analysis of the slag samples was performed by the central laboratory at the Boliden-Rönnskär smelter. This analysis was performed using X-ray emission spectrography. The morphology of the slag was determined using a Zeiss Gemini Merlin scanning electron microscope (SEM). The acceleration voltage was 20 kV and the emission current was 1.0 nA. Process data collected from the trials included the steam produced in the boiler and the heat lost through water cooling.

3. Results and discussion

3.1. Chemical analysis of slag

3.1.1. Trials with coal injection only

Figure 5 shows the concentrations of zinc in the slag for a representative batch with coal injection only. Figure 5 shows that the zinc concentration in the slag decreases linearly with time. The slope of the line provides the zinc reduction rate (wt-% min⁻¹). In addition to the zinc concentration, the SiO₂ and Pb concentrations are shown in Figure 5. The SiO₂ concentration increases slightly during the process, which is due to the decrease in the mass of the slag as zinc oxide is reduced and silica is introduced from the ash. Previous work showed that the tested coal consists of 25 wt-% SiO₂ [8]. The Pb in the slag is almost completely reduced in this batch.

Trials with higher coal injection rates, which in turn introduce a higher fixed carbon content, are expected to have higher reduction rates. Trials Coal-3 and Coal-4, are subject to similar conditions, except the coal injection rates differ by approximately 1 ton h⁻¹; trials Coal-7 and Coal-8 are also similar (Table 4). A lower zinc reduction rate is observed for trial Coal-3, which is expected. However, trial Coal-7 has the same reduction

<table>
<thead>
<tr>
<th>wt-%</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>MgO</th>
<th>Pb</th>
<th>S</th>
<th>SiO₂</th>
<th>Sn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
<td>3.4</td>
<td>2.2</td>
<td>0.2</td>
<td>2.1</td>
<td>30.2</td>
<td>0.8</td>
<td>0.9</td>
<td>1.1</td>
<td>30.6</td>
<td>0.2</td>
<td>8.8</td>
</tr>
<tr>
<td>Revert slag</td>
<td>2.7</td>
<td>10.2</td>
<td>0.2</td>
<td>25.9</td>
<td>2.3</td>
<td>27.8</td>
<td>10.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EAF dust</td>
<td>0.8</td>
<td>5.3</td>
<td>0.3</td>
<td>0.4</td>
<td>22.4</td>
<td>1.1</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4. Parameters during the trials.

<table>
<thead>
<tr>
<th>Marking</th>
<th>Batch time, h</th>
<th>Slag, ton</th>
<th>Revert slag, ton</th>
<th>EAF dust, ton</th>
<th>Coal ton h⁻¹</th>
<th>Plastic, ton</th>
<th>Secondary air km³ h⁻¹</th>
<th>Initial zinc content (wt-%)</th>
<th>Molar ratio (initial Zn/C + H₂)</th>
<th>Molar ratio (fixed carbon/C + H₂)</th>
<th>Zn reduction rate, (wt-% min⁻¹)</th>
<th>Efficiency of zinc reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal + PE -1</td>
<td>1.30</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>5.9</td>
<td>0.96</td>
<td>11.5</td>
<td>6.67</td>
<td>1.45</td>
<td>0.16</td>
<td>0.52</td>
<td>0.06</td>
</tr>
<tr>
<td>Coal + PE -2</td>
<td>2.00</td>
<td>92</td>
<td>0</td>
<td>0</td>
<td>5.6</td>
<td>1.30</td>
<td>10</td>
<td>8.2</td>
<td>1.43</td>
<td>0.09</td>
<td>0.53</td>
<td>0.07</td>
</tr>
<tr>
<td>Coal + PUR -1</td>
<td>2.00</td>
<td>94</td>
<td>0</td>
<td>0</td>
<td>5.6</td>
<td>3.00</td>
<td>10.5</td>
<td>7.7</td>
<td>1.46</td>
<td>0.10</td>
<td>0.50</td>
<td>0.07</td>
</tr>
<tr>
<td>Coal + PUR -2</td>
<td>2.00</td>
<td>94</td>
<td>0</td>
<td>0</td>
<td>5.6</td>
<td>3.00</td>
<td>10.5</td>
<td>7.8</td>
<td>1.46</td>
<td>0.10</td>
<td>0.50</td>
<td>0.08</td>
</tr>
<tr>
<td>Coal + PUR -3</td>
<td>1.45</td>
<td>86</td>
<td>0</td>
<td>0</td>
<td>5.6</td>
<td>2.80</td>
<td>10.5</td>
<td>9.1</td>
<td>1.54</td>
<td>0.14</td>
<td>0.48</td>
<td>0.09</td>
</tr>
<tr>
<td>Coal + PUR -4</td>
<td>2.00</td>
<td>88</td>
<td>0</td>
<td>0</td>
<td>5.6</td>
<td>1.30</td>
<td>10.5</td>
<td>9.3</td>
<td>1.31</td>
<td>0.11</td>
<td>0.56</td>
<td>0.07</td>
</tr>
<tr>
<td>Coal + SRM-1</td>
<td>1.50</td>
<td>95</td>
<td>4</td>
<td>0</td>
<td>5.6</td>
<td>0.70</td>
<td>10.5</td>
<td>7.4</td>
<td>0.80</td>
<td>0.19</td>
<td>0.75</td>
<td>0.06</td>
</tr>
<tr>
<td>Coal + SRM-2</td>
<td>1.50</td>
<td>95</td>
<td>0</td>
<td>0</td>
<td>5.6</td>
<td>1.30</td>
<td>10.5</td>
<td>7.1</td>
<td>0.87</td>
<td>0.17</td>
<td>0.70</td>
<td>0.06</td>
</tr>
<tr>
<td>Coal + SRM-3</td>
<td>1.75</td>
<td>91</td>
<td>0</td>
<td>0</td>
<td>5.6</td>
<td>1.40</td>
<td>10.5</td>
<td>7.2</td>
<td>0.86</td>
<td>0.14</td>
<td>0.70</td>
<td>0.06</td>
</tr>
<tr>
<td>Coal + SRM-4</td>
<td>2.00</td>
<td>83</td>
<td>3</td>
<td>2</td>
<td>5.6</td>
<td>1.04</td>
<td>10.5</td>
<td>7.4</td>
<td>0.80</td>
<td>0.13</td>
<td>0.74</td>
<td>0.07</td>
</tr>
<tr>
<td>Coal + SRM-5</td>
<td>2.00</td>
<td>93</td>
<td>0</td>
<td>0</td>
<td>5.6</td>
<td>1.30</td>
<td>10.5</td>
<td>7.4</td>
<td>0.83</td>
<td>0.13</td>
<td>0.72</td>
<td>0.07</td>
</tr>
<tr>
<td>Coal + SRM-6</td>
<td>1.75</td>
<td>98</td>
<td>0</td>
<td>0</td>
<td>5.6</td>
<td>1.20</td>
<td>10.5</td>
<td>7.1</td>
<td>0.84</td>
<td>0.15</td>
<td>0.72</td>
<td>0.07</td>
</tr>
<tr>
<td>Coal-1</td>
<td>2.00</td>
<td>97</td>
<td>0</td>
<td>0</td>
<td>6.3</td>
<td>11.5</td>
<td>8</td>
<td>1.26</td>
<td>0.11</td>
<td>0.61</td>
<td>0.06</td>
<td>74.3</td>
</tr>
<tr>
<td>Coal-2</td>
<td>2.00</td>
<td>97</td>
<td>0</td>
<td>0</td>
<td>6.3</td>
<td>11.5</td>
<td>8</td>
<td>1.26</td>
<td>0.11</td>
<td>0.61</td>
<td>0.07</td>
<td>78.0</td>
</tr>
<tr>
<td>Coal-3</td>
<td>1.85</td>
<td>66</td>
<td>5</td>
<td>0</td>
<td>5.6</td>
<td>10</td>
<td>9</td>
<td>1.18</td>
<td>0.11</td>
<td>0.61</td>
<td>0.08</td>
<td>77.4</td>
</tr>
<tr>
<td>Coal-4</td>
<td>1.50</td>
<td>65</td>
<td>4</td>
<td>2</td>
<td>6.5</td>
<td>11</td>
<td>9.8</td>
<td>1.31</td>
<td>0.13</td>
<td>0.61</td>
<td>0.11</td>
<td>88.3</td>
</tr>
<tr>
<td>Coal-5</td>
<td>2.00</td>
<td>99</td>
<td>0</td>
<td>0</td>
<td>6.7</td>
<td>11.5</td>
<td>9.6</td>
<td>1.33</td>
<td>0.12</td>
<td>0.61</td>
<td>0.09</td>
<td>84.8</td>
</tr>
<tr>
<td>Coal-6</td>
<td>2.00</td>
<td>57</td>
<td>5</td>
<td>0</td>
<td>5.6</td>
<td>10</td>
<td>9.5</td>
<td>1.18</td>
<td>0.10</td>
<td>0.61</td>
<td>0.09</td>
<td>87.4</td>
</tr>
<tr>
<td>Coal-7</td>
<td>1.75</td>
<td>52</td>
<td>5</td>
<td>0</td>
<td>5.6</td>
<td>10</td>
<td>9.8</td>
<td>1.18</td>
<td>0.11</td>
<td>0.61</td>
<td>0.11</td>
<td>87.6</td>
</tr>
<tr>
<td>Coal-8</td>
<td>1.50</td>
<td>52</td>
<td>8</td>
<td>0</td>
<td>6.5</td>
<td>11.5</td>
<td>7.1</td>
<td>1.29</td>
<td>0.11</td>
<td>0.61</td>
<td>0.11</td>
<td>87.1</td>
</tr>
<tr>
<td>Coal-9</td>
<td>2.00</td>
<td>97</td>
<td>0</td>
<td>4</td>
<td>6.4</td>
<td>10.5</td>
<td>6.3</td>
<td>1.32</td>
<td>0.11</td>
<td>0.61</td>
<td>0.06</td>
<td>81.1</td>
</tr>
<tr>
<td>Coal-10</td>
<td>1.75</td>
<td>79</td>
<td>3</td>
<td>2</td>
<td>6.4</td>
<td>11.2</td>
<td>7.2</td>
<td>1.29</td>
<td>0.11</td>
<td>0.61</td>
<td>0.08</td>
<td>83.2</td>
</tr>
<tr>
<td>Coal-11</td>
<td>1.50</td>
<td>80</td>
<td>0</td>
<td>0</td>
<td>6.3</td>
<td>11.5</td>
<td>6.9</td>
<td>1.26</td>
<td>0.11</td>
<td>0.61</td>
<td>0.09</td>
<td>83.3</td>
</tr>
</tbody>
</table>
rate as trial Coal-8, although the coal injection rate is lower. Comparing trials Coal-7 and Coal-8, the initial zinc content in trial Coal-7 is higher. The higher initial zinc content can be attributed to the higher activity of ZnO in the slag and thus a higher reduction rate is observed.

3.1.2. Trials with co-injection of plastic-containing materials and coal

The reduction potential of different plastic materials has been compared using the zinc concentration in slag versus time (zinc reduction rate). Figure 6(a–c) shows the variation in zinc concentration over time for the trials.
with the co-injection of coal and PE, PUR and SRM, respectively. The figures show that for all the tested materials, the zinc concentration decreases linearly with time, as observed in the trials with coal injection only. The rate of Zn reduction for all the trials is reported in Table 4. It is possible to compare the change in the zinc reduction rate due to the substitution of coal with different plastic materials. The average zinc reduction rate (Table 5) is highest for the trials with coal injection only. However, the zinc reduction rate is not significantly lower for the co-injection of coal and plastic, even though the rate of coal injection is decreased by 1 ton h$^{-1}$. The results suggest that reducing the coal consumption in the zinc-fuming process is possible by substituting it with plastic-containing materials. Among trials with co-injection of plastic-containing material with coal, the trials with PUR show the highest rate.

During the coal + PUR-4 trial, the injection system experienced technical difficulties and charging of the PUR stopped after 40 min. At the same time that the PUR injection stopped, the coal injection rate increased by 1 ton h$^{-1}$. Figure 7(a) shows the zinc concentration during this trial. As the PUR injection stops, the zinc reduction rate decreases from 0.08 to 0.07 wt-% min$^{-1}$, despite the increase in the coal injection rate. This finding demonstrates that PUR plays a role in zinc reduction. Similar phenomena occurred during the Coal-SRM-3 trial, but during this trial, the coal injection rate was not increased (Figure 7(b)). The zinc reduction rate decreases from 0.06 to 0.05 wt-% min$^{-1}$ when the SRM injection stops.

### 3.2. Zinc reduction efficiency for different reductants

Efficiency is a parameter that compares the ability of the tested materials to reduce the zinc contents of slag baths. The efficiency is calculated based on the following formula:

$$\text{efficiency} = \frac{\text{initial zinc molar content} - \text{final zinc molar content}}{\text{initial zinc molar content}} \times 100$$

The initial molar content of zinc in a slag bath is calculated from the average zinc content of the charged materials (both molten slag and cold charge). The final zinc wt-% from the slag characterisation is used to calculate the final molar zinc content. However, to calculate this value, the final mass of the slag must first be estimated. The total Fe concentration is used to estimate this value, because the total Fe content does not change during the batch. Thus, the change in concentration is related to the change in the total mass of the slag. The calculated efficiencies for all the trials are reported in Table 4. The average efficiency for each tested material is presented in Table 6. The efficiencies of the tested materials do not differ significantly, although the plastic-containing materials have less fixed carbon content compared to coal. These observations provide more evidence that fixed carbon is not the only important parameter affecting the zinc-fuming process.

The efficiency of the reductant is dependent on the amount of reducing elements and oxygen introduced during a batch. As coal is injected into the furnace, it combusts with air, producing gases such as CO$_2$, H$_2$O, CO and H$_2$. Later, the produced gases e.g. CO and H$_2$, plus the remaining fixed carbon, enter the slag and take part in the reduction. The ratio of produced (CO

### Table 5. Average Zn reduction rates and standard deviations.

<table>
<thead>
<tr>
<th>Reductant</th>
<th>Coal and PE</th>
<th>Coal and PUR</th>
<th>Coal and SRM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average rate (wt-% min$^{-1}$)</td>
<td>0.087</td>
<td>0.064</td>
<td>0.079</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.017</td>
<td>0.005</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Figure 7. The zinc reduction rate with co-injection of (a) coal and PUR-4 and (b) coal and SRM-3.
Table 6. Average value of molar ratios of reducing elements to oxygen, initial zinc to reducing elements, carbon to reducing elements and average efficiencies.

<table>
<thead>
<tr>
<th>Reductant</th>
<th>Coal</th>
<th>Coal + PE</th>
<th>Coal + PUR</th>
<th>Coal + SRM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ratio of (C + H₂)/O</td>
<td>1.26</td>
<td>1.43</td>
<td>1.45</td>
<td>0.80</td>
</tr>
<tr>
<td>Molar ratio of initial zinc/(C + H₂)</td>
<td>0.11</td>
<td>0.13</td>
<td>0.11</td>
<td>0.15</td>
</tr>
<tr>
<td>Molar ratio of fixed carbon /(C + H₂)</td>
<td>0.61</td>
<td>0.52</td>
<td>0.51</td>
<td>0.72</td>
</tr>
<tr>
<td>Efficiency of zinc reduction</td>
<td>82.9</td>
<td>72.7</td>
<td>79.4</td>
<td>72.2</td>
</tr>
</tbody>
</table>

The molar ratio of C and H in the reductants (both coal and plastic) to oxygen (in the air and the reductant) has been calculated for all the trials and is presented in Table 4. The average ratio for each tested material is presented in Table 6. The trials were designed to reduce the amount of coal used by partially substituting plastic materials, while keeping the (C + H₂)/O ratio constant. However, the injection system limits the amount of injected reductants; therefore, the ratio differs for the tested materials. The ratio is lower for the trials with co-injection of coal and SRM compared to the other trials, which suggests that the conditions are closer to complete combustion during the co-injection of the coal and SRM trials. Thus, the combustion products contain higher amounts of CO₂ and H₂O and a lower amount of the reductant gases, CO and H₂. The zinc content of the slag may also be compared to the amount of available reductant. This calculated value is the molar ratio of the initial zinc content to the molar value of C and H₂ in both the coal and plastic materials. The results are presented in Table 4, which shows that trials with an SRM injection have the lowest amount of reductant available compared to the amount of zinc in the slag that must be reduced. This finding explains the low efficiencies observed during these trials.

Despite having higher (C + H₂)/O ratios and similar Zn/ (C + H₂) ratios compared to trials with coal injection only, trials with PE and PUR injection show lower efficiencies. This result suggests that PE and PUR are less efficient reductants compared to SRM. The final parameter to compare is the molar ratio of fixed carbon to (C + H₂), where fixed carbon in both coal and plastic is

Figure 8. SEM images of the cross-section of slag collected during trials with (a) coal only, and with co-injection of coal and (b) PE, (c) PUR and (d) SRM.
taken into account (Table 4). Several authors [9,10] have reported that the fixed carbon of a reductant is the most important factor affecting the reduction efficiency. The average of the fixed carbon contents to the total injected reducing elements are reported in Table 6. Although the trials with SRM have the highest average molar ratio of fixed carbon to \((C + H_2)\), their average efficiency is not higher than that of the trials with coal injection only. PE and PUR contain higher volatile content than SRM (Table 2), which indicates that large portions of the reducing elements are in volatile form. Even though the average ratio of fixed carbon to reducing elements is higher for SRM, it does not have a higher average efficiency than PE and PUR. This finding further indicates that volatiles might also play a role in zinc reduction.

3.3. Morphology of slag

Figure 8(a) shows the cross-section of a slag sample collected during the trials with coal injection only. Figure 8 (b–d) shows the morphology of the slag samples...
collected during the trials with the co-injection of different plastic-containing materials and coal. The slag collected from the trials with coal injection only shows fewer pores compared to the slag collected during the trials with the co-injection of coal and the PE and SRM (Figure 8(b,d)). The higher porosity observed in the slags from the trials with co-injection of coal and PE and SRM suggest that PE and SRM reacted within the slag. The higher porosity may be related to the volume of volatiles that are released from PE, which has the highest volatile content among the plastic materials tested here (Table 2). The cross-section of the slag collected from a trial with co-injection of coal and PUR (Figure 8(c)) shows similar porosity as the slag from a trial with coal injection only (Figure 8(a)). Because the slag samples solidified quickly, pores observed in the slag samples could originate from bubbles within the slag bath. The large number of dispersed bubbles passing through the slag bath creates mixing, which promotes zinc oxide reduction. [15].

### 3.4. Steam production

Figure 9 shows the variation in steam production and heat loss to the cooling water during representative trials for each tested material. During the trials with co-injection of plastic materials and coal, the weight of the material in the plastic injection pressurised vessel is also reported, showing the loading and unloading sequence for the vessel. Figure 9(a) shows that the steam generation during the trials with coal injection only is approximately constant during the batch. Plastic materials are injected in a periodic manner; thus, the steam production also shows periodic behaviour. Trials with the co-injection of PE and coal (Figure 8(b)) show that with a slight delay, steam production is closely correlated to PE injection. A similar trend was observed for the trials with co-injection of coal and PUR (Figure 9(c)) and for coal and SRM (Figure 9(d)). The steam generation during the trials with coal injection only is approximately 400 kg min$^{-1}$; the steam production fluctuated between 400–600 kg min$^{-1}$, 500–750 kg min$^{-1}$ and 400–550 kg min$^{-1}$ for the co-injection of PE, PUR and SRM, respectively. The ratio of steam produced in kg min$^{-1}$ to plastic material charged is calculated for all the materials. The values are 1.6, 1.76 and 1.7 for PE, PUR and SRM, respectively. These results indicate that PUR has the highest steam production per injected material.

### 3.5. Heat lost through water-cooling panels

The heat lost to the water-cooling panel stays constant during the trials with coal injection only. During the trials with the co-injection of PE and coal, the heat loss through the water cooling panel increases significantly as soon as PE injection starts; however, the heat loss decreases after 20 min of PE injection and eventually reaches a plateau. A similar trend is observed for trials with co-injection of SRM and coal, although the extent of the increase is smaller. During the trials with PE and SRM injection, heat loss through water-cooling rises as soon as the plastic material is injected; however, for the trial with PUR injection, there is a 15-min delay before the water-cooling increases.

The water-cooling panel produces a frozen slag layer on the side, which protects the furnace interior from excessive heating. The heat from the slag is transferred through the slag bath first to the frozen slag and then to the water cooling panel, as shown in Figure 10. The heat loss to the water-cooling panel is proportional to the slag bath temperature and the thickness of the solidified slag at the wall. If the bath temperature increases, the frozen slag layer melts, resulting in a steeper temperature gradient through the slag layer. Scholey et al. [16] concluded that as the coal injection rate increases the solidified slag layer partially falls off due to intense mixing, leading to an increase in heat loss. Subsequently, the heat loss plateaus, which corresponds to the time required for a new slag layer to form and adhere to the water-cooled jacket. Similar behaviour was observed in the present study, which may be due to the high volume of released volatiles. Plastic materials have larger particle sizes and higher densities than coal. These differences lead to different trajectories and velocities for the particles. Therefore, plastic materials could be devolatilised in the vicinity of the tuyeres. The extra gases produced due to the devolatilisation of plastic materials can cause extra stirring and lead to the partial removal of the frozen slag layer near the tuyeres. Hence, the heat loss to the water-cooling panel will increase. The...
difference between the heat loss trends seen during trials with PE injection compared to PUR and SRM may be related to the devolatilisation behaviour of these materials. A previous study [8] shows that PE devolatilises rapidly at 480°C, and PUR and SRM decompose through two stages at a slower rate.

The proximate analyses show that the plastic materials decompose through the release of volatiles. A previous study [8] of these plastic materials shows that the volatiles consist primarily of hydrocarbons (CₙHₘ). At high temperatures in the furnace, the released volatiles breakdown into C and H₂. In the vicinity of the tuyere, the cracking of hydrocarbons consumes energy and may lead to a decrease in temperature. In other parts of the furnace, the released volatiles could combust and release heat. Given that the calorific values for the combustion of PE and PUR are higher than that of coal (Table 2), higher amounts of heat can be released into the bath during the trials with these materials.

Lastly, the rise in heat loss to water cooling panels suggests that the plastic-containing material reacts within the slag bath and not by passing through the slag bath and combusting at the top with tertiary air. The released volatiles can either participate in reduction or they can react with oxygen, which results in less oxygen availability to combust the coal, and thus the coal can participate in reduction.

### 3.6. Considerations about plastic materials application in industrial processes

The potential of different plastic-containing materials to serve as reductants in the zinc-fuming process was studied via industrial trials. The result shows that the zinc reduction rate for different tested materials does not show a significant change. However, applying of these materials at an industrial scale requires other considerations. The result shows that PUR has the highest steam production per kilogram of injected plastic. Additionally, despite having the highest available reducing elements during the batch (Table 6), the PUR does not have the highest efficiency in the process. Furthermore, although heat loss through water cooling increases during the trials with this material, the increase occurs with some delay after injection. All of the observed phenomena may be related to PUR being an extruded material. As the material is injected through the tuyere, it requires more time to heat up and devolatilise. The residence time of PUR within the slag bath may not be sufficient to complete the reactions. Thus, part of the material goes to the top of the furnace unreacted, where it combusts, leading to higher steam generation. Table 6 also shows that although the trials with injections of SRM have lower amounts of available reducing elements, the efficiency is not significantly affected. This finding shows that the ultimate analysis of material or the amount of reductant is not the only determining factor in the selection of alternative reducing agents. Finally, the difference in the devolatilisation rate of PE leads to the fast release of a large amount of volatiles. This phenomenon leads to a partial removal of the frozen slag layer and an increase in heat loss through water cooling. The results suggest that the utilisation of these materials during the process, at least under the current injection system, will lead to cracking and the failure of the water cooling panels.

### 4. Conclusions

To investigate the possibility of utilising plastic-containing materials in the zinc-fuming process, plant trials were conducted. Three plastic-containing materials, PE, PUR and SRM, were injected alongside coal for the process. The results of the different trials are quite scattered and the conclusions with respect to how the different materials can be compared are therefore indicative. The experimental results reveal the following:

- The zinc concentration in the slag decreases linearly with time for the trials with coal injection only, as well as it does for the co-injection of plastic materials with coal.
- The decrease in the coal injection rate is 1 ton h⁻¹, and substituting coal with plastic-containing materials does not result in a significant decrease in the zinc reduction rate.
- Although the reducing conditions for the SRM injections are the lowest (C + H₂/O), the reduction rate has the same order of magnitude as that of the other material combinations, showing that SRM is a promising alternative reductant.
- The amount of steam generated during trials with added plastic is higher than the amount of steam generated by injection of coal only.
- The heat lost through water-cooling panel increases during the trials with co-injection of plastic materials and coal and subsequently reaches a plateau.
- Despite having higher (C + H₂/O), the trials with PE and PUR do not show higher efficiency than the trials with injecting coal only.

### Disclosure statement

No potential conflict of interest was reported by the authors.
Funding

Financial contributions from Boliden Commercial, Vinnova supported strategic innovation program for the Swedish mining and metal producing industry, and SIP STRIM, Stena International Recycling and Kuusakoski Sverige AB are gratefully acknowledged. This study was conducted and to a lesser extent financed within the context, of CAMM, Center of Advanced Mining and Metallurgy, at Luleå University of Technology.

Notes on contributors

Samira Lotfiyan, Ph.D. in process metallurgy, works on both base metals production and thermal characterisation of materials. Recently, Samira Lotfiyan defended the Ph.D. with the title of ‘Alternative reducing agent in metallurgical processes’ (Dec. 2018).

Tommy Vikström, Industrial Ph.D. candidate in process metallurgy, and process development engineer in Boliden Mineral AB, works with zinc slag fuming and slag-related research.

Andreas Lennartsson, Associate Senior Lecturer in process metallurgy, works on base metal metallurgy with a focus on process modeling and distribution of minor elements. Among his recent publication is ‘Understanding the bottom buildup in an electric copper smelting furnace by thermodynamic calculations’ (2019).

Bo Bjorkman, professor in process metallurgy, works both on ferrous and non-ferrous base metals extraction. Among his recent publication is ‘Characterization of Slag-Metal Emulsion and Its Impact on Foaming Behavior and Slopping in the LD Process’ (2019).

Hesham Ahmed, Associate professor in process metallurgy, works on ferrous metallurgy and recycling of Li ion batteries. Among his recent work is ‘Developing the Oxidation Kinetic Model for Magnetite Pellet’.

Caisa Samuelsson, professor in process metallurgy, work on base metals extraction. Among her recent publication is ‘Characterization of Slag-Metal Emulsion and Its Impact on Foaming Behavior and Slopping in the LD Process’ (2019).

ORCID

Andreas Lennartsson © http://orcid.org/0000-0002-6655-0684

References


