Sustainable Management of the Plastic-Rich Fraction of WEEE by Utilization as a Reducing Agent in Metallurgical Processes

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Featured Application: The potential of the plastic-rich fraction of waste electronic and electrical equipment (WEEE) to partially substitute for coal in metallurgical processes was investigated.

Abstract: In modern society, there is a fast growth in the production of electrical and electronic equipment (EEE); however, rapid growth results in the frequent discarding of this equipment. During the treatment of discarded materials, a stream is generated that contains a high fraction of plastic materials, but also metals and oxides. This stream, which is called shredder residue material (SRM), is heterogeneous, which limits its recycling options. Utilizing this material in metallurgical processes allows the plastic fraction to be used as a reductant and energy source and the metallic fraction to be recycled and returned to the production of EEE. The aim of this study was to evaluate the potential of plastic-containing materials, especially SRM, as alternative reductants in metallurgical processes. The first step was to compare the thermal conversion characteristics of plastic-containing materials to the currently used reducing agent, i.e., coal. Three main candidates, polyurethane (PUR), polyethylene (PE), and SRM, were studied using a drop tube furnace and an optical single-particle burner. PE had the highest volatile content and the fastest conversion time, whereas PUR had the longest conversion time. Thereafter, plastic materials were tested at the industrial scale through injection to the zinc fuming process at the Boliden Rönnskär smelter. During the industrial trial, the amount of coal that was injected was reduced and substituted with plastic material. The results indicate the possibility of reducing the coal injection rate in favor of partial substitution with plastic materials.

Keywords: shredder residue material; plastic; metallurgical process; sustainable management; conversion characteristics

1. Introduction

The production of electrical and electronic equipment (EEE) is one of the fastest-growing sections of human activities [1]. With the expansion of the social economy, the demand for electronic products has rapidly increased [2]. During the 1960s, an average family possessed only a few electric devices: typically a radio, television, refrigerator, vacuum cleaner, and washing machine. Today, however, the number of electronic household appliances has greatly increased. This fast growth has led to the fast obsolescence and substitution of electronic devices. Thus, as the growth of EEE increases, the generation of waste electric and electronic equipment (WEEE) increases as well [1]. WEEE mainly...
consists of ferrous and nonferrous metals (such as Cu), and a large fraction of WEEE consists of plastic materials (Figure 1).

The global estimation of the amount of WEEE is in the range of 50 million tons annually [3]. While in 2016 about 45 million tons of WEEE were generated globally, this will reach about 52.2 million tons in 2021 [4]. The composition of WEEE is largely dependent on the type and age of the discarded equipment [5]. In Europe, the total quantity of plastics used for the production of electric and electronic products is 3 million tons per year. In total, 1.2 million tons of mixed WEEE plastics arise from the separated collection of WEEE in Europe per year [6].

Managing WEEE is important from both an environmental and an economic perspective. The processing of WEEE involves removing hazardous parts and shredding magnetic and eddy current separators to retrieve ferrous and non-ferrous metals. The remaining material contains a high fraction of plastics, in addition to some glass, ceramic, and metals (Figure 2). This heterogeneous fraction, which is called shredder residue material (SRM), is the most problematic fraction from WEEE.

The main plastic contents of SRM are as follows: acrylonitrile butadiene styrene (ABS), used in the casings of phones, microwave and flat screens; polystyrene (PS), used in refrigerators and small household appliances; and polypropylene (PP), used in components inside washing machines and dishwashers, and in the casings of small household appliances. A smaller fraction of plastics is polycarbonate (PC), which is used in housings for information and communication technology equipment (ICT); epoxy polymers are mainly used in printed circuit boards (PCB) [7].

The current options to process SRM are deposition in a landfill and incineration [8]. The options for treating SRM are limited. Another option to treat SRM is pyrolysis, which includes heating the material in the absence of oxygen. Pyrolysis turns the material into a liquid fraction, which can be used as fuel, and a solid fraction, which is ash and can be recycled [9]. The mechanical recycling of plastic waste is hindered by three main problems: the presence of hazardous substances, the degradation level of the polymer, and the miscibility of the plastics within WEEE. Hazardous substances include lead (Pb), which is used as a plastic stabilizer; cadmium (Cd), which is used as a pigment; and brominated flame retardants (BFR) used to prevent the products from burning. The use of these substances in new products is now restricted, but they can still be found in large amounts in certain waste streams. [7] Incineration as a method to recover the energy content has been a common practice for Sweden as it provides inexpensive district heating, but it is no longer carried out. Toxic compounds such as dioxins can be released from incinerators, which could be due to the high concentration of antimony and copper present in WEEE fractions, which favors their production [10].
One other possible option is the utilization of SRM in metallurgical processes. Some metallurgical processes deal with the production of metals from oxide ores (MeO), where the oxygen is removed through reaction with reductants such as coal or coke. Plastic material contains carbon and hydrogen, which might have the potential to substitute for coal in metallurgical processes, which require reducing conditions [11]. In addition to production from primary sources like ore, metallurgical processes also deal with secondary sources, such as slag, which is the byproduct of several metallurgical processes. Slag usually contains a significant amount of metal oxides. One method to recover the metals from slag is a fuming process, which involves treating the molten slag by the injection of a reducing agent into the slag bath. During the slag-fuming process, the oxides of zinc and lead are reduced by the injection of a coal-air mixture into the bath [12].

Through the utilization of SRM in nonferrous metallurgy, the plastic fraction can be used for reduction and energy supply. On the other hand, the metal content can be recycled through the processes and returned to the production of EEE. There are, however, very few studies that have examined the utilization of plastic as an alternative reductant [13–15]. The possibility of utilizing plastic material as a substitute for the current reductant and energy source has been studied in a full-scale trial at Umicore. These trials were performed with WEEE materials, which contained a high plastic content, with only coke and fuel oil as references. Energy balance calculations revealed that approximately 2/3 of the energy content of the WEEE plastics replaced the consumption of coke and fuel oil. The results showed that approximately 1/3 of the injected WEEE was used to increase the steam production [16].

The aim of this study was to study the potential of plastic-containing materials, especially SRM, as a reductant in metallurgical processes, where a zinc-fuming process was used as a case study. Three plastic-containing materials, namely polyethylene (PE), polyurethane (PUR), and SRM, were used. The first step was to compare plastic-containing materials to coal, particularly in terms of thermal conversion characterization. After a fundamental study at the laboratory scale, plastic materials were tested at the industrial scale through injection to the zinc fuming process at the Boliden Rönnskär smelter.

2. Materials and Methods

Proximate and ultimate analyses based on standard methods (Standards for the proximate analysis of coal: moisture SS 187155, ash SS 185157, and volatiles SS-ISO 562:2010. Standards for the proximate analysis of plastics: moisture SS-EN 14774:2009, ash SS-EN 14775:2009, and volatiles SS-EN 15148:2009. Fixed carbon was calculated. Ultimate analysis standard for coal: CHN ASTM D5373 and sulfur SS 187177, with oxygen calculated. Ultimate analysis standard for plastics: CHN SS-EN 15104:2011, with...
oxygen calculated) were performed for all the samples by the certified laboratory ALS Scandinavia AB, Sweden. An ultimate analysis was performed to determine the elemental compositions of samples, namely, C, H, N, O, and S. A proximate analysis was used to determine the moisture, volatile matter, ash, and fixed carbon content. Furthermore, the materials were tested for true density (Helium pycnometer, Accupyc II 1340, Micromeritics Instrument Corp. 4356 Communications Drive, Norcross, GA 30093-2901, USA); the results are presented in Table 1.

Table 1. Characterization of materials, including ultimate and proximate analyses and densities.

| Ultimate Analyses | H (wt %) | O (wt %) | N (wt %) | S (wt %) | C (wt %) | Ash (wt %) |
|-------------------|---------|---------|---------|---------|---------|----------|
| Coal              | 4.8     | 5.2     | 1.3     | 0.30    | 84.0    | 4.4      |
| SRM               | 6.1     | 12.9    | 1.4     | 0.20    | 57.3    | 22.1     |
| PE                | 11.6    | 1.6     | -       | 0.06    | 78.5    | 8.3      |
| PUR               | 6.2     | 15.3    | 6.0     | 0.03    | 61.7    | 10.8     |

| Proximate analyses | Moisture (wt %) | Volatile (wt %) | Fixed carbon (wt %) | Density (g/cm³) |
|--------------------|-----------------|-----------------|---------------------|-----------------|
| Coal               | 0.8             | 26.5            | 68.3                | 0.8             |
| SRM                | 8.0             | 67.3            | 2.6                 | 1.3             |
| PE                 | 0.3             | 89.1            | 2.3                 | 0.9             |
| PUR                | 1.6             | 80.8            | 7.1                 | 1.3             |

2.1. Conversion Characteristics under Oxidizing Conditions

All the plastic samples were provided by recycling companies; their ash content will most probably end up in the slag phase, apart from volatile metals, which will end up in the gas phase. The effect of particle size on the conversion characteristics of different plastic materials was studied. Plastic materials were crushed using a rotary knife mill to different particle sizes of 7, 5, 3, and 1 mm. The coal particle size was less than 38 µm, which is the conventional particle size for coal injection in the fuming furnace. However, this particle size was too fine for the conversion tests, thus, the conversion of the coal particles was not studied.

2.1.1. Drop Tube Furnace (DTF)

The first set of conversion experiments was conducted in a laminar-flow drop tube furnace. The reactor consisted of an alumina tube with heating compartments, as shown in Figure 3a. A detailed description of the furnace and test conditions is given elsewhere [17]. The furnace was heated to 1250 °C. Plastic particles fell directly into the high-temperature zone of the reactor through a water-cooled probe. The total heated length of the furnace was 2.3 m. To simplify the calculation, it was assumed that the drag force and gas velocity did not affect the velocity of the particles. The residence time of falling particles was calculated by assuming free fall. Thus, the residence time of the particles did not depend on the particle size. The residence time calculated was 0.65 s. The combustion products consisted of solid residue, which fell into a water-cooled char bin. The total flow of gas to the furnace was 3 L/min.

2.1.2. Optical Single-Particle Burner (OSB)

Another set of conversion experiments was performed with an optical single-particle burner (OSB). A schematic of the furnace is shown in Figure 3b. A detailed description of furnace and experiments has been provided elsewhere [17]. A stable flame at the bottom was provided by the combustion of CH₄ and the temperature of the flame was controlled by the ratio of CH₄ and O₂. The furnace contains a quartz windows, which stabilized the flow of gases and made it possible to observe the changes during the conversion. Gas temperatures were measured by a thin-wire thermocouple. During the experiments, first, the flame was ignited and stabilized before the sample was inserted into the center
of the furnace on a platinum wire-mesh plate. The temperature during the tests was set to 1250 °C, and the chamber was at atmospheric pressure. A 3CCD camera (CV-M9GE JAI) at a frequency of 30 Hz recorded changes in the sample. The experiments were repeated to ensure the representability of the results, especially for SRM, which is a heterogeneous material.

![Diagram](image)

**Figure 3.** Schematic illustration of (a) the laminar drop tube furnace (DTF), adopted from [18], (b) schematic of the optical single particle burner adapted from [19].

2.2. **Industrial Trial**

2.2.1. Description of the Zinc Fuming Process in Boliden Rönnskär

Industrial trials were conducted at the zinc fuming plant at the Boliden Rönnskär smelter. A simplified schematic of this process is shown in Figure 4. Pulverized coal was injected into the furnace through submerged tuyeres and utilized both for reduction and to supply heat for the process. The zinc and lead oxide contents of the slag bath were reduced, and the metal vapor formed was fumed off from the bath by the process gas. The process gas entered the combustion shaft, where it reacted with air. Post-combustion reactions generated heat and oxidized Zn and Pb. Subsequently, the gas that was produced after post-combustion entered a waste heat boiler (WHB), where its energy was recovered by producing steam. The gas was further cooled in the cooling tower and finally entered electrostatic precipitators (ESP) to recover ZnO and PbO as the mixed oxide. The process was batch-wise, where each batch takes about 2 h. During the batch, the zinc concentration in the slag bath changed from the initial value of approximately 10 wt % to 2 wt %.
2.2.2. Experimental Design and Sampling

The particle size of the plastic materials used in the industrial trials was less than 10 mm, which is much larger than the coal particle size, which was smaller than 38 µm. Thus, the plastic materials were introduced to the furnace through a different injection system than coal. Two sets of trials were performed, one with only coal injection as reference, and one set of trials with co-injection of coal and each plastic material. The main difference during the trials with injection of plastic material was that the coal injection rate was reduced and the plastic material was substituted for it. The initial idea of the industrial trial was to reduce the amount of injected coal and substitute it with plastic material, in such a way that the total amount of carbon entering the process remained the same. However, the amount of plastic material injected was dictated by the injection system due to technical difficulties. The trials included 11 batches with only coal injection, two trials with the co-injection of coal and PE, four trials with coal and PUR, and six trials with coal and SRM. Table 2 summarizes the conditions during the trial; a more detailed description of the trial has been published elsewhere [21].

Table 2. The description of the furnace and the process parameters; slag was not analyzed for all the possible elements.

| Description of Furnace | Amount and Type of Reductant during Trials |
|------------------------|------------------------------------------|
| Dimension of furnace, m | Coal, ton/h | Plastic on average, ton |
| Temperature of slag bath, °C | 1150–1250 °C | Coal | 6.3 | - |
| Slag, ton | Coal + PE | 5.6 | 1 |
| Air, kNm³/h | 30 | Coal + PUR | 5.6 | 3 |
| | | Coal + SRM | 5.6 | 0.9 |
| Composition of slag bath, wt % | Al₂O₃ | As | CaO | Cr | Cu | Fe | MgO | Pb | S | SiO₂ | Sn | Zn |
| | 3.4 | 0.2 | 2.0 | 0.2 | 1.4 | 30.0 | 0.8 | 1.2 | 0.8 | 30.0 | 0.3 | 8.9 |

The most important data from these batches were the changes in zinc concentration in the slag compositions. A slag sample was taken from the start of the batch with an interval of 10 min until tapping. Sample collection was conducted by inserting a steel rod through a tuyere on the opposite side of the plastic-injection zone. A chemical analysis of the slag samples was performed by the Central Laboratory of the Boliden Rönnskär smelter using X-ray emission spectroscopy. Furthermore, the steam generation and heat lost through water cooling panel were measured.

3. Results

Characterization of the material clearly indicated the main difference between coal and plastic materials. Table 1 shows that the volatile content of plastic materials was considerably higher than...
coal, while the fixed carbon was significantly lower. Among the plastic materials studied, PE had the highest volatile content and PUR had the highest fixed carbon.

3.1. Conversion under Oxidizing Conditions

3.1.1. Effect of Particle Size on Conversion in DTF

The combustion of particles was studied in the DTF. The amount of tar and soot that was observed during these experiments was not significant. No significant weight loss was observed for PUR and PE at all the particle sizes. SRM was the only material that reacted during the tests. Figure 5 shows the solid-residue yield for SRM at each particle size. Solid residue was calculated based on the ratio of the mass of the solid residue after the test to the mass of the original particle. The weight loss of the particles during the test corresponds to the extent of particle conversion. No weight loss occurred at a particle size of 7 mm. The limitation with the DTF is that conversion is only studied at certain residence times. The OSB was further used to study the conversion of plastic materials with respect to time.

Figure 5. Solid-residue yield for SRM with different particle sizes at 1250 °C.

3.1.2. Determination of Total Conversion Time by OSB

During conversion in an oxidizing atmosphere, particles could undergo ignition, devolatilization, and char combustion. It was possible to determine the time required for each phenomenon through the changes observed during the OSB test. One important parameter, in addition to the required time for each phenomenon, is the total required time for conversion. Total conversion time is defined as the sum of the ignition, devolatilization, and char-burnout times; by the end of this time, the particle is fully converted.

Figure 6 shows the average of total conversion time for all the tested materials at different particle sizes. PE had the shortest total combustion time and PUR had the highest total conversion time among the plastic-containing materials. SRM presented different total conversion times. At each particle size, the average SRM conversion time was between that of PUR and PE.
particles down, leading to a faster drop. As a result, the residence time of particles in the furnace was shorter than the calculated residence time.

3.2. Industrial Trial Result

Comparing the two tested methods revealed that no significant conversion was observed for PE and PUR at the DTF, while the devolatilization of particles began at the corresponding residence times in the OSB. This result could have been caused by the different dominant heat-transfer mechanisms in these methods. Radiation was the dominant heat-transfer method in the DTF, while convection was the main heat-transfer mechanism in the OSB. Another reason is that the input gas expands upon entering the DTF, as its temperature increases from room temperature to 1250 °C. This expansion pushes the particles down, leading to a faster drop. As a result, the residence time of particles in the furnace was shorter than the calculated residence time.

Figure 6. Total conversion times for the tested materials at different particle sizes.

Figure 7a,b shows the zinc concentration in the slag bath over the batch time of one of the trials with only coal injection, and one of the trials with coal and SRM, respectively. The slope of the line indicates the zinc-reduction rate (wt %/min). The average of zinc reduction rate and the standard deviation was calculated for the trials with each material and reported in Table 3.

Figure 7. Zinc-reduction rate with (a) coal injection, (b) the co-injection of coal and SRM.

The rate of coal injection during the trial with only coal injection was 6.3 ton/h, which was reduced to 5.6 ton/h and supplemented by 1 ton of SRM. The important finding is that, even though the coal injection was reduced by 0.7 ton/h, the zinc reduction rate was not significantly affected. This indicates that it is possible to partially substitute coal with plastic materials in a zinc fuming process.
Table 3. Average Zn reduction rates and standard deviations.

| Reductant          | Coal  | Coal and PE | Coal and PUR | Coal and SRM |
|--------------------|-------|-------------|--------------|--------------|
| Average rate (wt %/min) | 0.087 | 0.064       | 0.079        | 0.063        |
| Standard deviation | 0.017 | 0.005       | 0.009        | 0.003        |
| Average rate (wt %/min)/Molar content of (C + H$_2$) | 0.0096 | 0.0060     | 0.0064       | 0.0056       |

Among the trials with the co-injection of plastic materials and coal, the trials with PUR showed the highest zinc reduction rate. It is possible to calculate the amount of plastic material, which would correspond to the reduced coal injection, while the carbon amount entering the process remained the same. In that case, 1.5, 1.9 and 2.1 ton of PE, PUR and SRM, respectively, should have been injected to the process. However, the amount of PE and SRM injected was lower, while the amount of PUR injected was higher (Table 2). To have a better comparison between the plastic materials, the average rate of the total molar content of reducing elements (C and H$_2$) for trials with different plastic materials was also calculated and is presented in Table 3. Among the plastic materials, PUR had the highest rate per reducing elements, while SRM and PE were similar.

Another important change during the trials with injection of plastic materials was the steam generation. The steam generation during the trials with only coal injection was approximately 400 kg/min; while it increased to average amounts of 500 kg/min, 620 kg/min, and 475 kg/min for the co-injection of PE, PUR, and SRM, respectively. The ratio of the produced steam in kg/min to the plastic material that was charged were 1.6, 1.76, and 1.7 for PE, PUR, and SRM, respectively. The results indicate that PUR had the highest value for the calculated steam production per material injected. The increase in steam generation suggests that part of the plastic materials injected did not react in the slag bath and it combusted at the combustion shaft and participated in steam generation.

4. Discussion

The conversion characteristics and the industrial trial was discussed and the results from the conversion study are used in this section to understand the behavior of plastic materials in the process. Table 4 summarizes the experiments and summarizes the most important findings of the experiments.

Table 4. Summary of experiments and highlights of results.

| Experiment | Conversion Characterization | Industrial Trial: Reduction Potential |
|------------|----------------------------|---------------------------------------|
| Equipment  | Drop tube furnace-Single particle burner | Zinc fuming furnace |
| Particle size | 1–6 mm | Less than 10 mm |
| Material tested | PE, PUR, SRM | Coal, PE, PUR, SRM |

| Highlights |
|------------|
| PE has the shortest conversion time (only volatiles, as hydrocarbon), PUR has the longest conversion time (both volatiles and char), SRM shows a mixture of these behaviors. | It is possible to lower the coal injection rate and substitute it with plastic injection; steam generation increased, which suggested that part of the plastic goes to gas phase. |
| The conversion characteristic helps in understanding the plastic materials in the fuming process; parameters such as conversion time and product plays an important role in the efficiency of plastic materials. |

The results of the industrial trials indicate the potential of plastic materials as reducing agents. As these materials are injected alongside air to the furnace, they will go through thermal conversion. Conversion under oxidizing atmosphere has shown that these materials have different characterizations, which possibly leads to different interaction in the furnace. No studies have been found on the interaction of plastic materials in the zinc fuming process; however, the interaction of coal has been studied. In
In this study, the gas injected into the slag bath pushes the slag away and a plume is formed. Slag moves upward and falls back to the opposite direction of the gas injection. Slag starts to circulate, and new slag comes into contact with the gas plume [22]. Injected particles are carried away by the high-velocity gas jet. Some of the injected particles combust in the plume and generate bubbles, which get trapped in the slag bath and a foam is generated. Degerstedt [23] studied the injection phenomena in the zinc fuming furnace in Boliden Rönnskär by tuyere back-pressure measurement. Bubbles were reported to be formed, which later dispersed into small bubbles as they moved upward. Richards et al. [24], who conducted a comprehensive study on the zinc fuming process, also reported that the air-coal mixture discharges into the bath as a continuous series of bubbles, which, owing to the low modified Froude number, rise directly up the furnace wall.

Richards et al. [24] also mentioned that particles required to have a certain velocity and a minimum particle size managed to break through the surface tension and penetrate the slag. They assumed that the coal particles travelled at 50–80% of injected gas velocity; thus, particles larger than 0.7 µm have enough momentum to penetrate into the slag. Huda et al. [25] used a computational fluid dynamic (CFD) model to describe the same zinc fuming furnace that Richards studied. Their result also indicated that a fraction of coal penetrated the slag; however, there is debate about the role of penetrated particles. While Richards et al. suggested that the zinc fuming process was essentially controlled by the amount of coal that can be entrained in the slag, Huda et al. reported that the entrained coal particles had less influence on the overall fuming. Huda et al.’s simulation further predicted that a major portion of the injected coal (50%) was combusted in the tuyere gas column. Finally, it is possible that a fraction of the injected particles bypassed the process and went to the combustion shaft. A study of the fluid flow phenomena in the zinc fuming furnace at Boliden Rönnskär also confirmed that some of the coal bypassed the process and entered the post-combustion, as coal particles were captured in the gas phase over the slag bath [26].

All of these phenomena possibly occur in the process; however, their extent depends on the furnace, slag properties, the injection system, etc. During most of the batches in the industrial trial, 90 tons of slag was charged, which fills the furnace up to 1.2 m. Due to the turbulence caused by the gas injection and the foam generated by combustion of coal, the height of the slag bath increased. The height of the bath can oscillate by several meters during the process and can periodically splash a smaller amount to the top of the furnace (8 m). Some fractions of the injected particles combust in the plume, where the extent of the combustion depends on the conversion characteristic of the particles. The product of conversion consists of CO/CO₂ and H₂/H₂O, and it could also include volatiles. Reduction in the slag bath occurs when the oxides come into contact with the reducing gases CO/H₂ in the bubbles, i.e., at the interface of the slag/gas phase. The agitation caused by the sloshing and splashing of the slag accelerates the contact between the slag and gas phase. Unreacted particles and gases generated would either fall back into the slag bath due to the flow circulation or leave the slag bath, combust in the combustion shaft, and participate in steam generation.

The extent of conversion in the slag bath depends on the conversion time of particles. Timothy et al. [27] studied the total conversion time for single bituminous coal particles with particle sizes of 38–45 µm and reported that the total conversion time was 20–40 ms. All the plastic materials studied showed longer conversion times compared to the reported times for the single coal particles. Thus, the extent of conversion of the studied plastic materials at these particle sizes is possibly lower than that of coal during the process. The conversion tests indicated that plastics with smaller particle sizes have a shorter conversion time, so a decrease in particle size would possibly improve the conversion of plastic materials.

PE particles had the shortest conversion time; thus, it is expected that upon injection, PE would convert more compared to other plastics. Figure 8a shows the expected phenomena occurring by injection of PE. It was assumed that the injection of plastic materials would not affect the behavior of coal in the process. PE and coal particles flow upwards due to the gas, and as they ascend in the gas plume, they can go through combustion. Bubbles and unreacted particles could fall back into
the slag through recirculation. The gases that are generated through conversion are more likely to consist of CO/CO\(_2\), while the gases that are produced through the devolatilization of PE materials are mainly hydrocarbons (C\(_n\)H\(_m\)) [28]. It has been reported that when methane is used as a reductant, it needs to be externally cracked at high temperatures with oxygen-enriched preheated air to produce a reducing mixture. The slow breaking of carbon-hydrogen bonds can be the rate-limiting step in the zinc fuming process [29]. Thus, it is possible that, with the slow decomposition of hydrocarbons, the residence time of bubbles may not be enough to complete the cracking of hydrocarbons to participate in reduction reactions in the slag bath. This could be why PE efficiency in the zinc fuming furnace was not as expected.

PUR has the longest conversion time among the studied plastic materials. PUR was injected in extruded form and broke into different lengths during injection. Smaller particles were expected to have a shorter conversion time, while the larger particles took a longer time for conversion. The released volatiles however, consisted of fewer hydrocarbons due to the presence of a high amount of O in the structure, so some of the volatiles were in the form of CO/CO\(_2\) [28]. Furthermore, PUR has an aromatic structure and could form a char during conversion. Once a particle was entrained in the slag, in addition to volatiles, the C in the char could produce CO by the Boudouard reaction (C + CO\(_2\) = 2CO), as shown in Figure 8b. Finally, a fraction of PUR reached the top of the furnace unreacted or partially reacted; here it oxidizes and participates in steam generation.

Finally, SRM consists of different types of plastic materials that consequently have different conversion times and different conversion characteristics. Conversion studies showed that some of the SRM only decompose by devolatilization, while others can also produce char, which could further participate in reactions in the slag bath. SRM consists of different particle sizes, just as it consists of materials with different grindability. Thus, while the conversion of smaller particles might be completed, some fractions could pass through the slag bath unreacted. A schematic illustration of the possible interaction mechanisms of SRM in the process is shown in Figure 9. The variety of the conversion characteristics and times observed for SRM improves its potential as a reducing agent.

**Figure 8.** Schematic illustration of possible phenomena by plastic materials injection: with (a) PE and (b) PUR in the fuming furnace, unreacted particles will react at the top of the slag bath or in the combustion shaft and participate in steam generation; bubbles and particles recirculate by the motion of the slag.
Figure 9. Schematic illustration of possible phenomena by injection of SRM in a fuming furnace.

Although this study focused on the utilization of plastic materials in the zinc fuming process, it is possible to utilize them in other metallurgical processes as well. While implementing the plastic materials as a substitute for the conventional reducing agents, such as coal, it must be noted that the most important difference is the number of volatiles developed. The process needs to be designed in such a way that it can utilize the developed volatiles. On the other hand, one of the limitations of utilizing SRM is the ash content, which could contaminate the final product. One of the limitations in this study was that the composition of gas phase was not analyzed. Combustion of SRM could lead to the release of gases such as Cl, which could lead to corrosion in the furnace. Furthermore, to implement the injection of plastic materials, the emission of different gases, such as Br₂, Sb, and NOx (from the nitrogen from PUR), should be investigated.

SRM is a complex, heterogeneous material, and its current methods of treatment (deposition or incineration) are not only a waste of resources, but also an environmental hazard. By utilizing this material in metallurgical processes, the plastic fraction could help with reduction and the metal fraction can be recycled and returned to production, which is a step towards a circular economy.

5. Conclusions

The potential of plastic materials as an alternative reducing agent in metallurgical processes was studied, with the aim of partially substituting for the coal in the process. In the first step, the thermal conversion characteristics of the materials were studied. In the next step, the reduction potential was studied through an industrial trial at Boliden Rönnskär smelter.

- PE and PUR were not converted during the DTF test, which could be due to the fast drop of materials and the heat transfer mechanism.
- The zinc concentration in the slag bath decreased linearly over time; the slope indicates the zinc reduction rate. The decrease in the coal injection and substitution with plastic-containing materials did not lead to a significant decrease in the zinc reduction rate. This suggests the possibility of partially substituting for coal with plastic materials.
Steam generation increased during the trial with co-injection of plastic materials. The increase in steam generation suggests that part of the plastic material injected did not participate in reactions in the slag bath and went to post-combustion.

Generation of reducing gases such as CO and H$_2$ and their residence time in the slag bath are the important parameters in the efficiency of the reductant.

PE had the shortest conversion time; however, the volatiles released only consisted of hydrocarbons, which require a long time to decompose. PUR and SRM in the slag bath had the possibility to convert by the reaction of fixed carbon in char.

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