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RESEARCH ARTICLE



## Evaluating the potential of plastic-containing materials as alternative reducing agents

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### ABSTRACT

The amount of discarded plastic-containing materials is increasing, and one option to help with this issue is to use these materials in bath smelting processes. The injection of plastic-containing materials to partially substitute coal in zinc-fuming processes has been studied in an industrial trial at Boliden–Rönnskär smelter. To evaluate the potential of plastic-containing materials, thermodynamic calculations were performed in this study. In the first step, a thermodynamic calculation was performed for trials with only coal injection, and then this calculation was applied to trials with the co-injection of plastic materials. The thermodynamic calculation shows that not all the injected coal participates in the reactions within the slag. Similarly, the calculation with the co-injection of plastic-containing materials shows that different amounts of each plastic material participate in the reactions within the slag bath.

### RÉSUMÉ

La quantité de matériaux contenant du plastique et mise au rebut augmente, et une option pour aider avec ce problème est d'utiliser ces matériaux dans les procédés de fusion de bain. On a étudié l'injection de matériaux contenant du plastique pour substituer partiellement le charbon dans les procédés de volatilisation du zinc lors d'un essai industriel au four de fusion de Boliden–Rönnskär. Pour évaluer le potentiel des matériaux contenant du plastique, on a effectué des calculs thermodynamiques dans cette étude. Au cours de la première étape, on a effectué un calcul thermodynamique pour les essais avec uniquement des injections de charbon, et l'on a ensuite appliqué ce calcul aux essais de co-injection de matériaux plastiques. Le calcul thermodynamique montre que ce n'est pas tout le charbon injecté qui participe dans les réactions avec la scorie. Similairement, le calcul avec la co-injection de matériaux contenant du plastique montrait que différentes quantités de chaque matériau plastique participent dans les réactions avec le bain de scorie.

### ARTICLE HISTORY

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### KEYWORDS

Shredder residue material; reducing agent; sustainable management; base metal production; industrial trial; recycling; thermodynamic calculation

## Introduction

With the development of science and technology, the electronics industry has become one of the fastest growing sectors in the world. At the same time, large amounts of waste electrical and electronic equipment (WEEE) are generated worldwide. WEEE contains a variety of valuable materials, such as metals, glass, plastics and oxides. Several studies and developments have been performed on recycling the valuable metals of the WEEE through ferrous and non-ferrous metallurgy [1]. During the shredding of WEEE, a mixed shredder residue material (SRM) is generated, which contains mixed amounts of plastics, metals and oxides [2]. Despite having both energy (plastic) and metal value (ash content), a high portion of SRM goes to landfill. One sustainable method to utilise this material is through bath smelting processes.

In this way, the plastic fraction can be used as both a reductant and a fuel, and the metal value can be recycled. One example of a bath smelting process is zinc fuming, which involves the reduction of zinc from zinc-containing slag by injection of coal and air. In a previous study, the authors investigated the injection of two pure plastic-containing materials and SRMs through industrial trials in a zinc fuming plant of the Boliden–Rönnskär smelter [3]. The finding indicates that plastic-containing materials can partially substitute coal in the process. However, the main question remains, of the extent of plastic material participation in reactions within the slag bath. There are few studies [4] available on the utilisation of plastic materials in zinc fuming processes. However, several researchers have studied the role of coal in zinc fuming reaction using different methods.

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## Literature study

The first thermodynamic study of the zinc fuming process was performed by Bell et al. [5] in 1955 who concluded that there is a thermodynamic equilibrium between the bath and the gases leaving it. The thermodynamic calculation in their paper was based on C and H oxidation and the reduction of ZnO, plus the reaction of H<sub>2</sub>O with CO. Their calculation was based on the heat and mass balance as well as equilibrium consideration, and provides a reasonable simulation of the zinc fuming rate during operation. Blaskett [6] used a simple equilibrium model similar to Bell et al. [5] to predict the performance of a plant trial. The actual performance showed that fuel consumption was 10% greater than the estimated figures. However, in these calculations ZnO was the only reacting species in the slag. In 1967, Kellogg [7] developed a model that considered reactions of other elements in slag such as lead and Fe, in addition to the heat and mass balance. Although the slag was not fully described, Kellogg successfully described the zinc fuming process. In 1980, Grant [8] adopted the model from Kellogg and further developed the model by including more slag components and describing the derivation of their activities. One clear drawback with these thermodynamic calculations is the lack of an accurate description of the chemistry of the slag and the activities of species. Jak et al. [9] calculated the equilibrium condition in the zinc fuming process using a thermodynamic database in FACT and compared the result to experimental measurements. While in previous models, the mass balance was calculated based on the reactions of a few elements in the slag, in this calculation, the minimisation of Gibbs free energy of a large slag system was used. The result indicates that the zinc fuming process is principally equilibrium controlled; however, as the zinc fuming progress and reaches a lower zinc concentration, the reactions become increasingly limited by kinetic factors.

Equilibrium calculations, however, fall short of describing the poor performance of natural gases and light oils as fuel in the zinc-fuming process. Quarm [10] in 1965 in his publication argued that the process is controlled by kinetic factors and is related to an exchange in the iron oxidation state. The fuming furnace was extensively analysed by Richards [11] in 1985. Based on their findings, the authors concluded that the fuming process is kinetically controlled, namely, by entrainment of coal particles and by the rate of ferrous oxidation. From mathematical modelling, the authors reported that the fuming efficiency increases with the increase of the residence time of coal particles in the slag. The level of ferric iron in the slag was also identified as an important factor that affects the kinetics of zinc-fuming.

One of Richards's pieces of evidence for claiming that the furnace is kinetically controlled is that some of the carbon passes through the bath without reacting. Ward [12] in his publication argues that an equilibrium calculation can only be applied for the part of the coal that reacts in the reaction system and stated that the authors have successfully applied equilibrium models to slag fuming process, where the reaction of coal does not proceed to completion. The findings indicate that despite local variation in the process condition, at least in deep bath processes, the overall zinc fuming operation approaches equilibrium.

## Objectives of this study

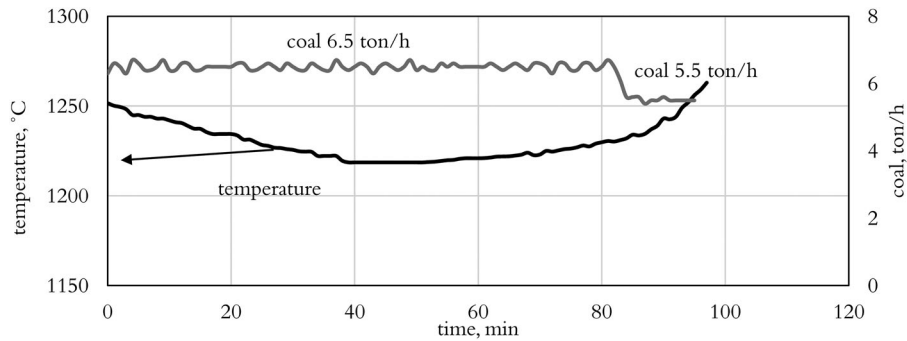
The aim of this study was to evaluate the potential of plastic materials, in particular, SRM to partially substitute coal as reductant in the zinc fuming process. To determine the possibility of utilisation of plastic materials, an industrial trial was performed at the Boliden-Rönnskär smelter [3]. In this study, thermodynamic calculation using FactSage 7.1 was performed and used as a tool to identify and compare the reduction potential of studied plastic materials. The zinc concentration at equilibrium is compared to the zinc concentration in slag bath from the experimental result of the industrial trial.

The first step of the calculation was performed with only coal. The most important change during the batch is the zinc concentration in the slag, thus the calculated zinc concentration was compared with the zinc concentration measured during the trial. The result indicates the extent of coal that participates in the reactions within the slag bath. This finding is used for the calculation of trials with only coal injection. Similarly, a comparison of the calculated and experimental zinc contents in the slag is used to determine the extent that plastic materials participate in the reactions. Furthermore, the effect of the addition of SRM on process conditions, especially the slag chemistry, is investigated.

## Materials and method

### Description of the zinc fuming process in the Boliden-Rönnskär smelter

The conventional fuming furnace practice is a batch operation and involves charging, a fuming cycle and heating up the slag before tapping out. Coal is injected with primary and secondary air into the furnace and reduces the oxides in the slag. During the fuming cycle, the coal injection rate remains constant and decreases only during the last stage, prior to the tapping out the slag, as shown in Figure 1. Figure 1 also shows the



**Figure 1.** Change in temperature of the slag during the batch, with respect to the change in the coal injection rate.

variation in the temperature of the slag during the batch. The reduction reactions are endothermic and cool down the slag. Towards the end of the batch the extent of reduction reactions decreases, which increases the temperature of the slag. Furthermore, during the final stage of the batch the coal injection rate is decreased, resulting in higher combustion (higher  $\text{CO}_2/\text{CO}$ ), which rapidly increases the temperature of the slag.

The content of ZnO and PbO in the slag bath is reduced, and the metal vapour is fumed off by process gases. The gas phase ascends to the top of the furnace, where it oxidises with tertiary air injected at top of furnace and ZnO is formed. Then, gas will go to the boiler, where its energy will be used to produce steam and pre-heat secondary and tertiary airs; as a result the temperature of the gas drops. Finally, the gas goes to the cooling tower, where by water spray it reaches room temperature. A schematic of the process is presented in Figure 2. At point (A), as marked in Figure 2, which is approximately 2 m above the tertiary air injection, the temperature was previously measured. The temperature varied

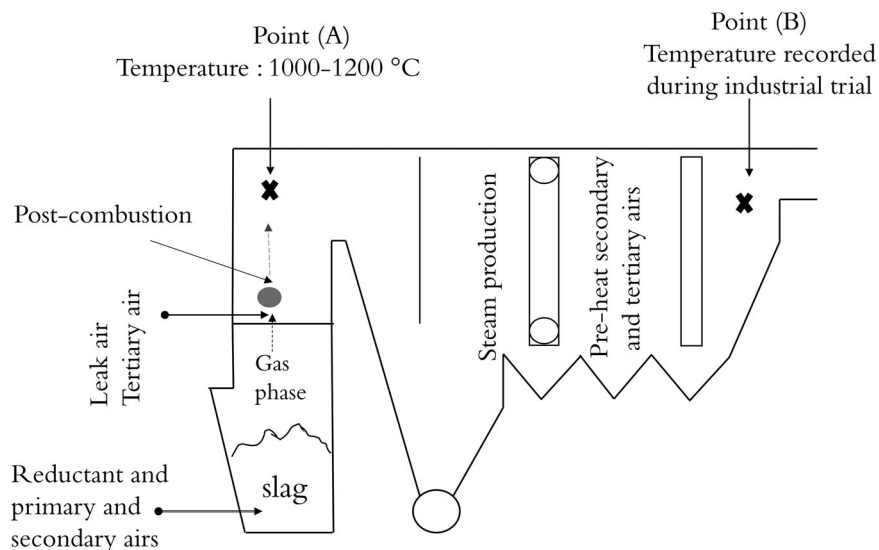
between 1000°C and 1200°C. However, during the industrial trial the temperature at point (A) was not measured. At Point (B), the temperature was recorded during industrial trials, which indicates the temperature of the gas immediately before entering the cooling tower.

### Materials and description of the industrial trials

Three plastic-containing materials, polyethylene (PE), polyurethane (PUR) and SRM, were selected for the industrial trials. The average particle size of the plastic materials was 7 mm, and the coal was pulverised to 38  $\mu\text{m}$ . Table 1 shows the ultimate and proximate analysis of the materials used in trials.

### Description of slag

Chemical analysis of the slag samples was performed by the central laboratory of the Rönnskär smelter, using X-ray emission spectroscopy. The initial composition of the slag for selected trials is reported in Table 2.



**Figure 2.** Schematic of different parts of the fuming process, including the fuming furnace and the boiler.

**Table 1.** Ultimate and proximate analysis of the coal and plastic materials.

Ultimate analysis					
	H (wt-%)	O (wt-%)	N (wt-%)	S (wt-%)	C (wt-%)
Coal	4.8	5.2	1.3	0.30	84.0
SRM	6.1	12.9	1.4	0.12	57.3
PE	11.6	1.6	-	0.06	78.5
PUR	6.2	15.3	6.0	0.03	61.7
Proximate analysis					
	Moisture (wt-%)	Volatile (wt-%)	Fixed carbon (wt-%)	Ash (wt-%)	
Coal	0.8	26.5	68.3	4.4	
SRM	8.0	67.3	2.6	22.1	
PE	0.3	89.1	2.3	8.3	
PUR	1.6	80.8	7.1	10.5	

### Description of the industrial trial conditions

The conditions during the plant trials are presented in Table 3, a detailed description of the operation condition during industrial trials is provided elsewhere [3]. Figure 3 shows the flow sheet of the process, including the temperature and pressure of the gas phase. The data collected from the plant trial includes the slag composition and steam production collected at 10-min intervals after all the slag has been charged to the fuming furnace.

### Thermodynamic calculation

FactSage 7.1 [13] was used for thermodynamic calculations using the data from the industrial trials. The first step was to formulate the thermodynamic calculation steps for the trials with only coal injection. Elements such as Cr, Cu, As and S are excluded from the calculation due to their low concentration.  $\text{Al}_2\text{O}_3$ , CaO, FeO,  $\text{Fe}_3\text{O}_4$ , MgO, PbO,  $\text{SiO}_2$  and ZnO are used as the inputs for the thermodynamic calculations. The gas phase is assumed to be ideal and is taken from Fact PS. All possible pure solids and pure liquids from Fact PS and Fact Oxides are selected. The solutions were

selected from the FT-Oxide database, A-Spinel, A-Monoxide and A-Olivine. The following assumptions were made:

- The slag bath is assumed to be well stirred and therefore can be considered uniform in temperature and composition.
- The composition of the slag is not normalised, as normalisation of the slag would lead to a wrong estimation of the Zn content in the slag bath.
- Based on the analysis of the slag, 4 wt-% of the total Fe is calculated as  $\text{Fe}_3\text{O}_4$ , and the rest is assumed to be FeO.
- The whole slag charge participates in the reaction (the effect of slag frozen on the wall is neglected).
- The reducing agents, both the coal and plastic materials, consist of C, H and O based on the ultimate analysis. The ash, S and N contents are neglected.
- The temperature of the slag bath, and thus the final temperature in the calculation, is assumed to be 1250°C and constant during the batch.
- During trials with co-injection of coal and plastic materials, it is assumed that there is no interaction between coal and plastic materials.
- These calculations only consider the equilibrium in the process, and the kinetic parameters are not considered.

Data during trial was collected every 10 min; thus the calculations were performed for the interval of 10 min. The calculation method is shown in Figure 4. In the initial step of the calculation, air and reductant amount injected in 10 min and initial slag composition are used as input. The calculation results in a slag phase (slag-1) and a gas phase (gas-1). The resulting slag composition (slag-1) is used as the input for the next calculation step (next 10 min). The gas phase from each calculation step is used as the input for the post-combustion with the

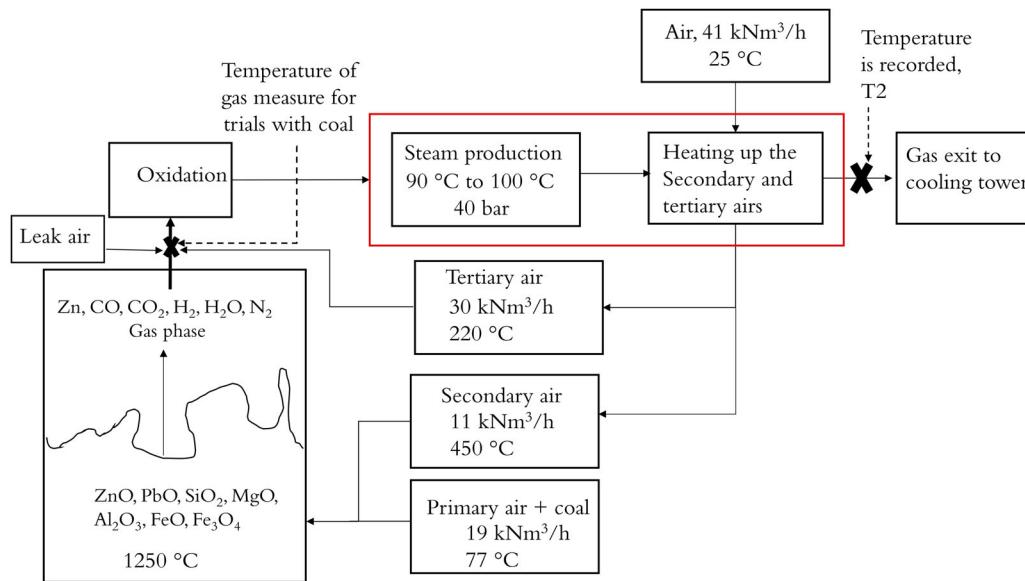
**Table 2.** Initial composition of slag used during trials, note that the slag is not analysed for all possible elements, and oxygen in the form of metal oxides is not accounted for, and thus the balance is not 100%, wt-%.

	$\text{Al}_2\text{O}_3$	As	CaO	Cr	Cu	Fe, total	MgO	Pb	S	$\text{SiO}_2$	Sn	Zn
Coal	3.4	0.2	2.0	0.2	1.4	30.0	0.8	1.2	0.8	30.0	0.3	8.9
Coal + PE	3.6	0.2	2.2	0.2	1.9	33.6	1.0	1.1	1.0	30.1	0.2	8.3
Coal + PUR	3.1	0.2	1.8	0.2	1.5	30.5	0.8	1.7	0.8	29.3	0.4	9.2
Coal + SRM	3.9	0.2	2.3	0.1	1.2	33.2	0.9	1.4	0.8	30.9	0.4	8.0

**Table 3.** Operational conditions during industrial trials.

	Primary air, $\text{kNm}^3 \text{h}^{-1}$	Secondary air, $\text{kNm}^3 \text{h}^{-1}$	Tertiary air, $\text{kNm}^3 \text{h}^{-1}$	Coal, $\text{tons h}^{-1}$	Plastic, ton per batch	Slag, ton per batch	Time per batch, h
Coal	19	11.5	30	6.3	–	97	2:00
Coal + PE	19	10	30	5.6	1.3	92	2:00
Coal + PUR	19	10.5	30	5.6	3	94	2:00
Coal + SRM	19	10.5	30	5.6	1	88	2:00





**Figure 3.** The simplified flow sheet describing the process, the inputs to the process (air and coal), and the schematic of post-combustion with tertiary and leak air.

tertiary air (Figure 4). The resulting gas phase from post-combustion with tertiary air will lose its heat when producing steam and pre-heating the tertiary and secondary air. During this industrial trial, the temperature of gas after post-combustion is not measured. Based on measurement from previous trials, it is assumed that the temperature of the gas after post-combustion with the tertiary air during the trials with coal injection remains constant at 1150°C. Further, the temperature of the gas before it leaves to the cooling tower was recorded during the industrial trials. Thus it is possible to calculate the heat that the gas will produce as a result of cooling. This heat should correspond to the heat required to pre-heat the airs and produce steam. However, the connection between the furnace and the shaft is not sealed at this point; therefore, an unknown amount of air is also introduced to furnace, which is called leak air. The first step was to estimate the amount of leak air, by comparing the heats from the thermodynamic calculation and the experimental data. The amount of leak air estimated will further be used to back calculate the rise in temperature of the gas phase after post-combustion for trials with co-injection of coal and plastic materials.

## Results and discussion

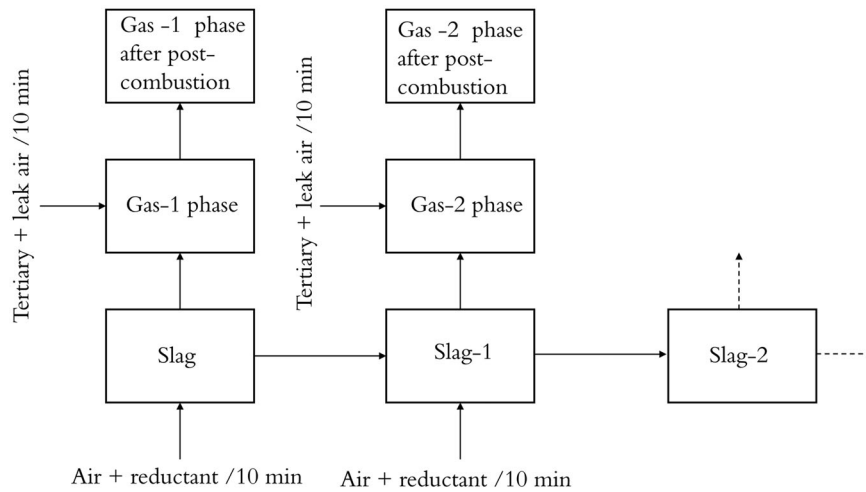
### Comparison of zinc reduction from the industrial trial with coal injection and the result of the thermodynamic calculations

During the industrial trial, 12 batches were conducted with only coal injection, which are used as reference

batches. The thermodynamic calculation was performed for several batches. Figure 5 shows the experimental measurement of the zinc content in the slag and the corresponding thermodynamic calculation values for the trial with only coal injection for a selected batch. Figure 5 compares the calculated zinc fuming rate with different amount of coal is reacting within the slag bath. The thermodynamic calculation assuming the complete utilisation of coal (100 wt-%) shows a 0.5–1.5 percentage point difference to the experimental result. To reach the same zinc concentration level as experimentally measured one, the amount of coal used in the calculation has to be reduced compared to the amount of coal injected to the furnace during industrial trials. The result shows that for the case that thermodynamic calculation was performed with 85 wt-% of the injected coal, the result of calculation is similar to the zinc concentration measured during the industrial trials. Other batches show that the coal utilisation must be at 80–90 wt-%, giving an average value of 85 wt-%. To simplify the following calculations, it is assumed that 85 wt-% of the coal participates in the reactions. In other words, based on the calculations, it is assumed that the utilisation of coal in the process is 85%.

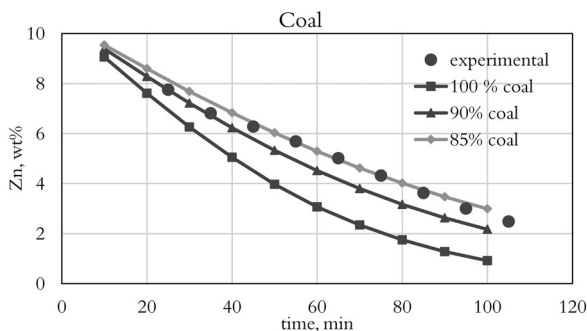
### Determining the extent of leak air

Figure 5 shows that 15 wt-% of coal does not react within the slag bath and goes directly to the post-combustion with the tertiary air. Thus, in addition to the gas phase from the calculation, 15 wt-% of the coal is used for post-combustion with tertiary air. To estimate the leak



**Figure 4.** The stepwise calculation, primary, secondary air and coal are added at a rate of mole per 10 min, the slag phase goes to the next calculation, while the gas phase goes to the post-combustion with the tertiary and leak air.

air, various amounts of air were added to the calculation. The heat is calculated by cooling down the gas phase from 1150°C to 370°C. The heat required to produce steam and pre-heat the air calculated that was from industrial trial is compared to the heat released from cooling down of the gas with various amounts of leak air. The amount that matches the required heat is selected. The steam production during the plant trials with only coal injection remains at a constant level of 30 ton h<sup>-1</sup> during the batch; thus only one step of calculation is presented. Both the heat required to produce steam and pre-heat the secondary and tertiary air and the calculated heat are presented in Table 4. The results show that when the leak air is 10 kNm<sup>3</sup> h<sup>-1</sup>, the energy is matched. However, there are sources of heat loss in the system that are not measured, which means the efficiency of the system is not 100%. Thus a certain unaccounted heat loss should be considered. Further, the value is



**Figure 5.** Comparison of the results of zinc concentration in the slag bath from the thermodynamic calculation with the experimental results from the industrial trial. The calculation has been done at 1250°C, in the calculations different percentage of coal is used, e.g. 100% coal means, 100% of coal injected during industrial trial is used for the calculation.

selected to be representative of several batches. Therefore, an estimation of 20 kNm<sup>3</sup> h<sup>-1</sup> is more realistic as it matches the heat in several batches. That is, approximately 2 GJ heat is assumed to represent the heat loss in the system.

#### *Comparison of the zinc reduction from the industrial trial with co-injection of plastic materials and the result of the thermodynamic calculations*

The thermodynamic calculation was performed, for trials with co-injection of plastic materials and coal, where 85 wt-% of the coal reacting within the slag bath was kept constant, and the amount of plastic that reacted was varied. This is based on the assumption that co-injection of plastic materials does not change the extent of coal participation during the batch. The final temperature for the calculation was 1250°C, the same as the calculations with only coal injection. Figure 6 shows the comparison of the experimentally measured and calculated zinc contents in the slag bath for the trials with injection of plastic-containing materials. The result for the trial with PUR injection (Figure 6a) shows that the calculation with 85 wt-% of the coal and 100 wt-% of the PUR reacting within slag shows up to 1 percentage point difference to the experimental result in Zn wt-% within the slag bath. To describe the experimental results, the amount of PUR must decrease to 60 wt-% in the calculation, which means that 60 wt-% of the PUR participates in the reactions in the bath.

Figure 6(b) indicates that the calculated zinc content for the trials with injection of PE shows up to a 2 percentage point difference with the measured Zn content of the bath. To describe the experimental data, the PE must be

**Table 4.** The calculated heat required for steam production and heating up the tertiary and secondary air for a trial, and the calculated heat produced from cooling down the calculated gas after post-combustion with the tertiary and leak air, from 1150°C to the cooling tower temperature (370°C).

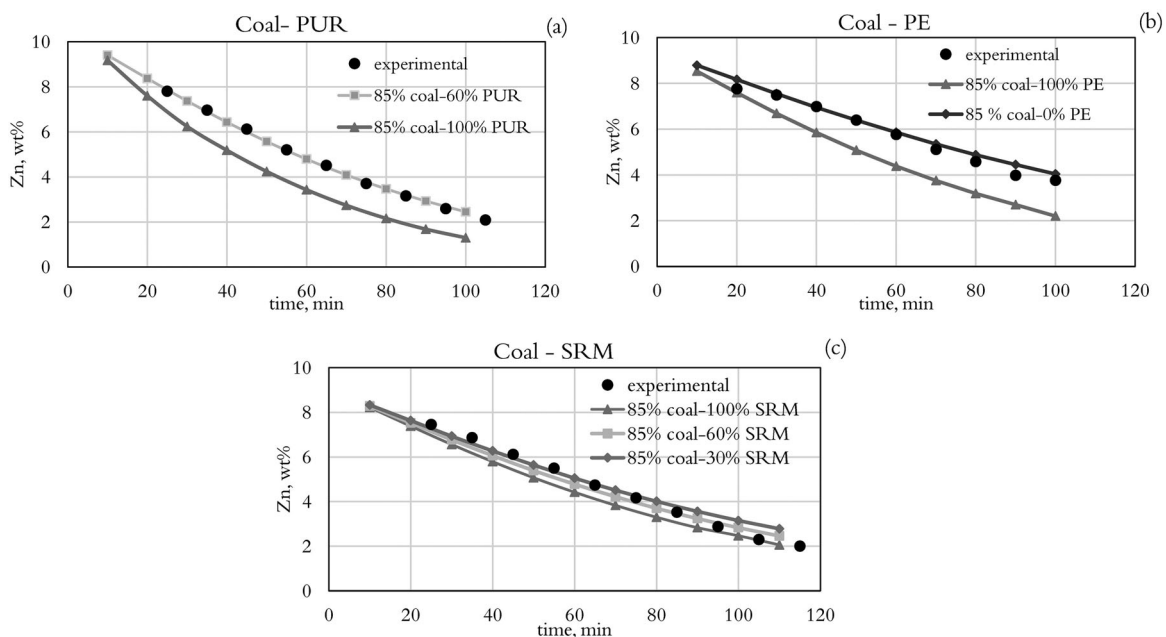
Measured during trial		Calculated based on measured data – Coal			Calculated heat by addition of various leak air, $\text{kNm}^3 \text{h}^{-1}$		
Final temperature of gas °C	Steam $\text{kg min}^{-1}$	Steam production GJ	Pre-heat airs GJ	Sum of heat for steam and pre-heat air GJ	10 GJ	20 GJ	30 GJ
370	460	13.4	2.04	15.4	16.0	17.7	19.7

reduced to 0 wt-%, which indicates that the PE probably does not participate in the reaction within the slag bath. Figure 6(c) shows that in the trials with injection of SRM, less difference is observed between the calculated and experimental Zn contents, when 100 wt-% of the SRM is used for the calculation. Reducing the SRM reacting in the bath to 30 wt-% up to 60 min gives a better agreement with the experimental results, while after 60 min, the calculation with 60 wt-% of the SRM shows a better agreement. The results from the other batches also show that at different times during the batch, different amounts of the SRM being added give a better agreement with the experimental results. For the following calculations, it was assumed that 60 wt-% of the SRM is needed to describe the experimental data.

#### Comparison of the calculated energy that is released from the off-gas with the experimental data

The gas phase from the calculation and the unreacted materials (plastic and coal) goes to the post-combustion

with the tertiary and leak air ( $20 \text{ kNm}^3 \text{h}^{-1}$ ). The plastic material was injected in a periodic manner; thus the steam production during the trials with co-injection of plastic and coal shows a periodic behaviour. To simplify the calculation, the average value for a time step (10 min) was calculated assuming that this value stays constant during the trial. The calculated heat values from cooling down the gas are reported in Table 5. The heat required to produce steam and pre-heat the air was calculated from the experimental data. Furthermore, the amount of lost heat (2 GJ) must be added to attain the total energy that should be released by cooling down the gas phase. The summation of all heat that is required is reported as the total heat required (Table 5) and compared to calculated heat produced by cooling down the gas phase. The result indicates that the heat produced by cooling down the gas from 1150°C is insufficient to both produce steam and pre-heat the airs. The calculation shows that for the gas to release the required energy, a temperature of 1350°C is required for trials with PUR injection, and 1300°C for trials with PE and



**Figure 6.** Comparison of the results of the calculation at 1250°C with the results of the experimental measurement of the Zn content of the bath, for the trials with injection of coal (a) PUR, (b) PE, (c) SRM. In all calculations, 85% of coal injected is used and different percentage of plastic materials added. For example, 85% coal – 100% PE shows the calculation where all PE injected during industrial trial is assumed to participate in equilibrium.



**Table 5.** The amount of heat required for steam production and pre-heating the air for trial with co-injection of PE, PUR and SRM with coal, calculated for the third step (after 30 min), and the calculated heat produced from the cooling down of the gas from various temperatures.

Calculated based on measured data – Coal + PE						Calculated heat produced by the cooling down gas from various temperatures (°C)			
Measured during trial		Heat required							
Final temperature of gas °C	Steam kg min <sup>-1</sup>	Steam production GJ	Pre-heat air GJ	Lost heat GJ	Total heat GJ	1150 GJ	1250 GJ	1300 GJ	
370	571	16.6	2.0	2.0	20.6	17.3	19.7	20.8	
Calculated based on measured data - Coal + PUR						Calculated heat produced by cooling down gas from different temperatures (°C)			
Measured during trial		Heat required							
Final temperature of gas °C	Steam kg min <sup>-1</sup>	Steam production GJ	Pre-heat air GJ	Lost heat GJ	Total heat GJ	1150 GJ	1250 GJ	1300 GJ	1350 GJ
400	624	18.1	2.0	2.0	22.1	17.2	19.6	20.8	22.0
Calculated based on measured data- Coal+ SRM						Calculated heat produced by cooling down gas from different temperatures (°C)			
Measured during trial		Heat required							
Final temperature of gas °C	Steam kg min <sup>-1</sup>	Steam production GJ	Pre-heat air GJ	Lost heat GJ	Total heat GJ	1150 GJ	1250 GJ	1300 GJ	
400	480	13.9	2.0	2.0	17.9	14.8	16.9	18.0	

SRM injection. This means that the gas phase will have a higher temperature after post-combustion during trials with plastic materials. The result agrees with the fact that some portion of the plastic material does not react in the slag bath and leads to high energy generated during post-combustion, which increases the temperature of the gas after post-combustion.

### Parameters influencing utilisation of SRM in the process

Among the studied plastic materials, the most interesting material to use as a possible reducing agent is SRM, since currently there is not an attractive alternative way to utilise this material. Thus it is desirable to increase the substitution of coal by SRM in fuming processes. In this section, a simple mass balance, based on an industrial trial and thermodynamic calculations is presented, to calculate the amount of SRM required to totally substitute coal during the fuming process. Additionally, the thermodynamic calculation is used to estimate the probable changes in the process. The following assumptions were made:

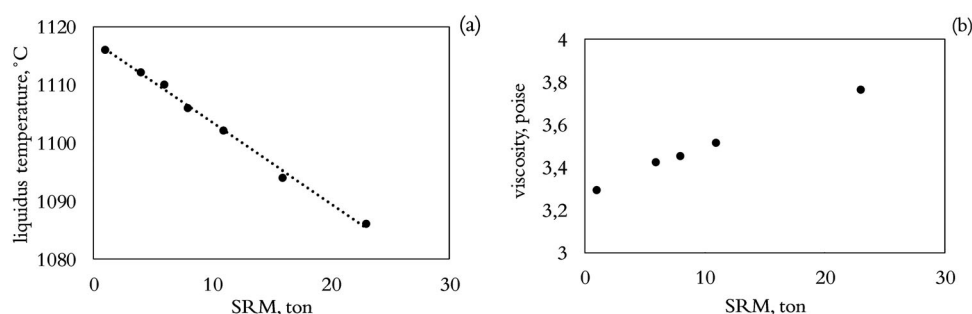
1. The zinc reduction rate remains approximately the same: meaning the amount of C used in the calculation remains the same. (To calculate the corresponding amount of SRM to coal, the C content has been used. As a result, a slightly higher amount of hydrogen will be used.)
2. The utilisation efficiency of SRM would remain the same; 60 wt-% of the injected material will participate in the reactions in the slag bath and 40 wt-% goes to the post-combustion.

The total amount of C used during the industrial trial with coal and SRM is used to calculate the amount of SRM needed to fully substitute the coal. Thus the total C that is required is calculated based on the summation of C coming from 11.2 tons of coal with 85% utilisation and 1 ton of SRM with 60 wt-% utilisation. The result shows that approximately 23 tons of SRM is needed to fully substitute coal. A thermodynamic calculation was performed with 23 tons of SRM. The gas phase produced from the calculation goes for post-combustion, in addition to 40 wt-% of the SRM. It is assumed that the temperature of the gas after post-combustion with the tertiary air is 1300°C, which was estimated for the trial (Table 5). The heat generated by cooling down the resulting gas phase from 1300°C to 370°C is calculated. Subtracting this value by the heat required to pre-heat the air and lost heat will give the heat available to produce steam. The result estimates that 636 kg min<sup>-1</sup> of steam is generated by utilising 23 tons of SRM, in the absence of coal. Since the amount of C used for the calculation is the same as the trial with coal and SRM, the calculated steam generation is similar to the steam generated in the trial. The difference is probably due to additional H coming from the SRM, which contains more H compared to coal. This result is based on the assumption that by increasing the amount of SRM from 1 ton to 23 tons, the extent of participation in the reactions in the slag and post-combustion with the tertiary air does not change, which is an extensive extrapolation.

Two other cases were calculated with 6 and 11 tons of SRM. These values were selected to represent cases between the industrial trial (1 ton of SRM) and the calculated case with only SRM (23 tons). It is possible to calculate the amount of coal needed to keep the total

**Table 6.** The chemical composition of SRM ash.

Element in ash	Ca	Si	Cu	Al	Mg	Ti	Cr	Fe	Zn	Na
Wt-%	12.9	12.6	11.5	11.0	2.6	2.3	0.6	0.4	0.3	0.1
Other elements detected in ash in ppm level	Pb, Mo, Se, V, Co, Cd, As, Be, Sb, Ni, Mn									

**Figure 7.** The calculated changes in (a) the viscosity and (b) liquidus temperature of the slag at the final stage during fuming due to the addition of SRM.

amount carbon the same. The assumptions that are made are similar to those in the previous calculation, with the addition that the utilisation efficiency of coal remains the same and 85 wt-% of the injected material participates in the reactions in the slag bath. The result indicates that by increasing the SRM to 6 and 11 tons, it is possible to reduce the coal injection rate to 4.5 and 3.3 ton h<sup>-1</sup>, respectively.

Another possible change in the process due to the addition of SRM is a change in the composition of the final slag due to the accumulation of SRM ash. Table 6 shows the elemental composition of the ash content in SRM. As SRM is injected alongside air, it is assumed that the elements in the ash will form corresponding oxides.

SRM is gradually added to the process, and at the end of the process, a considerable amount of ash is accumulated in the slag. The change in the composition of the final slag might affect the viscosity of the slag and the liquidus temperature. To estimate the change in viscosity, the viscosity module in FactSage 7.1 is used. Only elements with wt-% higher than 1 in the ash, are considered. It is assumed that the slag temperature remains constant at 1250°C. The final composition of the slag is extracted from the last step of the calculation, which includes both the addition of ash coming from SRM and the change in the amounts of ZnO and PbO due to reduction. Figure 7(a) shows that the viscosity of the slag increases as the amount of SRM increases. The Equilib module of FactSage 7.1 has been used to determine the liquidus temperature of the slag with the addition of various amounts of SRM (Figure 7b). It can be observed that as the SRM addition changes from 1 ton to 23 tons, the liquidus temperature of the slag decreases by 40°C. The decrease of the liquidus temperature and the increase of the viscosity could be related to

the addition of Al<sub>2</sub>O<sub>3</sub> to the slag, as Mostaghel et al. [14,15] reported in their study of the effect of the addition of Al<sub>2</sub>O<sub>3</sub> to slag after the fuming process in the Boliden-Rönnskär smelter. Additionally, the increase of the SiO<sub>2</sub>/Fe ratio could lead to a decrease of the liquidus temperature, as was stated by Hayes et al. [9]. The viscosity and liquidus temperature of the slag during final step are important for tapping out the slag. A change of the viscosity of the slag affects the foaming of the slag, which is an important parameter in controlling the process [16].

### Concluding remarks towards application

In their study of the zinc fuming furnace, Richards et al. [11] developed a mathematical model using a plant data analysis. Results of their model showed that the coal injected in the furnace can react in one of the three ways: first, 55 wt-% combusts in the tuyere gas column; second, 33 wt-% of the total injected coal entrains in the slag; and third, 12 wt-% bypasses the bath completely. The coal particles that are entrained in the slag undergo devolatilisation, producing a bubble around the particle. The bubble further ascends in the slag bath, and the remaining fixed carbon reacts with the CO<sub>2</sub> and produces reducing CO gas. The finding of this study shows that 15 wt-% of the injected coal does not participate in the reactions within the bath, which agrees with the findings of other researchers. The calculation with the current assumptions shows that participation of PE in reactions in the slag bath was less than PUR and SRM. This result is based on current assumption, such as no interaction between coal and plastic materials. In reality, it is possible that by co-injection of coal and plastic materials, the extent of coal

interaction would change and part of PE participates in reactions within slag bath.

Similarly, plastic materials can be divided into three fractions during the process: the fraction that will combust, the fraction that entrains in slag and, finally, the part that will bypass the process. The extent of each fraction can be correlated with the thermal characterisation of the plastic materials. A previous study showed that PE devolatilised rapidly, while the devolatilisation of PUR and SRM was slower [17]. In addition, PE is mainly decomposed as volatiles, which most likely react rapidly in front of the tuyere. This could be the reason that PE does not participate in reactions within the bath, according to the calculations. Notably, the combustion of volatiles will lead to the release of heat, which could increase the temperature of the slag bath. In this study, the calculation was performed at the same temperature as that in the trials with only coal injection. Calculations at different temperatures could lead to different results. The temperature of the slag bath during the trials with the injection of plastic materials was not measured. Further, the descriptions of the coal and plastic materials are simplified in the calculations performed in this study. Plastic material mainly decomposes by releasing volatiles, and the actual composition of the released volatiles will affect the kinetics of the reactions. These facts cannot be modelled using thermodynamics calculation. Although PUR and PE have similar ultimate analyses, the PUR proximate analysis shows fewer volatiles compared to PE, and it also produces char. PUR is known to have a longer reaction time than that of PE. Thus it is more possible that a higher fraction of PUR would penetrate into the slag. In addition, PUR is agglomerated in an extruded form, and cylinder particles could break at different lengths during the injection. Therefore, the reaction time of particles with different sizes will be different. Additionally, PUR requires more time to devolatilise; thus the calculation shows that 60 wt-% of PUR will react within the slag bath. SRM is an inhomogeneous material that consist of different types of plastics. Therefore, the combustion characteristic of these materials is different. While a fraction can react rapidly, similar to PE, another fraction can have a longer combustion time and penetrate into the slag. This result shows the importance of experimental trials, which can be combined with thermodynamic calculations to gain a further understanding of the reaction mechanisms.

## Conclusion

Thermodynamic calculations have been used in addition to plant trials at the Boliden–Rönnskär smelter; with the aim of understanding the potential of plastic materials to

substitute coal in bath smelting processes. In this study, thermodynamic calculations are used to estimate the extent that coal and plastic materials will participate in reactions within the slag bath.

- A thermodynamic calculation was first performed for trials with only coal injection; the result showed that 15 wt-% of the coal does not participate in the reactions within the slag bath.
- Thermodynamic calculation for the trials with the co-injection of plastic materials with coal showed that plastic materials contributed to reactions in the slag bath with various extent. The calculations with current assumptions show that PE has the lower level of contribution compared to PUR and SRM.
- Thermodynamic calculation shows that although plastic materials can have a similar ultimate analysis, the extent that they contribute to reactions in the slag bath also depends on the proximate analysis.
- The addition of SRM is restricted by parameters, such as steam generation and the change of the viscosity of the slag.

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No potential conflict of interest was reported by the authors.

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