Exergy based efficiency analysis of pyrometallurgical processes

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Abstract

Exergy based efficiency analysis provides a powerful tool for optimizing industrial processes. In this paper, the use of this technique for pyrometallurgical applications is explored in four steps. First, the exergy concept is introduced, the outline of exergy calculations is presented and the role of a reference state is discussed. Second, it is shown that an unambiguous exergy calculation for pyrometallurgical streams with a complex, unknown phase composition is not straightforward. Hence, a practical methodology is proposed in which a suitable phase-based stream description is estimated prior to the actual exergy calculation. For this, the equilibrium phase composition is calculated while all known stream properties are incorporated as boundary conditions. Thirdly, the proposed methodology is validated by recalculating literature results. This reveals significant deviations for exergy values of the same pyrometallurgical streams. Our results are probably more accurate due to the incorporation of additional phase related information. And fourthly, a full analysis of a zinc recycling process is presented. In a base case scenario, the total exergetic efficiency turns out to be only 1.2%. Based on this result, different process modifications are suggested and quantitatively evaluated. We find that significant efficiency gains are possible.

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1 Introduction

Pyrometallurgical processes consume natural resources and emit waste products on a large scale. However, these resources are not inexhaustible and the ecosystem's capacity to absorb waste streams is limited^[1,2]. Faced with major challenges such as peak oil and climate change, people become increasingly aware of the need for more sustainable industrial development. Reducing the ecological footprint of the pyrometallurgical industry is therefore a key challenge^[3]. Recent research confirms that, under the right socio-economic conditions, efficiency optimization of industrial processes can be an important step towards increased industrial sustainability^[4].

Figure 1: Calculation of the efficiency ratio of a process from its process streams

In general the efficiency η of a process corresponds to the ratio of the total amount of useful production over the total amount of input this production requires. This is depicted in Figure 1. However, a quantitative determination of this efficiency ratio is not straightforward for pyrometallurgical processes. Since these processes often handle both mass and energy streams, they are described with separate mass and energy balances. However, these descriptions don't allow an unambiguous determination of a relevant process efficiency for two reasons. First there is a dimensional problem. Since mass streams and energy streams are expressed in different units (kg vs. J), the calculation of a single process efficiency is not possible. A second reason is that these balances are solely based on the laws of mass and energy conservation. The second law of thermodynamics, which imposes a theoretical upper limit on the efficiency of a process, is ignored. However, this law has important practical, economical and ecological implications that have been discussed in detail by Ayres^[5].

A process description based on the thermodynamic quantity 'exergy' is more suited for process efficiency analysis. Basically, the exergy content of a process stream describes to what extent the stream can be used to drive the process, taking into account thermodynamic limitations as imposed by both the first and second law. In addition, using an exergetic approach solves the dimensional problem, since exergy can be calculated and expressed in joules (J) for energy

streams as well as for mass streams. In this way it is possible to determine a single, relevant exergetic efficiency ratio that can be used for consistent process comparisons.

Although the thermodynamic concepts behind exergy were already developed by Carnot and Gibbs in the 19th century, only in the last decades this concept has been adopted on a larger scale for process analysis. This was promoted by the work of Kotas^[6] and Szargut, Stewart and Morris^[7-9] in the 1980's. Since then, along with the increasing attention for sustainable development, a rapidly growing number of successful exergy analyses have been reported. These are mainly situated in the fields of ecology, thermomechanics and (bio-)chemistry, ranging from a detailed level, for efficiency optimization of individual processes, to a larger scale, for evaluations of integral flowcharts. An extensive overview is published by Dewulf et al.^[10]. In the last decade, exergy analysis is also finding more entrance as a tool to evaluate the efficiency of pyrometallurgical processes. Most of the relevant publications here are dealing with iron- and steelmaking applications. Akayima and Yagi^[11] and Shigaki et al.^[12] made a rather theoretical analysis on the thermodynamic boundaries of traditional ironmaking in general. Costa et al.^[13] compared the exergetic efficiency of different steel production systems in a more practical way. Nogame et al.^[14] and Ziebig and Stanek^[15,16] focussed in particular on blast furnaces. Finally, the exergetic performance of ladle furnaces during steelmaking has been analysed by Camdali and Tunc^[17,18] and by Mapelli and Baragiola^[19]. The number of studies regarding non-ferrous applications is much smaller. To our knowledge, in the last decade, only Ayres and co-workers published exergy analyses on traditional high temperature non-ferrous processes^[20,21].

As far as can be derived from the publications, these studies all use a similar calculation methodology to determine the exergy content of process streams. In practice, they directly apply the same routines that are traditionally used for exergy calculations on a wide variety of non-metallurgical process streams with simple compositions. However, in this way the presence of multiple phases and possible non-equilibrium conditions is often ignored. Therefore the methodology needs some modifications before it can be used for exergy calculations on pyrometallurgical streams that typically have a complex composition. Only in the work of Reuter and co-workers on recyclability of metals^[22-24] we find an adapted approach for exergy calculations on metallurgical streams, although this is not indicated explicitly. They focus on the separation and contamination of metals during recycling processes and do not consider any high temperature steps in detail. However, their results are relevant because they include exergy calculations for typical metallurgical streams like aluminum metal with impurities.

In the present article, the use of exergy based process efficiency analysis is extended towards pyrometallurgical applications in a more systematic way. This results in a calculation methodology

that accounts for the particular compositional properties of high temperature streams.

In section 2, first the general outline of an exergy calculation for energy and mass streams is presented. Subsequently, the important choice for an adequate reference state is discussed. In section 3, a practical methodology, optimized for pyrometallurgical exergy calculations, is proposed. Further on, an implementation is presented, based on the thermodynamic calculation software FACTSAGE. In section 4, exergy results obtained with this methodology are compared with literature data. In section 5, the results of a case study on the exergetic efficiency analysis of a zinc recycling process are presented. Section 6 summarizes the results and concludes the paper.

2 Exergy calculation

By definition, the exergy B of a stream is the maximum amount of thermodynamic work that this stream can perform when it evolves towards thermodynamic equilibrium with its reference environment by interacting with this environment only ^[25]. As a consequence of the second law of thermodynamics, this maximum work can only be generated by an ideal reversible process. The efficiency of a reversible process thus represents an upper limit on the efficiency of real processes. In terms of exergy, this efficiency is expressed as

$$\eta_B = \frac{B_{products}}{B_{input}} \quad (1)$$

and equals 100% in case of an ideal reversible process. However, the energetic efficiency of this process, expressed as

$$\eta_E = \frac{E_{products}}{E_{input}} = 1 - \frac{E_{waste}}{E_{input}} \quad (2)$$

can be less than 100%. A prime example is an ideal Carnot process operating between a heat reservoir at high temperature and the environment. The process extracts thermal energy from the high temperature reservoir (an input stream) and converts it into work (a product stream). However, as dictated by the second law of thermodynamics, only a fraction of the thermal energy supplied by the high temperature reservoir can be converted into work. The remaining energy is lost towards the surrounding in the form of waste heat at environmental temperature. This waste stream is not used to drive the process. Hence, according to equation 2, the energetic efficiency of a Carnot process will be below 100% although it operates in a reversible way. On the other hand, the exergetic process efficiency does equal 100% because, due to the reversibility of the process, the generated work equals the exergy flow in the high temperature heat stream. In addition, the waste heat contains no exergy because it is in equilibrium with the environment. Finally it should be remarked that exergy is only conserved by reversible processes. In real, non-reversible

processes, an amount of exergy ΔB is destroyed. These irreversibilities can be calculated according to the relation of Gouy-Stodola^[26]:

$$\Delta B = T_0 \Delta S \quad (3)$$

where ΔS is the total amount of entropy generated in the system and the environment due to the irreversibilities in the process.

2.1 Exergy content of energy streams

Reconsider the ideal Carnot process operating between a high temperature heat reservoir and a reference environment. The work generated in this reversible process equals the exergy content of the high temperature heat stream. Therefore, the exergy content of a thermal energy stream can be calculated through the use of the Carnot efficiency η_c :

$$\begin{aligned} B_{thermal} &= E_{thermal} \cdot \eta_c \\ &= E_{thermal} \cdot \frac{T - T_0}{T} \end{aligned} \quad (4)$$

For most other energy streams in pyrometallurgical applications the exergy content equals the energy content. An integral transformation of e.g. electrical or mechanical energy streams into useful work without any emission streams is possible in theory.

2.2 Exergy content of mass streams

Analogous to a thermal energy stream that derives exergy from a temperature difference compared to the environment, a mass stream derives exergy from a deviant composition, pressure or temperature. The exergy in a mass stream can be calculated in three steps as the work that is required to separate this stream from its reference environment using reversible processes. Due to the reversible character of these processes, it is exactly the same amount of work that can be exerted by the stream during the evolution toward equilibrium with the environment. Figure 2 illustrates these steps.

Figure 2: The different steps during an exergy calculation for a mass stream

1. The first step involves extracting all chemical elements in the stream from the reference environment in their standard state at environmental pressure p_0 and temperature T_0 . The corresponding elementary exergy B_{el} in the stream is calculated from the elementary composition n_k of the stream and the standard molar exergy b_k^{ref} of the corresponding elements k :

$$B_{el} = \sum_k n_k b_k^{ref} \quad (5)$$

The standard molar exergy b_k^{ref} is the exergy of one mole of a pure chemical element in its standard state. This standard state is the most stable appearance of the pure element at T_0 and p_0 . For example, b_C^{ref} equals the exergy of a mole of pure graphite (carbon), b_{Fe}^{ref} is the exergy of a mole ferrite (iron) and b_O^{ref} is the exergy of half a mole of gaseous O_2 . These values, which are dependent on the reference environment, are tabulated in literature^[8,27-29]. The choice of the environment will be discussed in the next paragraph.

2. In the second step, still at reference conditions (p_0 , T_0), the different phases i in the stream are formed. The formation energy $\Delta G_{f,i}$ equals the work that is generated/required in this step and indicates the exergy difference between the stream of individual elements and the actual stream at reference conditions. At this point, the exergy is solely derived from chemical phenomena and is often referred to as the chemical exergy of the stream:

$$B_{ch} = \sum_i \Delta G_{f,i} + B_{el} \quad (6)$$

Notice here that the phases in a stream are not necessarily stable at reference conditions. This is e.g. the case for a stream of steam. Since the stable state of water at reference conditions is the liquid state, and not the vapor phase, the formation energy ΔG_f for water vapor needs to be extrapolated for T_0, p_0 conditions.

3. In the final step, physical phenomena are also taken into account by calculating the work required to change the temperature and pressure of the stream from reference conditions to the actual stream conditions. This work involves a change in enthalpy and entropy and equals the physical exergy of the stream, as is outlined by Moran and Sciubba^[30]:

$$B_{ph} = (H - H_0) - T_0(S - S_0) \quad (7)$$

In summary, the total exergy of the stream can be calculated as:

$$B = \sum_k n_k b_k^{ref} + \sum_i \Delta G_{f,i} + (H - H_0) - T_0(S - S_0) \quad (8)$$

2.3 The reference state

The choice for a reference environment will influence the result of an exergy calculation through the b_k^{ref} , H_0 and S_0 terms. Scientific agreement exists about the physical properties of such a reference environment: a temperature of 298.15 K (25 °C) and a pressure of 1 atm. The definition of a chemical composition for the reference environment is less straightforward. Since the exergy in a stream depends on its non-equilibrium with the environment, this environment itself needs to be in a thermodynamic equilibrium. On the other hand, to make exergy values relevant for industrial efficiency and sustainability evaluations, the properties of the reference environment need to match the conditions in the earth's ecosystem as close as possible. This ecosystem however is pre-eminently not in equilibrium. Several methods have been suggested to overcome this contradiction^[31]. In this work, the reference compound method is adopted. The method was first suggested by Szargut and has gained general acceptance for exergy analysis of industrial processes^[8].

In the reference compound method, for each chemical element a compound is selected based on two conditions. First, the compound must represent a prevalent form in which the element is represented in the ecosystem, i.e. in the lithosphere, hydrosphere or atmosphere. Second, the compound must have a high thermodynamic stability. However, since prevalent compounds typically are the most probable products of the interaction between the chemical element and the

environment, they often have a high thermodynamic stability. Hence, for most elements the selection of a reference compound is rather straightforward. E.g. the reference compound of oxygen is O_2 (from the atmosphere), for silicon it is SiO_2 (lithosphere) and for sodium it is Na^+ (hydrosphere). Also, for each compound, a standard concentration is assigned. This is the concentration at which the compound is present in its part of the environment (in its sphere). It is derived from geochemical data and does not necessarily correspond to the equilibrium concentration. The exergy content of the reference compound at its reference concentration is then arbitrarily set to zero. In this way the unstable thermodynamic properties of the ecosystem can be taken into account. Next, the molar exergy content of the pure reference compound can be calculated as the partial energy released, or work performed, during an ideal mixing operation that dilutes the pure compound to its reference concentration. For this, it is assumed that the atmosphere and the lithosphere can be described as ideal solutions of reference compounds:

$$\bar{G}_{ideal}^{mix} = -RT_0 \ln x_{ref} \quad (9)$$

In case of ionic reference compounds from the hydrosphere, this calculation is more complicated since the formation of the ion needs to be taken into account. For this, it is assumed that the formation occurs in a standard electrochemical cell with a hydrogen electrode. For more details we refer to the work of Szargut et al.^[8]. Finally the standard molar exergy b_k^{ref} for a pure chemical element can be calculated with the formation energy $\Delta G_{f,i}$ of the corresponding reference compound. This is the inverse of the second step in an exergy calculation as outlined in the previous paragraph.

3 Pyrometallurgical exergy calculations in practice

According to equation 8, the outcome of an exergy calculation depends both on properties of the environment and the stream. The availability, quality and processing of this data will thus determine the accuracy of the result.

3.1 Data quality

The properties of the reference environment are defined through b_k^{ref} values. For most common elements, these values were first tabulated by Szargut et al.^[8] in 1988. Ideally, this dataset should be the same for any exergy analysis. However the availability of accurate geochemical data is still limited. Therefore unequal $\bar{G}_{ideal}^{mix}$ values or alternative reference compounds can be found when consulting different data sources. It is particularly the case for elements that are less abundant on

earth. Consequently, b_k^{ref} values have been reviewed regularly, based on updated geochemical and thermodynamic values. The deviations between different commonly used b_k^{ref} datasets are more extensively discussed by De Meester et al.^[28] and Rivero and Garfias^[29]. It is through such discussions, and an increasing knowledge of the environmental chemistry, that future convergence towards a generally accepted and standardized dataset^[24] will be possible. This is advisable since comparisons between exergy values and exergetic efficiencies from different studies are only meaningful if the same set of environmental data is used. And it is through such comparisons that exergy analyses can be employed for process selection and optimization.

$\Delta G_{f,i}$, H , S and n_k represent properties of the stream. The n_k values describe its elementary composition. In practice, their accuracy is only limited by the measurement technique used to determine the stream composition. The other values depend not only on the elementary composition but also on the phase constitution of the stream. In the majority of exergy analyses a rough compound based stream description is used. After all, most measuring techniques only determine an elementary composition, which is often extrapolated to a compound based description. From a thermodynamic viewpoint, this approach suggests that the stream consists of pure elements or compounds, each representing a separate phase. Such a description is well suited for materials without solution phases. However, in typical pyrometallurgical high temperature streams such as slag, sinter, matte, metal ... different compounds often combine and form complex solution phases. Therefore an accurate quantification of $\Delta G_{f,i}$, H and S values requires that the phase compositions and fractions must be fully characterized as well. As a consequence, exergy analyses solely relying on compound based stream descriptions are not optimal and should be avoided, at least for most pyrometallurgical applications. When looking at the previously published exergy analyses mentioned in the introduction, only Reuter and co-workers took the formation of different solution phases explicitly into account^[22-24]. Therefore we suspect that the results of most of the other analyses^[11-21] can be improved.

A probable explanation for the omission of phase related information in most studies is the fact that experimental techniques to quantify relevant data can be time consuming and are not always possible. A pragmatic (partial) solution to this problem could be the use of thermodynamic equilibrium calculations to estimate phase related data. In the next paragraph, we propose a practical, semi-analytical methodology that allows an integration of both approaches.

3.2 A semi-analytical methodology

In the past, a large amount of generic data has accumulated with respect to the thermodynamic characteristics of different phases in pyrometallurgical streams. When this information is combined with the averaged stream composition, an equilibrium phase distribution of the stream can be calculated. This is done by minimizing the free energy in the stream as a function of the phase constitution while taking the temperature, pressure and composition of the stream as boundary conditions^[32]. Consequently, the calculated phase constitution can be used for exergy calculations. The major advantage of this approach is the possibility to incorporate phase related information into exergy analyses even if only basic compositional information is available. It thus eliminates the need to gather additional experimental data. A possible drawback is the inherent inability to account for non-equilibrium conditions in the phase constitution of specific streams when only relying on generic thermodynamic data.

In practice, often a limited amount of information on the phase constitution of a particular material stream is known. This happens for example when only qualitative observations on the phase structure are done. Nevertheless, these observations can point at possible non-equilibrium conditions in the stream despite that the phase constitution cannot be fully quantified. A semi-analytical calculation approach could then be used to obtain the best possible estimation on the actual phase morphology. It should allow the integration of measured data in the modeling process by imposing additional boundary conditions during the calculation of the stream description. For example streams that are quenched from a high-temperature equilibrium state can conserve their phase constitution when kinetic barriers prevent the formation of more stable low temperature phases. If this is observed, the formation of these low temperature phases can be suppressed during the equilibrium calculation that searches for the most stable combination of phases. Consequently, the calculated result will not represent an absolute equilibrium state, but will provide a stream description that is closer to reality. Exergy calculations based on this description should thus be more accurate.

We translated this semi-analytical approach into a practical methodology for exergy calculations. The methodology can be applied for very diverse streams in a consistent way, while the calculation itself can still be tailored in function of the available data, to obtain the highest possible accuracy. Our implementation relies on the thermodynamic calculation software FACTSAGE and accompanying databases^[33]. This software allows the calculation of an equilibrium composition of a system by minimizing its free energy. It uses databases containing generic expressions for the free energy of different components and phases, including complex solution phases in pyrometallurgical streams. The detailed methodology is presented in figure 3 and illustrated with a detailed exergy calculation on lead blast furnace slag in appendix A.

Figure 3: Flowchart of the calculation routine to perform an exergy calculation according to the semi-analytical methodology

After initialization, the equilibrium state of the stream is calculated at the temperature T and pressure p of the stream. In this state, both solution phases and pure compound phases can be present. By setting the status of each phase as a boundary condition prior to the equilibrium calculation, information from qualitative observations can be incorporated. The possible formation of phases with an 'active' status is taken into account, whereas the formation of phases with a 'dormant' status is prohibited during the calculation.

In the next calculation loop, the total exergy content of the stream is calculated as the sum of the exergies of the different phases that are present in the obtained equilibrium. This is reasonable since the configurational entropy increase in the stream due to the macroscopic mixing of these phases is negligible compared to the entropy generated by atomistic level effects within the phases. Consequently, according to the law of Gouy-Stodola (equation 3), the exergy effect due to mixing of the phases in the stream can also be neglected.

In the calculation loop, the chemical, physical and total exergy of each phase needs to be determined. This requires knowledge of the formation energy $\Delta G_{f,i,0}$, enthalpy H_0 and entropy S_0 of the phases in the stream at reference conditions. As mentioned before, these values sometimes need to be extrapolated since the phases are not stable, and thus not measurable, at reference conditions. This is often the case for high-temperature solution phases. To make such an extrapolation, one by one, the phases are isolated in a separate system and the equilibrium state of this system is calculated while suppressing the formation of any other phases (by setting their status to dormant). A first calculation at T and p yields phase values for H and S . Subsequently, this calculation is redone for environmental conditions, at T_0 and p_0 . Since the formation of all other phases is explicitly suppressed, the calculated minimal energy state will contain only the isolated phase at T_0 and p_0 , although this phase could be unstable at these conditions. From this state, extrapolated values for H_0 and S_0 are derived. Afterwards the difference in Gibbs free energy is calculated between this constrained equilibrium state and a system with the same elementary composition but where the matter is present as pure chemical elements in their stable reference state at environmental conditions. This difference equals the standard formation energy $\Delta G_{f,i,0}$ of the phase under consideration. With this elementary composition, the elementary exergy of the phase can also be calculated. This is done in the last step of the loop, together with the calculation of the physical, chemical and total phase exergy. When the iteration of the loop over the different phases is completed, the different exergy values for all the phases are summed to obtain a total value for the stream.

When partial quantitative data for a stream is available (e.g. when the composition and total amount of only some phases is measured), this information cannot be directly incorporated into the

presented calculation methodology. The reason for this is that the FACTSAGE routines do not allow imposing boundary conditions on the concentration of phases during an equilibrium calculation. In this case, best practice is to consider the stream as two distinct imaginary streams. A first one would consist of the known phases and thus have a predefined composition and phase constitution. The second one would consist of the remaining compounds with an unknown, to be calculated phase constitution. For both imaginary streams the exergy can be calculated with the proposed methodology. Finally, the sum of these exergy values equals the exergy content of the original stream.

We implemented the methodology using FACTSAGE 6.1. We also noticed that the use of versions below 6.0 of this software could lead to incorrect results^[34].

4 Validation and discussion

To assess the performance of the suggested semi-analytical methodology, we compare our results with literature data. For this, we selected 4 representative pyrometallurgical streams from earlier published exergy analyses. The first criterion for this selection is the availability of a detailed and complete description of the stream properties. A second criterion is that the formation energy (ΔG_f) of the streams is not negligible compared to their elementary exergy (B_{el}). This excludes streams consisting of relatively pure metal or energy carriers like cokes and natural gas. According to equation 8, the chemical exergy values for these streams are almost entirely dependent on the chosen reference environment. Because this choice is unaffected by the calculation method, the influence of using our semi-analytical is marginal for these streams. Both our recalculated results and the literature exergy values are presented in table I.

The calculation for the first stream, lead slag, is elaborated in appendix A. The calculations for the other streams are done in a similar way, using data from the FTOXID53, FTMISC53 and FACT53 databases, with this priority. In addition, for condensed streams, the formation of gaseous compounds is suppressed during the equilibrium calculations. And since in none of the cases phase related information is available, no additional boundary conditions are imposed. To ensure that a consistent reference environment is chosen, values for b_k^{ref} are taken the same as in the original literature sources.

Table I: Literature values and recalculated exergy values for pyrometallurgical streams at atmospheric pressure. (a) deviation = $(B_{\text{recalculated}} - B_{\text{literature}}) / B_{\text{literature}}$

	Literature	Recalculation, compound based		Recalculation, phase based		Source
	B (kJ/kg)	B (kJ/kg)	Deviation ^(a)	B (kJ/kg)	Deviation ^(a)	
Pb slag at 1473 K (1200 °C)	2035	2071	+1.78%	2104	+3.41%	Szargut et al. ^[8]
EAF slag (B _{ch} only)	1438	1376	-4.36%	1330	-7.51%	Camdali and Tunc ^[17,18]
Pb sinter at 723 K (450 °C)	787	838	+6.51%	571	-27.41%	Szargut et al. ^[8]
Copper matte at 298 K (25 °C)	5226	5232	+0.12	4657	-10.87%	Ayres et al. ^[20]

- Szargut et al. analyzed the lead blast furnace slag. This process stream leaves the furnace at 1473 K (1200 °C) with a weight based composition of 39.02% FeO, 22.79% SiO₂, 16.83% ZnO, 13.36% CaO, 4.44% Pb, 3.23% CaS, 0.34% CuO. When we recalculate the exergy in this stream, assuming that only these compounds are present, our result deviates only 1.78% from the literature value. The deviation increases when we remove the compositional restrictions. In this case, our equilibrium calculations indicate that solution phases are formed (see appendix A). At the high temperature of the stream, most of the oxides will combine in a single slag phase (93.1 wt%). The other oxides accumulate in a wustite rich monoxide phase (2.3 wt%). In addition, some liquid metallic lead (4.2 wt%) and traces of metallic iron will be present. The presence of solution phases and metallic lead in lead blast furnace slag has also been observed experimentally^[35]. Therefore, this phase based description is probably more accurate compared to the pure compound based description used by Szargut et al.
- Camdali and Tunc published exergy analyses for EAF-furnaces. In reference [18] we found a value for the chemical exergy of EAF slag. The composition of this stream corresponds to 34.42% CaO, 20.98% FeO, 15.21% SiO₂, 10.97% MnO, 6.78% Fe₂O₃, 5.47% Al₂O₃, 4.86% Cr₂O₃, 0.98% P₂O₅, 0.33% CaS. However, the temperature of this stream is not mentioned in the paper, although it is required to make an accurate estimation of the stream phase constitution. Therefore we assume a temperature of 1873 K (1600 °C), which is mentioned in reference [17] and probably covers the same process data. Camdali and Tunc only published the chemical exergy content of the stream. So in our calculations, we also ignored the contribution of the physical exergy. When comparing the results, we observe a similar trend as in the case of the lead blast furnace slag: the deviations increase when we account for the formation of solution phases. In our phase-based calculations, the compounds are almost completely dissolved in one single oxide slag phase. In absolute terms however, the deviations are larger and inverted compared to the literature result for EAF slag.

- Szargut et al. also determined the exergy of sintered lead ore at a temperature of 723 K (450 °C) with a weight based composition of 37.36% PbO, 20.38% Fe₂O₃, 13.03% SiO₂, 10.08% CaO, 7.43% ZnO, 6.45% FeO, 3.9% ZnS and 1.37% CuO. By assuming the same composition, we obtain a significant higher exergy value. However, when we take into account the formation of solution phases, we find a stream composition with a much lower energy state. Our calculations point out that most of the compounds will be dissolved in either a spinel phase (31.8 wt%), a lead silicate phase (31.2 wt%) or an iron-calcium-silicate phase (19.6 wt%). Such a composition also corresponds to the observations made by O'Keefe et al.^[36], who investigated the composition of lead sinter in more detail.
- Ayres et al. calculated the exergy in a matte stream, an intermediate product during copper production. They described the stream as consisting of 55.6 % Cu, 11.1 % Pb, 22.2 % S, 7.8 % FeO, 2.2 % Ni and 1.1 % Zn. We obtain very similar exergy values when using the same composition. However, it is unlikely that sulfur will be present as a pure compound in such a high concentration. Our calculations confirm that the elements will form sulfites and sulfates. When taking this into account, the exergy values show a larger deviation.

The differences between our compound based recalculations and the literature data can only be explained by the use of inconsistent thermodynamic datasets. Since the calculation routine, reference state and stream compositions are identical, according to equation 8, a different outcome should be due to deviant enthalpy and entropy values. For the lead slag stream, the lead sinter stream and the copper matte stream, this resulted in a higher exergy compared to the literature values. Only for the EAF slag stream, our value was smaller. Although the deviations are limited, they stress the importance of always using the most accurate available thermodynamic data. From this point of view, since we used the most recent version of the specialized FACT53 database, we assume that our results are more accurate.

When comparing the phase based results against literature values, part of the deviations can again be explained by the use of inconsistent datasets. This is similar to the compound based results. However, since the differences here are much larger, there is clearly an additional influence from the use of the recalculated, phase based stream composition. Because these descriptions often resemble the real stream constitution more closely, we assume that also in this case our results are more accurate.

Based on these observations, we can conclude that for streams comparable to the ones considered here, exergy calculations based only on compound based descriptions could be significantly inaccurate. Secondly, we notice that the application of the semi-analytical approach often results in significantly lower exergy values. As will be shown further, this is even required for

streams that contain only chemical exergy, like the copper matte (or where only the chemical exergy contribution is considered, e.g. the EAF slag). Switching to the proposed semi-analytical approach can only result in higher exergy values when there is a physical exergy contribution. This is the case for the lead blast furnace slag, where we notice a small overestimation.

Chemical exergy

When applying the semi-analytical approach, the equilibrium state of a stream is calculated. For this calculation, the stream is considered as a closed system that could contain all possible pure compounds and solution phases. Its equilibrium composition is calculated by minimizing the total Gibbs energy in this system. Consequently, solution phases will be present in the resulting equilibrium state of the stream if their formation energy ΔG_f is negative:

$$\Delta G_f = \Delta H_f - T\Delta S_f \leq 0 \quad (10)$$

If the temperature of a stream corresponds to the reference temperature T_0 , it only contains chemical exergy. Its exergy content is thus described by equation 6. From this equation it can be seen that chemical exergy will always be minimized when starting from the thermodynamic equilibrium state of the stream, as is the case in our calculations.

Physical exergy

Contrary to the chemical exergy, the physical exergy of a stream will not always decrease when solution phases are considered during the equilibrium calculation. E.g. for the lead blast furnace stream, our calculations indicate that oxide solution phases will be present in the equilibrium state of this stream. This leads to a higher calculated exergy value compared to the compound based approach. However, since these solution phases are formed, their formation should result in a smaller Gibbs energy content for the stream. It means that solution phases in streams can carry more exergy although they are thermodynamically more stable than a corresponding stream of individual compounds. This paradoxical result can be explained. For the calculation of its equilibrium composition, a stream is considered as a closed system. In this system, solution phases will form from their pure compounds if this results in a lower free energy content:

$$\Delta G = \Delta H - T\Delta S \leq 0 \quad (11)$$

Here, ΔG , ΔH , ΔS correspond to the mixing reaction of pure compounds, required to form a solution at the temperature and pressure of the stream. According to equation 7, the observed increase in physical exergy during this mixing should equals:

$$\Delta B = \Delta H - T_0\Delta S \geq 0 \quad (12)$$

According to the second law of thermodynamics, during any spontaneous mixing reaction in a closed system, entropy is generated and thus ΔS is positive. With this information and the previous

expressions it can be derived that the formation of a more stable (equilibrium) phase is accompanied with an increase in physical exergy only if

$$0 \leq T_0 \leq \frac{\Delta H_f}{\Delta S_f} \leq T \quad (13)$$

To meet this condition, the enthalpy content of the stream should increase during the formation of a solution phase. Meanwhile the formation energy of the solution phase should remain negative and thus the enthalpy change needs to be compensated by an entropy increase, multiplied by T (equation 11). On the other hand, this entropy increase should be limited, so that its product with the reference temperature T_0 is insufficient to compensate for the enthalpy increase (equation 12). In other words, the increase in physical exergy should more than offset the decrease in chemical exergy. This rather exceptional situation is promoted by a large difference between T and T_0 and a low entropy increase during the phase formation. These conditions can be met in high temperature slag phases that often consist of solution phases with a regular internal structure and a rather low configurational entropy content.

5 Case study on a zinc recycling process

A full exergetic efficiency analysis of a recently developed zinc recycling process is presented. This case study will illustrate the potential of exergy analyses as a process optimization tool for pyrometallurgical applications. The process itself is described and extensively modeled by Verscheure et al.^[37-39] The exergy analysis is based on data generated with their model. However, it should be mentioned that this model only accounts for theoretical process parameters; the influence of the practical implementation is not considered. As a consequence, the real efficiency of the process will be lower than the calculated efficiency. For the exergy calculations, the earlier introduced semi-analytical approach is used in combination with the FACT50 thermodynamic database and a reference environment as defined by De Meester et al.^[28] The relevant properties of the different process streams can be found in the appendix B.

5.1 Presentation of the process

The process allows to extract pure zinc oxide from neutral leach residue (NLR), a zinc oxide rich by-product of traditional hydrometallurgical zinc production. It is a continuous fuming process that takes place in a single reactor, depicted in Figure 4.

Figure 4: The reactor for the zinc recycling process [38]

NLR Feedstock is heated, melted and reduced by a combination of methane gas and petroleum coke (petcoke), a derivate from the oil industry. Petcoke, residue and fluxes are added through the top of the reactor; the methane gas is mixed with plasma gas and injected in the melt at the bottom of the reactor. This highly energetic plasma gas consists of primary blast air that is heated and ionized by an electric arc. The extra energy supplied by this plasma gas allows to reach temperatures as high as 1673 K (1400 °C) in the reactor. At these temperatures, metallic zinc evaporates and accumulates in the upper part of the reactor. Addition of secondary blast air will cause this zinc vapor to oxidize and to form fine zinc oxide particles. These particles are removed from the post combustion zone together with the off-gases. After filtering, they provide a source of relatively pure zinc oxide that can be used as a high grade feedstock for hydrometallurgical production of zinc metal. The remaining slag and matte in the reactor are regularly tapped off through the bottom of the reactor.

5.2 Analysis of a base case

The exergy content of the different process streams is calculated in a base case scenario as presented by Verscheure et al.^[37]. In this scenario, only the produced zinc oxide is accounted as useful product. The other output streams are considered waste streams. The outcome of this calculation is presented in table II. A more detailed description of the different streams is included in appendix B.

Table II: Exergy flows in a base case

Exergy flow rate (kJ/s)	Input	Output	
		Product	Emission
PetCokes	23979		
Electricity	21600		
Methane	7060		
Leach residue	1281		
Flux	223		
Secondary blast air	17		
Primary blast air	12		
Zinc oxide		677	
Off-gas			19344
Slag			12826
Matte			1823
Heat losses			4972
Total	54172	677	38965

Several factors limit the process efficiency. The so called internal exergy losses can be calculated by subtracting the total exergy output from the total input. These losses are due to thermodynamic irreversibilities in the process and are equal to 14530 kJ/s. But this is still rather small compared to the exergy that is lost through the highly exergetic emission streams. These external losses account for 38965 kJ/s. In addition, the exergetic content of the useful product stream is rather low (677 kJ/s). This is due to the high chemical stability and therefore low exergetic content of zinc oxide. According to equation 1, this yields a low global process efficiency of 1.2%.

The low efficiency indicates that significant enhancements can be realized. However, to be able to make suggestions for process optimization, first the exergy losses need to be located. To be able to do this, we divide the reactor into 3 subsystems. This is represented in figure 5.

Figure 5: A subdivision of the reactor in a preheater, fumer and afterburner section

With the model of Verscheure et al., we are able to calculate the internal exergy exchanges between these subsystems. The reduction gas represents an exergy transfer of 24316 kJ/s. The heat flow from the post combustor to the fumer equals is 1294 kJ/s and the fuming gas corresponds to 27444 kJ/s. With this information we can construct an exergy flow diagram for the whole process, depicted in figure 6. It allows also calculate an exergetic efficiency for each of the subsystems. For this, the internal streams are considered as input streams or as useful output product streams for the subsystems. Notice here that the global process efficiency cannot be calculated as the product of the efficiencies of the individual subsystems. This due to the recirculation of the post combustion heat, which is a useful product when considering the post combustor subsystem but not when considering the whole process.

Figure 6: The exergy flows for the base case scenario represented in a Sankey diagram

5.3 Efficiency optimization

To increase this efficiency, different process modifications can be considered. As the Sankey diagram shows, the preheater only accounts for some minor internal losses. Since no emission streams are generated here, only internal losses are present. The exergetic efficiency of the preheater equals 81.2%, so no major gain can be achieved here.

Optimization of fumer

The efficiency of the fumer is 53.7 %. When considering this subsystem, we notice that the slag stream accounts for the majority of the exergy losses. The matte stream, heat losses and internal losses represent smaller efficiency decreases. Hence reducing the exergy content of the slag emission stream offers the most promising way for optimization. This slag has a temperature of 1615 K (1342 °C). Consequently, the exergy in this stream can be divided in a physical exergy part, equal to 2726 kJ/s, and a chemical exergy part, equal to 10100 kJ/s. Although the chemical exergy is far larger, optimization on this part is not straightforward. As outlined in section 2, the chemical exergy of the slag depends on its composition. But this composition is optimized for the

fuming process, partly by the addition of fluxes. This means that the properties of the slag cannot be altered without completely redesigning the process. However, when the slag can be used as an input stream for other processes, e.g. in the construction industry, its chemical exergy could be classified as a product stream. In that case, the overall process efficiency can be calculated as 19.9%. Currently, a lot of research is done on this transformation of slag from an emission stream into a useful product, e.g. as aggregate or fertilizer. This is however outside the scope of the present article.

In a similar way, recovery of heat from high temperature slag allows a partial transformation of the physical exergy into a useful stream. A detailed exergetic study on this topic was carried out by Bisio^[40], based on data from a heat recovery technology described by Pickering et al.^[41] Bisio investigated the efficiency of heat exchangers that recover heat from blast furnace slag at 1773 K (1500 °C) to generate useful hot air and superheated steam product streams. Two configurations were considered, resulting in exergetic efficiency values of 27.1% and 30.3% for the heat exchangers. If we assume that the energy in the slag can be recovered with the same average exergetic efficiency of 28.7%, the limit to the fumer efficiency can be estimated at 2.7%. Of course this is only a very rough estimation since the initial temperature difference and the influence of the composition on the heat conduction properties are not taken into account.

Optimization of post combustor

According to the Sankey diagram, the efficiency of the post combustor is far lower than for the other subsystems, around 7.2%. Hence, the largest efficiency gain can be achieved here. This subsystem can be optimized in two ways: by reducing the exergy losses or by increasing the exergy content of this product stream. This is possible since the zinc oxide is processed in this subsystem.

To reduce the exergy losses, we consider the off gas stream that contains the majority of the exergy losses in the process. Due to the high temperature of these gasses at 1823 K (1450 °C), their physical exergy (12924 kJ/s) is larger than their chemical exergy (6420 kJ/s). Consequently, the most promising optimization technique is energy recuperation, similar to the heat recovery from the slag in the fumer subsystem. Additional useful by-products such as steam or electricity can be generated in this way. However, the composition and the thermal properties of the off-gas are not optimized for use in steam boilers. The efficiency of these boilers will be limited by construction restrictions that are for example imposed by the corrosive properties of the gas. We estimate the upper boundary for the energetic efficiency of these boilers at 85% while they cool the off-gasses to 1073 K (800 °C). This would result in a total process efficiency of 11.6%, under ideal

circumstances. Of course, this efficiency will be lower in practice, depending on the specific implementation. In a next step, this steam could be used to generate electricity by steam generators in a Rankine cycle. The non reversible operation of the steam turbine and the electrical generator will create additional losses. The resulting maximal process efficiency will thus be lower and is estimated at 7.0%.

The other way to optimize the post combustor subsystem is to enlarge the exergy content of the zinc oxide product stream. However, since the production rate is limited by the zinc content of the feedstock, this can only be achieved by increasing the specific exergy content of the product. Zinc oxide has a low specific exergy content due to its high chemical stability. Pure zinc metal has a specific chemical exergy content that is 16.5 times larger compared to zinc oxide. Consequently, producing metallurgical grade zinc instead of zinc oxide could improve the efficiency. This is possible by avoiding the reoxidation reaction and capturing the zinc fumes by unsaturated lead in a lead condenser, followed by a liquation step to separate the zinc metal^[42]. The maximal metal efficiency of a condenser operating between 723 K (450 °C) and 833 K (560 °C) is estimated at 94%^[43,44]. In this case the useful product is zinc metal saturated with lead. Also the composition of the off-gas will change. Based on these assumptions, the maximal obtainable exergetic efficiency of this modified process is estimated at 10.8%. However, this estimation does not account for the energy consumption and thermodynamic irreversibilities of a real lead condenser.

Conclusion

A comparison of the investigated optimization scenarios is presented in table III. It shows that the overall efficiency improves the most if the slag can be considered as a useful product. For this, a transformation of the slag into a useful input stream for other processes is required. From a thermodynamic viewpoint, the next best optimization would be to extend the reactor with boilers to produce steam as an additional product. But steam is not easily transported and can only be counted as a useful product if a customer process is available nearby. If this is not the case, steam can also be converted into electricity. This by-product is always useful because the process itself can be a customer. However the generation of the electricity results in important additional exergy losses. Therefore, the use of a lead condenser can be an alternative with an in-between efficiency. A drawback of this condenser is its complex and difficult operation. Finally, energy recovery on the slag stream could also be considered for process efficiency enhancement.

Table III: A comparison of different optimization scenarios

Scenario	Estimated exergetic process efficiency
Reuse of slag (product)	19.9 %
Energy recovery from gas, steam production	11.6 %
Use of lead condensor for zinc production	10.8 %
Energy recovery from gas, electricity production	7.0 %
Energy recovery from slag	2.7 %
Base case	1.2 %

Here we want to stress once more that this study is based on theoretical considerations only, without looking at real life implementations. We also notice that some of the proposed process optimizations, in particular those involving heat recovery techniques, are rather straightforward. They probably could also be identified without the use of an exergy analysis. However, the exergetic quantification allows comparing them in an unambiguous way with other totally different optimization scenarios. According to the authors, this is the most important advantage of exergetic process analysis.

6 Summary

The outcome and the accuracy of an exergy analysis are mainly determined by two factors. Firstly there is the choice of a thermodynamic reference state; secondly there is the used stream description. As a consequence, great care should be taken when comparing different exergy analyses. Only when a consistent dataset and methodology is used, a straightforward comparison is possible.

An evolution towards a universally accepted reference environment, based on the reference compound method, can be noticed. However, until such a standardized environment is widely introduced, the result of exergy analyses will depend on inconsistent reference data. And even when agreement on a standardized environment exists, the reference data will need to be updated regularly, based on new geochemical data from earth's changing environment. As a consequence, for each new analysis, the most recent data should be used. Care should also be taken when choosing a description method for the process streams, in particular for pyrometallurgical streams. Although previous exergy calculations for such streams are reported in literature, these analyses often do not account for the complex phase structure of such streams. However, our results show that the incorporation of phase related information could cause significant deviations on the calculated exergy values. Therefore, we propose a semi-analytical approach to combine the

available, experimental stream data with generic thermodynamic phase related information. In this way the highest possible accuracy is obtained in practice. A comparison with the existing results from literature suggests that this approach could have a significant impact on the outcome of the calculation. Moreover, the results obtained with this approach will probably be more accurate if the expressions for the thermodynamic stability of the phases are selected with care and used in a consistent way over the different phases.

To summarize, we can state that comparisons between different exergy analyses are only possible when a consistent and unambiguous methodology is followed. In this paper, we presented such a method, tailored for pyrometallurgical exergy analyses. It is a semi-analytical method that incorporates information about the actual phase configuration into exergy calculations. In combination with carefully selected thermodynamic data for these phases, this method can provide more accurate exergy values compared to traditional compound-based calculations. In this way, exergy analysis becomes useful for the optimization of pyrometallurgical processes. This is illustrated by the analysis of a zinc recycling process that shows how exergy analysis can be used to select, evaluate and compare different processes based on their thermodynamic efficiency. In a base case scenario the exergetic efficiency of this process is only 1.2%, but it can be considerably increased by using energy recuperation techniques or optimizing the output streams. This efficiency increase results in a reduction of emissions and an increase of the process sustainability.

List of symbols

η	efficiency
Δ	change of a quantity
n	Amount [mole]
B, b	Exergy [J]
E	Energy [J]
G	Gibbs energy [J]
H	Enthalpy [J]
S	Entropy [J / K]
T	Temperature [K] ([°C])
p	Pressure [pa]
x	Mole fraction
subscript / superscript	
0	Property of the environment
c	Property of an ideal (reversible) Carnot process
ch, ph	Property derived from chemical phenomena (ch) or physical phenomena (ph)
el	Property derived from the elementary composition, without phase formation
f	Property of a formation reaction
i, k	Index for counting phases (i) or chemical elements (k)
ref	Based on a reference composition
B, E	Based on an exergy balance (B) or energy balance (E)

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Figure 1: Calculation of the efficiency ratio of a process from its process streams

Figure 2: The different steps during an exergy calculation for a mass stream

Figure 3: Flowchart of the calculation routine to perform an exergy calculation according to the semi-analytical methodology

Figure 4: The reactor for the zinc recycling process [38]

Figure 5: A subdivision of the reactor in a preheater, fumer and afterburner section

Figure 6: The exergy flows for the base case scenario represented in a Sankey diagram

Appendix A: Exergy calculation for lead blast furnace slag

Like most other exergy related studies, we adopt the calculation principles outlined by SZARGUT, MORRIS AND STEWARD, 1988^[8]. However, during the practical implementation, we incorporate phase related information whereas most other studies rely on a compound based stream description. To illustrate the methodology, and to compare both approaches, the results of Szargut et al. are recalculated for a high temperature slag stream from a lead blast furnace. The calculation is done using FACTSAGE V.6.1. Data is taken from the FTOXID53 oxide solutions database and FACT53 compound database. The reference environment is defined the same as in the work of Szargut et al.

The slag has a (weight based) composition of 39.02% FeO, 22.79% SiO₂, 16.83% ZnO, 13.36% CaO, 4.44% Pb, 3.23% CaS, 0.34% CuO, its temperature is 1473 K (1200 °C) and the pressure equals 1 atm. We perform an exergy calculation for 1 kg of this stream.

First the equilibrium state is calculated. Here, we consider the formation of all solid and liquid phases available in the databases. If duplicate compounds are present, the information in the FTOXID53 is given priority. If multiple solution phases from the FTOXID53 describe a similar system, we select the most appropriate one based on the database documentation. For gaseous components we assume ideal gas behavior, but their formation is suppressed because we know that slag is a condensed stream. However, the same results are obtained when allowing the formation of gaseous species, indicating that they are not stable anyway.

In the calculated equilibrium state, the following phases are present in the system:

- 93.1% Slag solution phase (FToxid-SLAGA): 37.54% FeO, 23.86% SiO₂, 17.25% ZnO, 16.61% CaO, 1.20% FeS, 0.97% Fe₂O₃, 0.95 SiS₂, 0.56% CaS, 0.54% ZnS, 0.32% Cu₂O, 0.16% PbO, 0.03% Fe₂S₃, 0.01% Cu₂S
- 2.31% Wustite rich solution phase (FToxid-MeO_A): 79% FeO, 15.15% ZnO, 5.68% Fe₂O₃, 0.18% CaO
- 4.30% Liquid lead (Pb_liquid)
- 0.29% Solid Iron (Fe_fcc)

This result indicates that most of the oxides will combine to form a single solution phase, which will affect the total enthalpy and entropy content of the stream and thus also its exergy value. In the next step, these enthalpy and entropy values are calculated, both at stream conditions and at reference conditions. As explained in section 3, we do this by repeating equilibrium calculations for each phase individually. The results are summarized in table A.I.

Next, the formation energy of the phases is calculated. It is also done with FACTSAGE for each phase

individually, by calculating the change in free energy during the formation reaction of the phase out of its elements in their reference state. The resulting formation energy values can be found in table A.1. In addition, the reference states per element are listed in table A.II.

Finally, the elementary exergy in the stream is calculated, based on its elementary composition and standard exergy values determined by Szargut et al. This is also summarized in table A.II.

Table A.I and A.II now contain all information required to calculate the exergy content of the stream according to equations 5-8. This yields a chemical exergy of 1484.35 kJ/kg, a physical exergy of 619.43 kJ/kg and a total exergy content of 2103.78 kJ. In section 4, these values are compared with the results of Szargut et al.

Table A.I: Calculated thermodynamic phase properties

Phase	Mass	Stream conditions		Reference conditions		
		1473 K (1200 °C), 1 atm		298 K (25 °C), 1 atm		
	(g)	Enthalpy (J)	Entropy (J/K)	Enthalpy (J)	Entropy (J/K)	Formation energy (J)
FToxid-SLAGA	931.08	-6.18E+06	2.24E+03	-7.17E+06	9.53E+02	-6.80E+06
FToxid-MeO_A	23.07	-6.77E+04	4.73E+01	-8.86E+04	1.95E+01	-8.19E+04
Pb_liquid	42.96	7.30E+03	2.32E+01	-8.36E-01	1.34E+01	4.61E+02
Fe_fcc	2.89	2.31E+03	4.33E+00	4.12E+02	1.86E+00	2.80E+02
Stream	1000	-6.24E+06	2.32E+03	-7.26E+06	9.87E+02	-6.88E+06

Table A.II: Elementary exergy calculation

Element	Reference state	Standard exergy	Amount	Elementary exergy
	FACTSAGE phase name	b^{ref} (kJ/mol)	n (mol)	B_{el} (kJ)
Pb	solid-FACT53	232.8	2.14E-01	49.9
Zn	solid-FACT53	339.2	2.07E+00	701
O ₂	gas-FACT53	3.97	1.75E+01	34.8
Fe	solid-1-FACT53 bcc	376.4	5.43E+00	2040
Si	solid-FACT53	854.6	3.79E+00	3240
Ca	solid-1-FACT53	712.4	2.83E+00	2020
S	solid-1-FACT53 orthorhombic	609.6	4.48E-01	273
Cu	solid-FACT53	134.2	4.27E-02	5.74
Stream				8370

Appendix B: Process stream data

In tables B.I, B.II and B.III the properties of the process streams are listed. The matter streams are all at standard pressure ($P_0=1$ atm) and the given compositions are weight based.

Table B.I: Properties of the process input streams in the base case scenario

Stream name	Temperature	Composition
Leach residue	298 K (25 °C)	53.0% ZnFe ₂ O ₄ , 17.9% ZnSO ₄ , 9.5% PbSO ₄ , 5% SiO ₂ , 4.8% H ₂ O, 4.6% CaSO ₄ , 2.2% Cu ₂ O, 1.2% Al ₂ O ₃ , 1.1% Zn ₂ SiO ₄
Flux	298 K (25 °C)	54.3% CaCO ₃ , 39.8% MgCO ₃ , 4.8% H ₂ O
Petcoke	298 K (25 °C)	95.2% C, 4.8% H ₂ O
Methane	298 K (25 °C)	100% CH ₄
Primary blast air	298 K (25 °C)	23.3% O ₂ , 76.7% N ₂
Secondary blast air	298 K (25 °C)	23.3% O ₂ , 76.7% N ₂
Electricity		21.6 MW

Table B.II: Properties of the process internal streams in the base case scenario

Stream name	Temperature	Composition
Reduction gas	3663 K (3390 °C)	1.2% H ₂ O, 2.9% OH, 3.4% O ₂ , 3.7% NO, 7.6% CO, 8.1% O, 71.4% N ₂
Fuming gas	1615 K (1342 °C)	1.6% Pb, 4% PbS, 7.7% H ₂ O, 11.5% CO, 16.5% Zn, 28.5% N ₂ , 29.4% CO ₂
Post combustion heat	1823 K (1550 °C)	1.55 MW

Table B.III: Properties of the process output streams in the base case scenario

Stream name	Temperature	Composition
Zinc oxide	1823 K (1550 °C)	98.6% ZnO, 1.4% PbO
Off-gas	1823 K (1550 °C)	48.2% N ₂ , 33.3% CO ₂ , 6.5% H ₂ O, 6.0% Zn, 3.5% PbO, 1.3% SO ₂
Slag	1615 K (1550 °C)	37.3% FeO, 13.1% CaO, 11.4% Fe ₂ O ₃ , 9.7% SiO ₂ , 9.2% FeS, 6.7% MgO, 3.4% ZnO, 3.4% CaS, 2.4% Al ₂ O ₃ , 1.9% MgS
Matte	1615 K (1342 °C)	25.5% S, 17.6% Fe, 42.2% Cu, 9.6% Zn, 5.0% Pb.
Heat side wall post combustor	1702 K (1429 °C)	3.39 MW
Heat top post combustor	1604 K (1331 °C)	0.95 MW
Heat fumer	1556 K (1283 °C)	1.74 MW

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