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Opportunity for using steelmaking/EAF or BOF laden dust to desulphurise hot metal

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Abstract

In order to promote recycling of basic oxygen furnace (BOF) zinc laden dust, desulphurising hot metal using ZnO or Zn has been researched on a laboratory scale and the possibility of developing a new desulphurisation (De-S) method is explored. Directly as a result of sublimation of ZnS at 1460 K, the driving force for desulphurisation with Zn or ZnO increases with increasing temperature beyond this sublimation temperature, thus potentially making Zn based reagents useful for high temperature desulphurisation reactions. Feasibility reactions were also performed to confirm that ZnO can effectively react with FeS (from 1473 to 1653 K) or with Fe-Csat-S(1473-1673 K) to remove S. There is therefore potential for the utilisation of ZnO laden waste dust as an additional or alternative reagent for desulphurisation.

Introduction

The iron & steel industry generates over 30 million tonnes (MT) of dust each year worldwide, comprising up to 2 wt% of iron and steel produced, containing ZnO, arising in the various iron and steel making units. The top gas dust can vary from 2-5 wt% ZnO in the iron blast furnace (BF), while it may be further concentrated into a lower volume but more concentrated ZnO fraction by using a hydrocyclone. The basic oxygen steelmaking furnace (BOF) accounts for over half the dust produced in the steel industry, typically in a slurry form containing over 4 wt% ZnO. In some operations in the BOF, the ZnO is concentrated to beyond 30 wt% by repeated recycling of the dust so that it is acceptable for further processing by the Waelz kiln process. The electric arc furnace (EAF) is responsible for generating over one third of all steel industry dust, containing 20-40 wt% ZnO in a very fine morphology, making the dust difficult to handle and treat. Secondary steelmaking processes, especially where vacuum is used, can generate very concentrated ZnO (> 50 wt%) dust in relatively smaller amounts. ZnO-laden wastes are mostly in the form of dry dust, slurry, sludge or wet cake containing useful values of Zn, C, Fe and lime and are mostly landfilled at a considerable economic and environmental cost.¹⁻³ Despite a considerable volume of research over the last two decades,⁴⁻⁸ economically viable routes for utilising or recycling zinc oxide dusts are not yet available.

The ZnO dust problem will become even more important, due to a healthy growth (+ 5%) in the consumption of galvanised steel combined with a 10% or more annual growth in the EAF steelmaking in the last decades. As more and more of the galvanised steel is returned for recycling in the near future, higher amounts and richer concentration of ZnO dust would become available for treatment and/or disposal. Steelmakers have wished to avoid Zn & ZnO from their furnaces, as dust is a source of operational nuisance and environmental costs and perhaps the reason why the possibility of using ZnO dust as a reagent has not been seriously explored. Given the growth in galvanised steel, the presence of Zn in steelmaking is inevitable and a novel solution for treating or utilising zinc oxide containing material is suggested in this paper.

Sulphur is an unacceptable impurity in steel and its removal in the iron and steelmaking process is vigorously pursued. The best conditions for removing sulphur arise in the carbon saturated hot metal before it is charged to the BOF.⁹ The most common practice is to desulphurise hot metal (De-S) in ladles by using magnesium (as salt coated granules to moderate the violent reaction) at 0.5 to 1 kg t⁻¹ hot metal (THM) or CaC₂/CaO in the 6 - 10 kg t⁻¹ hot metal range, either singly or in combination to achieve levels of sulphur in the < 200 ppm range. It is a surprising fact that very little information is available in the literature concerning the interaction between Zn and ZnO with molten iron despite its inevitable presence in iron and steelmaking furnaces. In the BF the Zn input arises from the iron ore/sinter/pellet charge. Over 95% of the Zn can ultimately escape with the dust as an oxide. Zn can also recirculate within the BF from upper bosh to mid-stack, causing coke disintegration leading to reduced permeability. It is reported that hot metal from the BF may retain up to 10 ppm¹⁰ Zn. In both the BOF and the EAF, Zn input arises from the recycled scrap and virtually all of the Zn reports in the exhaust gas as oxide dust particles. In a laboratory experiment it has been shown that by using pressures greater than the vapour pressure of Zn, up to 0.4 wt% Zn can dissolve in steel at 1873 K. When calculated for 1 atm pressure, the solubility decreases to the ppm levels.¹⁰ While some solubility is seen as essential for promoting reaction with sulphur in the hot metal phase, such low solubility is fortuitous as treatment with ZnO for desulphurising hot metal will not result in any significantly higher Zn content in the hot metal. Given the demand for galvanised steel, the presence of Zn is inevitable. The steel industry is in need for a novel solution to deal with the Zn arising in the dust. This research project has explored a new solution for converting a burden into an opportunity by utilising ZnO-based dust as a reagent for desulphurising hot metal. Hence, a significant part of the dust can be upgraded in value for internal use within the steel industry itself.

The sublimation of ZnS - thermogravimetric analysis (TGA)

For ZnO to react with sulphur in the hot metal, the product ZnS must be relatively stable under the chemical conditions prevailing in the hot metal. In order to investigate stability of ZnS at elevated temperatures, TGA was carried out in a NETZSCH apparatus by heating ZnS under a Helium atmosphere. In a typical run, 10 mg of ZnS was placed in an alumina crucible, while a reference crucible was kept empty. The sample was heated to 1200°C at a heating rate of 5°C/min and kept isothermally for two hours before cooling down to room temperature. Measurements were recorded and analysed using software provided by NETZSCH.

As shown in Figure 1, the weight loss begins at approximately 930°C and is completed by 1200°C. The rate loss is accelerated at $T > 1180^{\circ}\text{C}$ (1453 K), indicating that 1453 K is the sublimation point for ZnS. The implication of these findings is significant with respect to desulphurisation reaction. Not only is the driving force higher at $T > 1453\text{K}$, the reaction product is gaseous at $T > 1453\text{K}$ and thus will be eliminated from the reaction zone resulting in the renewal of the reaction. Therefore, kinetic factors are favourable for the desulphurisation reaction.

Thermodynamic considerations

The currently available thermodynamic data for ZnS at elevated temperatures is based on extrapolation from the low temperature data and is thus incorrect as the data does not include the effect of phase transformation of ZnS from a solid phase to a vapour phase at 1450 K. A phase transition into a gaseous phase should help in increasing the thermodynamic driving force for desulphurisation reactions with increasing temperature beyond $T > 1453\text{K}$. The key reactions to be considered for desulphurising hot metal with ZnO are given below:

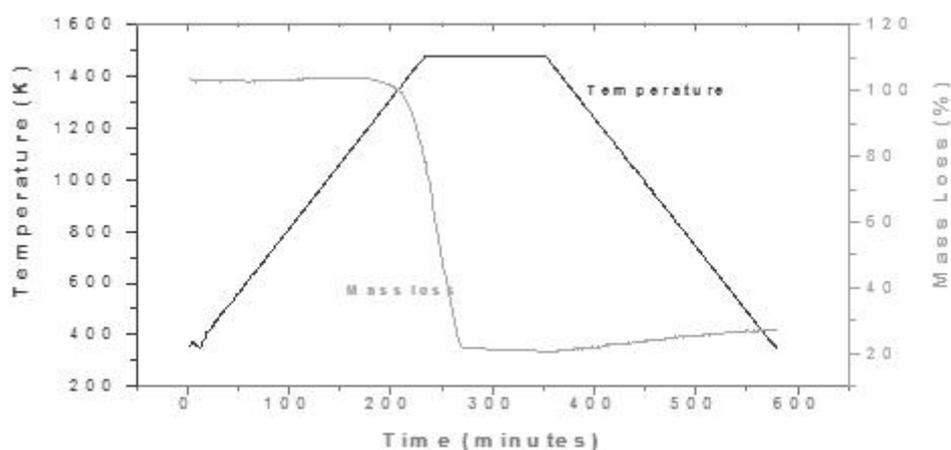
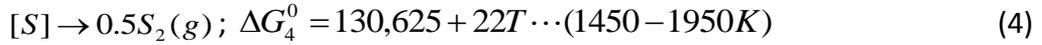
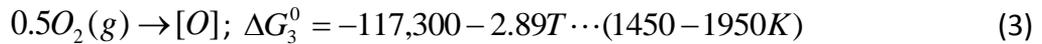


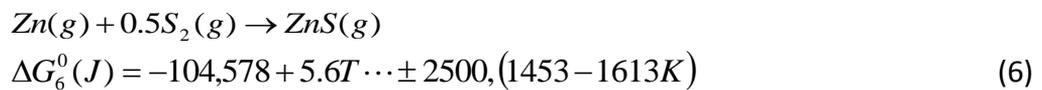
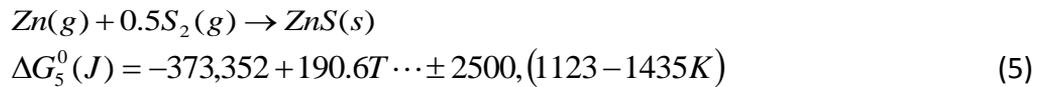
Figure 1: TGA Data on ZnS



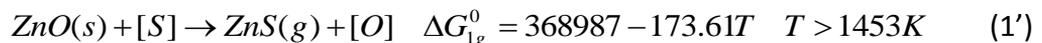
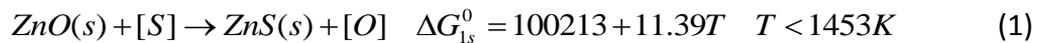
The reaction (1) may be derived from combinations of the partial reactions (2), (3), (4), (5) and (6). Thermodynamic data for reactions (2), (3) and (4) are well established in the literature. In order to evaluate the thermodynamics of reactions (5) and (6) the following galvanic cell was used in the temperature range 1123-1613 K, and the emf results shown in Fig. 2 and 3:^{11,12}

Pt, Mo, MoO₂ / Ytria Stabilised zirconia / ZnO, ZnS, SO₂, Pt

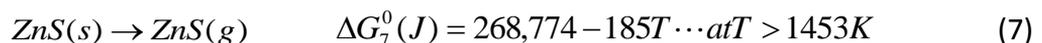
According to the formula $\Delta G_i^0 = -nFE^0$ and the results determined by the galvanic cell we can get the thermodynamic data of reaction (5) and (6) :



Combining (2) + (3) + (4) + (5) or (6) together, one obtains:



(1) - (1') =



We can calculate that the reaction direction for (1) is dependent on the content of oxygen in the hot metal. At a temperature of 1623 K (1350°C) and at a value of [O] < 0.001559%, i.e < 16 ppm, the reaction:

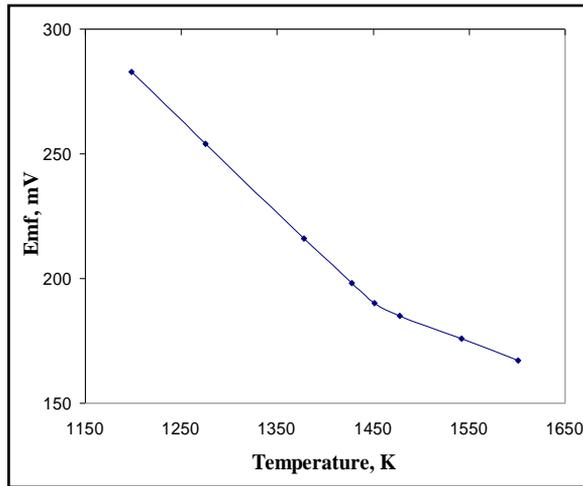


Figure: 2 Emf vs T



is favourable. Figures 2 and 3 present the thermodynamic data as determined in the laboratory. In a carbon saturated hot metal, typically, $[\text{O}] < 1.6 \times 10^{-5}\%$; is in the ppb range. The thermodynamic calculations derived from the experimental research suggests that, in a carbon saturated hot metal ($[\text{O}] < 0.1\text{ppm}$), ZnO can potentially be used as a desulphurising reagent . The free energy values at 0.1 ppm oxygen are more negative at all temperatures as shown: $\Delta G(J) = 368987 - 269.35T$. Applying the data to hot metal at 1700 K, containing 0.1 ppm oxygen, the equilibrium concentration of sulphur is calculated as 1.85 ppm.

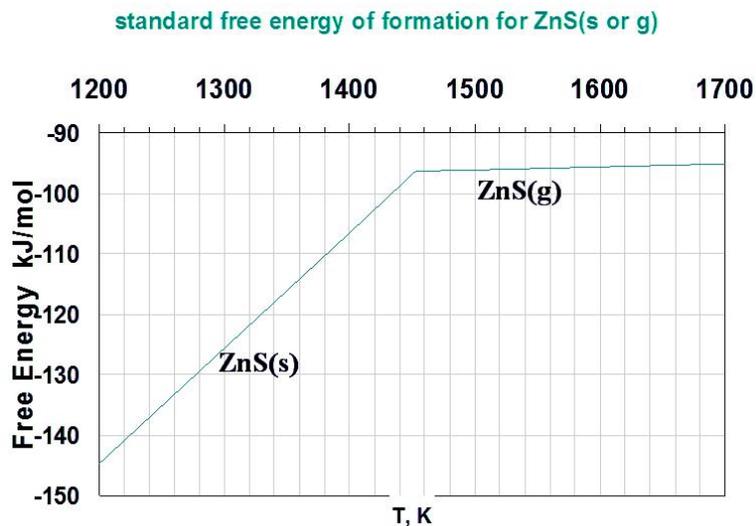


Figure 3: The standard free energy of formation for ZnS

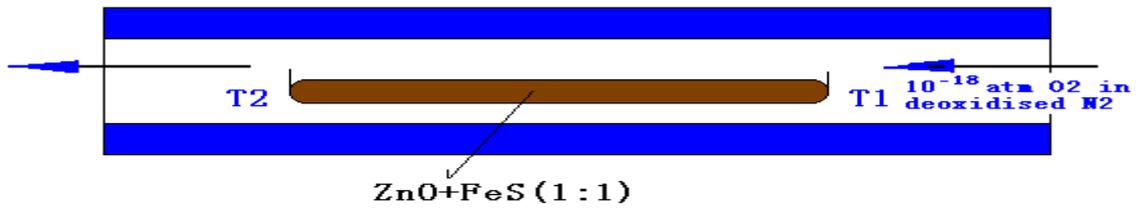


Figure 4: Formation of ZnS in a Temperature Gradient Furnace (a schematic sketch)

Formation of ZnS(g)

The implications of forming ZnS as a gaseous product in a desulphurisation reaction is significant for minimising the problem of sulphur reversal from retained slag after skimming. It may be possible for the gaseous product to be collected from the exhaust gas as condensed ZnS. A high grade ZnS may be available as a by-product for zinc producers and for the chemical industry.

Experiments were carried out to demonstrate that ZnS can be formed in the gaseous state as a direct result of the desulphurisation reaction, and can then be condensed at lower temperature. The feasibility of transporting sulphur from the liquid iron phase as ZnS vapour was demonstrated in a simple experiment, as depicted in Figure 4. FeS was mixed with ZnO in 1:1 molar ratio and heated in a temperature gradient furnace with a flow of deoxidised nitrogen (10^{-18} atm partial pressure of oxygen). The arrangement of the alumina boat containing the reaction powder was such that in the first run, the hot end ($T > 1653$ K) faced the gas, while in the second, the profile was reversed, that is the cold end ($T < 1453$ K) faced the gas. The reaction was allowed to proceed for 60 minutes after which the furnace was cooled to 303 K while keeping nitrogen gas flowing. The boat containing the powder was weighed before and after the run. Products of the reaction were examined by SEM/EDX and XRD. Figure 5 illustrates the sequence of the reaction between ZnO and FeS, following the first run in which the hot end ($T_1 > 1653$ K) faced the incoming gas in the direction of decreasing temperature. Zinc sulphide was formed at the hot end and transferred

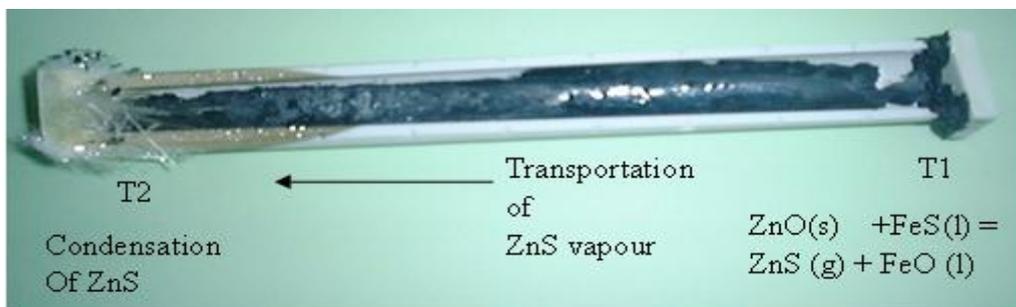


Figure 5: $T_1 > 1653$ K; $T_2 < 1453$ K; ZnS formed at T_1 and condensed at T_2

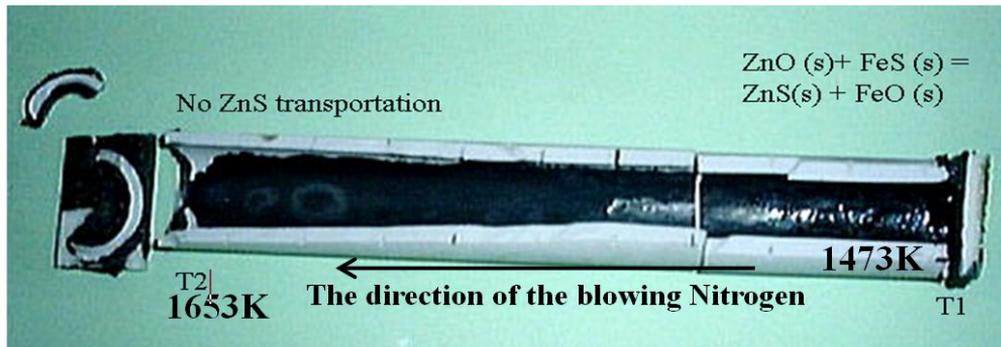


Figure 6: T1: 1473 K and T2: 1653 K; ZnS formed at T1, but has escaped from the ceramic boat at T2

through the nitrogen atmosphere to the cold end, $T_2 < 1453$ K, where it condensed. No ZnS was collected at the hot end.

In the second run, where the temperature profile was reversed, in order to minimise condensation, all the zinc sulphide formed at the cold end, which was maintained at 1473 K, escaped from reactor. This was confirmed by its absence from the alumina boat as seen in Figure 6. Most of the ZnS was found to be condensed on the furnace tubular wall and in the exhaust gas line. It is confirmed, therefore, that in both the above experiments, ZnS is eliminated from the reaction zone containing ZnO and FeS.

Industrial trials

An industrial scale trial was carried out with a 300 tonne KR De-S equipment, in order to investigate the feasibility of the reaction $ZnO(s) + [S] \rightarrow ZnS(s/g) + [O]$ in the carbon saturated hot metal on a larger scale. The test program schematic is described in Figure 7. The tests were organised at the third KR De-S set of Shougang Jingtang steelworks in China. The KR process is flexible with respect to the De-S reagent used, hence suited for this trial. Pure ZnO granular powder (1-3 mm) was used as the desulphurising agent. These are commercially available as chemical reagents, under the name of "active grain zinc oxide". A hole was cut on the flue and a mesh sieve was fixed in order to collect any condensed ZnS product. A photograph of the De-S trial is shown in Figure 8.

BOF or EAF dust is also being used instead of pure ZnO in on-going work. The results are not yet available. All other components in the dust are considered valuable or neutral. For example, CaO/MgO provide additional desulphurising power and basicity (countering the acidic components such as silica) to the dust. Carbon is useful for reducing ZnO and any iron oxide. The iron oxides can add iron value to the metal. It

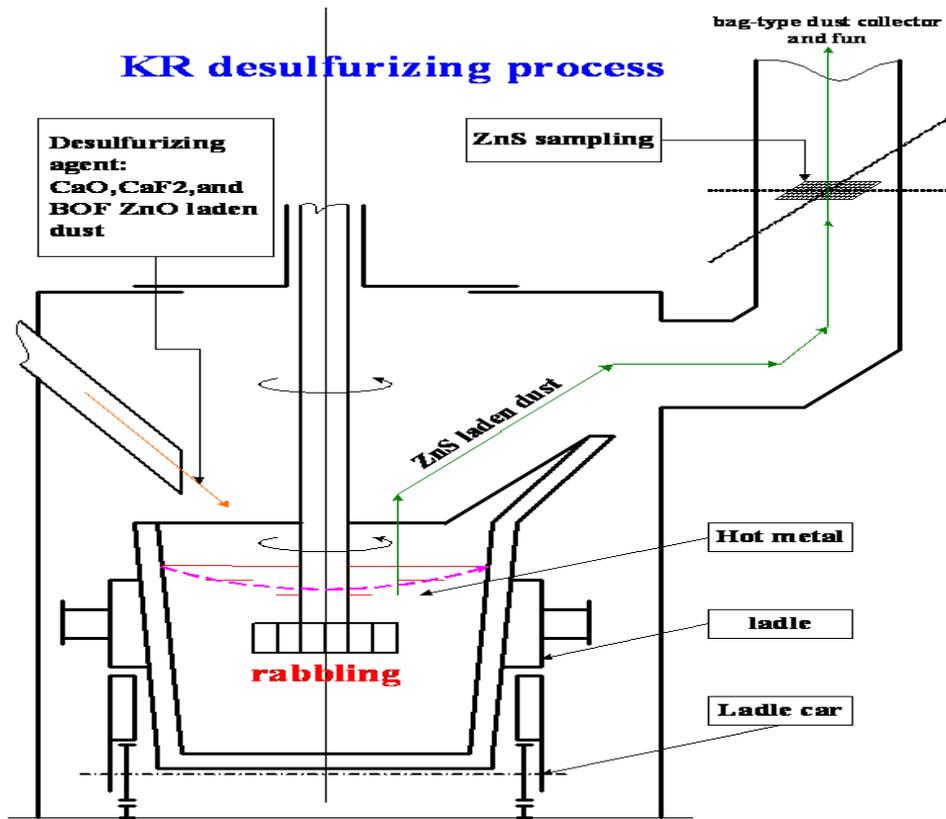


Figure 7: Trial using ZnO desulphurisation on KR Equipment

should also be realised that pre-treatment methods such as plasma processes can provide a highly enriched ZnO product that can be directly used as de-S agent for the hot metal. The KR desulphurising method is utilised in a number of steelworks in the world. It is generally a simple process and easy to control. A typical technological procedure is schematically shown below in Figure 9.



Figure 8: A photograph of the De-S process

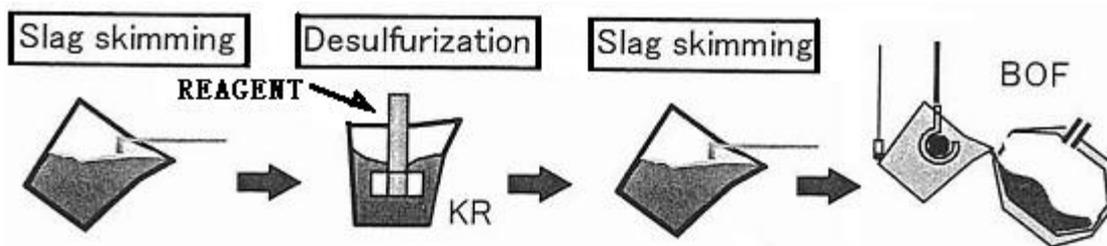


Figure 9: KR desulphurisation method

As shown, initially, the carry-over slag from the BF is skimmed followed by desulphurisation (De-S) with the selected reagents such as CaO, CaC₂, CaO + Mg or pure Mg, by mechanical rabbling with reagents being simultaneously added. The remaining slag is skimmed in order to avoid S-reversion into the metal in the BOF. Because of the two slag skimmings, the treatment time is relatively long, *i.e.* 40-45 minutes. As a consequence, iron and temperature losses are also relatively high.

Details concerning a typical trial in this work using ZnO are now described. The amount of hot metal charged was 287 tonne with an initial carry-over slag of nearly 3 tonne. After the first skimming, the amount of slag left was 345 kg. A total of 200 kg of ZnO, corresponding to 0.7 kg t⁻¹ of hot metal (THM) was added and rabbled in the liquid metal. The amount of ZnO input was sufficient for reacting only with a total of 79 kg of S in the hot metal and the carry-over slag. The amount of ZnO input was deliberately kept lower than the stoichiometric requirement (1.5 kg per THM, assuming 100% S removal) in order to control the violence from the reactions. The composition of the slag (only key components are tabulated) is given in Table 1, both before and after desulphurising with ZnO.

Table 1: Slag Composition (Before and After De-S)

Components	Wt% (Before De-S)	Wt% (After De-S)
SiO ₂	38.1	38.9
CaO	29.3	35.9
FeO	12.4	2.9
T-Fe	9.7	2.3
MnO	6.5	0.9
S	1.05	0.33
R = CaO/SiO ₂	0.77	0.92

The De-S reagent ZnO has desulphurised S in the slag from 1.05 to 0.33 wt%, amounting to removal of 2.35 kg of S, corresponding to 6 kg of the ZnO for the De-S reaction, from the 200 kg input. It should also be noted that the slag composition has altered, whereby the wt% of FeO, T-Fe and MnO have decreased considerably, while

the relative amount of CaO/SiO₂ has increased from 0.77 to 0.92. These values indicate that Zn (g) arising from the treatment in the hot metal is able to desulphurise the BF carry-over slag, and also participate in partial reduction of FeO, MnO and some SiO₂. The hot metal composition and temperature are given in Table 2.

Table 2: Hot Metal Composition and Temperature (Before and After De-S)

Element	Wt% (Before De-S)	Wt% (After De-S)
C	5.09	4.7
Si	0.3	0.29
S	0.055	0.044
Temperature, °C	1450	1416

The total amount of S arising from the 287 tonne hot metal is 157.8 kg (for 0.055 wt%) of which 31.5 kg of S was removed in this process. From stoichiometrical considerations, 80 kg of ZnO is used up in the De-S reaction with the hot metal. Combining De-S from both the slag and the hot metal, a total of 34 kg of S has been removed, requiring 86 kg of ZnO by stoichiometry, corresponding to a 43% ZnO utilisation. Even at a relatively low input of ZnO, there was violence in the bath. Utilisation of 43% is quite impressive, given no special effort (such as salt coating used with Mg) was made to decrease the violence from the reactions. ZnO losses can be expected because of the violent reactions (assumed from vaporisation of Zn and ZnS and the exothermicity of ZnS formation and from participating in reduction of other oxides). Based on the preliminary recovery value, the amount of ZnO required is around 3.2 kg per THM, which can be possibly decreased by tempering the high rate of reaction. Some of the escaping dust was captured in order to check the composition of the dust. The dust contained 1.11 wt% of ZnS confirming that a ZnS product is formed by De-S reaction and removed from the molten metal/slag into the exhaust gas phase. Much of the dust was made of Fe oxides and metallic Fe (T - Fe of 68%), but also contained minor amounts of C, CaO, MnO and SiO₂ but without any ZnO. The hot metal suffered a temperature loss of 34°C.

The ability of ZnO to achieve slag desulphurisation is very useful, as slag skimming step(s) can be eliminated in the KR process, which will result in a lower treatment time and thus lower both the iron loss and the temperature drop. S reversion problem will also be greatly decreased. Some of the Zn is able to participate in reduction of oxides, thereby decreasing Zn utilisation for the De-S reaction. Recovery of Fe and Mn is only to be seen as an advantage. Loss of Fe in the dust can be decreased by tempering the De-S reaction by optimising the rate of feeding from

further trials. Methods for fully recovering ZnS will be developed in future trials in order to obtain valuable by-products.

Conclusions

Continued growth in the use of galvanised steel and EAF steelmaking have ensured the increasing relevance of Zn in steelmaking and can cause ZnO related problems in the well established recycling chain in the steel industry. This research has provided new insight on the thermochemical data which is of vital value to the steel industry, made even more valuable by providing the possibility of developing low-cost reagents based on ZnO dust for desulphurising hot metal with a number of benefits:

- Reduction in the environmental costs of disposing ZnO laden dust;
- Savings in expensive Mg;
- Increase in iron yield;
- Minimise disruption to the well-established recycling system in the iron steel industry;
- Utilisation of C and lime in the dust;
- Formation of ZnS (g) at $T > 1453$ K results in greater thermodynamic driving force with increasing temperature;
- Elimination of the product ZnS from the hot metal resulting in the renewal of the reaction;
- Reduction in slag skimming time due to removal of ZnS in the gas phase;
- Minimum S reversion problems;
- Formation of Zn vapour *in-situ* in the hot metal from ZnO is advantageous for the reactions;
- Exothermicity of ZnS formation tempered by ZnO reduction (endothermic);
- Low solubility of Zn in hot metal is beneficial to desulphurisation as the amount of S is lowered towards the end of desulphurisation;
- Recycling of ZnO generated within the steel plant towards attaining a zero waste strategy;
- Generation of Zn and/or Zn (containing ZnO) from the dust for direct metallic desulphurisation; and
- Potential availability of concentrated ZnS in the exhaust dust as a valuable by-product.

The availability of enriched ZnO by pre-treatment of steel dust using plasma processes or the Waelz kiln process offers another avenue for using the dust. This will take away the pressure from pre-treatment process to produce high specification ZnO. Preliminary results with pure ZnO have shown promising results as an alternative De-S agent. Provided the steel dust is directly used or ZnO derived from

the dust is used, one can envisage the availability of a low-cost De-S agent that can allow re-use of waste products as valuable reagents. Further trials are required to achieve the full potential of the new process.

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