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

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Introduction

- **ZnO-laden dust in iron & steelmaking**
- **Interaction of Zn with Fe**
- **Desulphurisation of hot metal**
- **Thermodynamic issues for using ZnO (or Zn) as a desulphurising agent**
- **Experiments**
- **Results**
- **Potential Benefits**
- **Ongoing trials and Conclusions**

ZnO-laden dust in iron & steelmaking

- **From: sintering plant; blast furnace, basic oxygen furnace; vacuum degasser; electric arc furnace; millscale**
- **Estimated worldwide at over 30 million tonnes per year of dust containing ZnO**
- **Range of concentration - from few % to over 50 % Zn - but there is a trend towards upgrading**
- **Growth in galvanised steel consumption will make the problem even more serious**

Interaction of Zn with Fe

- **Most of the Zn input escape from iron and steelmaking units as an oxide with the dust**
- **Solubility of Zn in Fe reported to be at parts per million levels**
- **Methods for recovering Zn by reacting agglomerated ZnO-laden dust at the surface of molten iron have been reported**
- **Can ZnO react with sulphur in the hot metal?**

Desulphurization of hot metal

- Sulphur is an unacceptable impurity in steel and the best opportunity for removal is from the hot metal external to the blast furnace
- Commonly removed using Mg (as salt coated granules to moderate the violence) at 0.5 to 1.0 Kg/THM, CaC_2 and CaO at 6-10 Kg/THM, by mono-, co- or multi-injection using lance
- S reduction from over 0.05 % to less than 0.02 %
- Time in minutes: Desulphurisation : 15 ; Analysis : 3 + 3 ; Skimming: 7-9

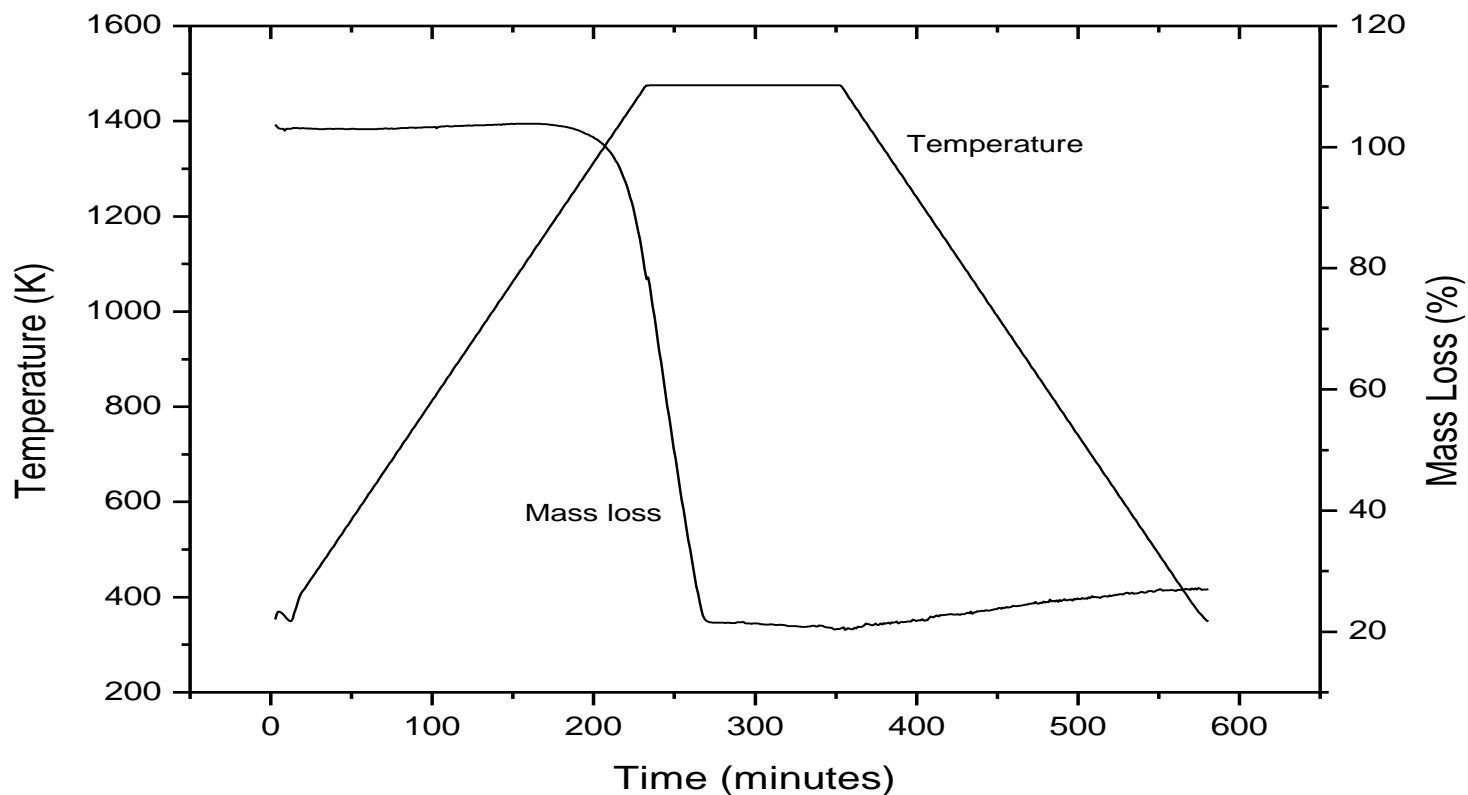
Thermodynamic Issues for Using ZnO as a Desulphurising Agent

- $\text{ZnO} + \underline{\text{S}} \rightarrow \text{ZnS} + \underline{\text{O}}$ at $T > 1450 \text{ K}$
- (1) $\text{ZnO} \rightarrow \text{Zn (g)} + \frac{1}{2} \text{O}_2 \text{ (g)}$
- (2) $\frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \underline{\text{O}}$
- (3) $\underline{\text{S}} \rightarrow \frac{1}{2} \text{S}_2 \text{ (g)}$
- (4) $\text{Zn(g)} + \frac{1}{2} \text{S}_2 \text{ (g)} \rightarrow \text{ZnS (s or g)}$
- Anomaly in the data concerning reaction (4)

Thermodynamic Issues with ZnS

- **Solid ZnS is reported to sublime ~1450 K**
- **From the current thermodynamic data for ZnS formation in the gas and in the solid phase, the calculated sublimation point is 2300 K**
- **Original Richardson & Jeffes data has been extrapolated (uncritically) by many investigators to hot metal temperatures**
- **Experiments are required to resolve the anomaly and establish new free energy data**

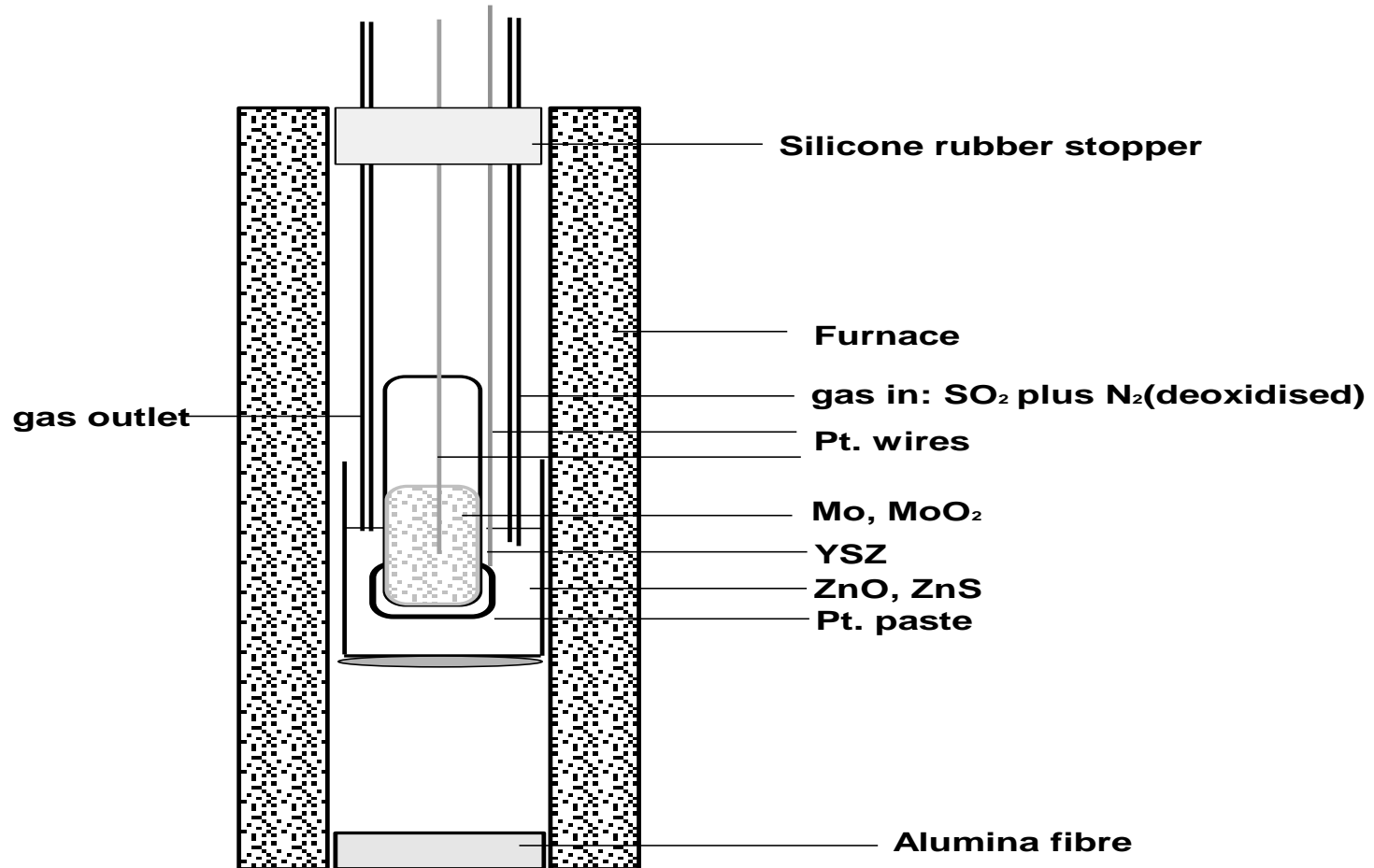
Thermogravimetric Analysis of ZnS in He



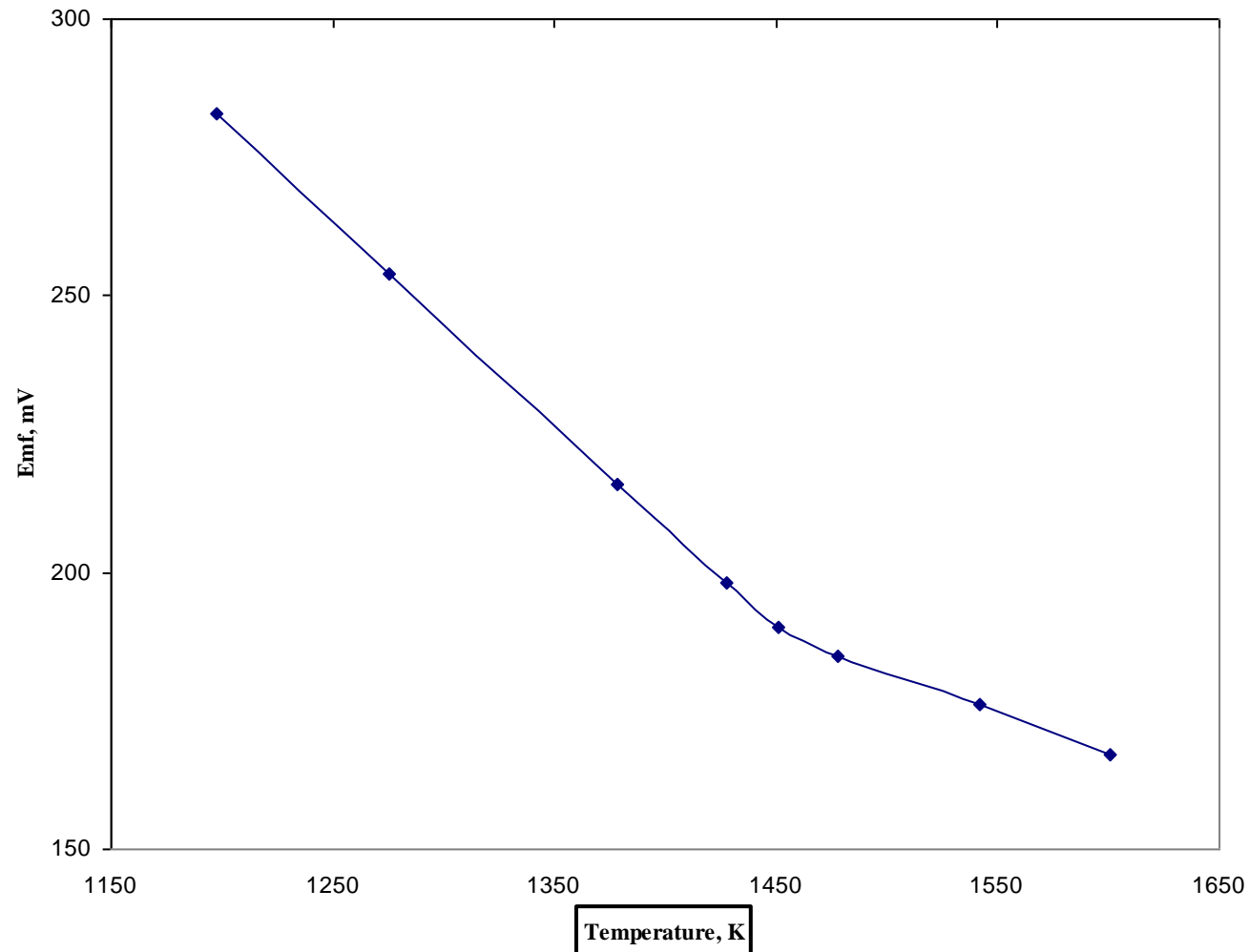
Evaluation of Thermodynamic Data

- Mo, MoO₂ | YSZ | ZnO, ZnS, SO₂ (5000 ppm in nitrogen deoxidised with Mg)
- An Oxygen concentration cell at T: 1123 – 1613 K
- At T > 1453 K, ZnS (s) → ZnS (g), sublimation of ZnS makes the experiment very cumbersome
- Cell designed to allow ZnS to sublime
- It is assumed that pZnS = 1 atm in the cell at T > 1453 K

Cell Design - Schematic



Cell Electromotive Force vs Temperature

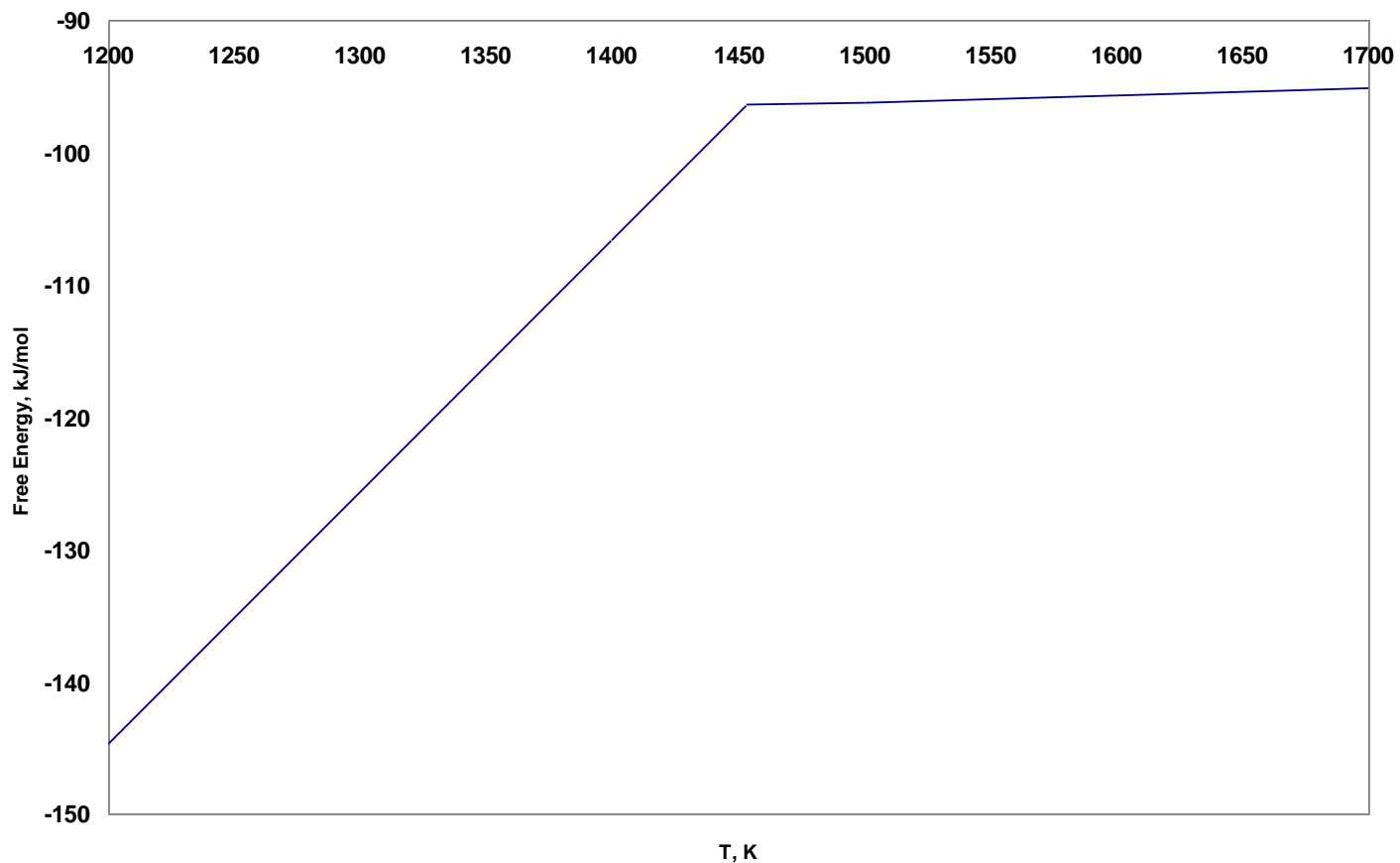


Relevant Thermodynamic Data

- For ZnS (s): $\Delta G^\circ = -373,352 + 190.6 T$ (J)
- For ZnS (g): $\Delta G^\circ = -104,578 + 5.6 T$ (J)
- Estimated Error in above data: $\pm 2,500$ J
- At $T < 1453$ K agreement with the literature data is excellent
- At $T > 1453$ K, enhanced stability for ZnS due to phase change
- At 1700K, in a C-satd. hot metal equilibrium $S < 0.1$ ppm with ZnO, whereas with CaO it is 13 ppm S

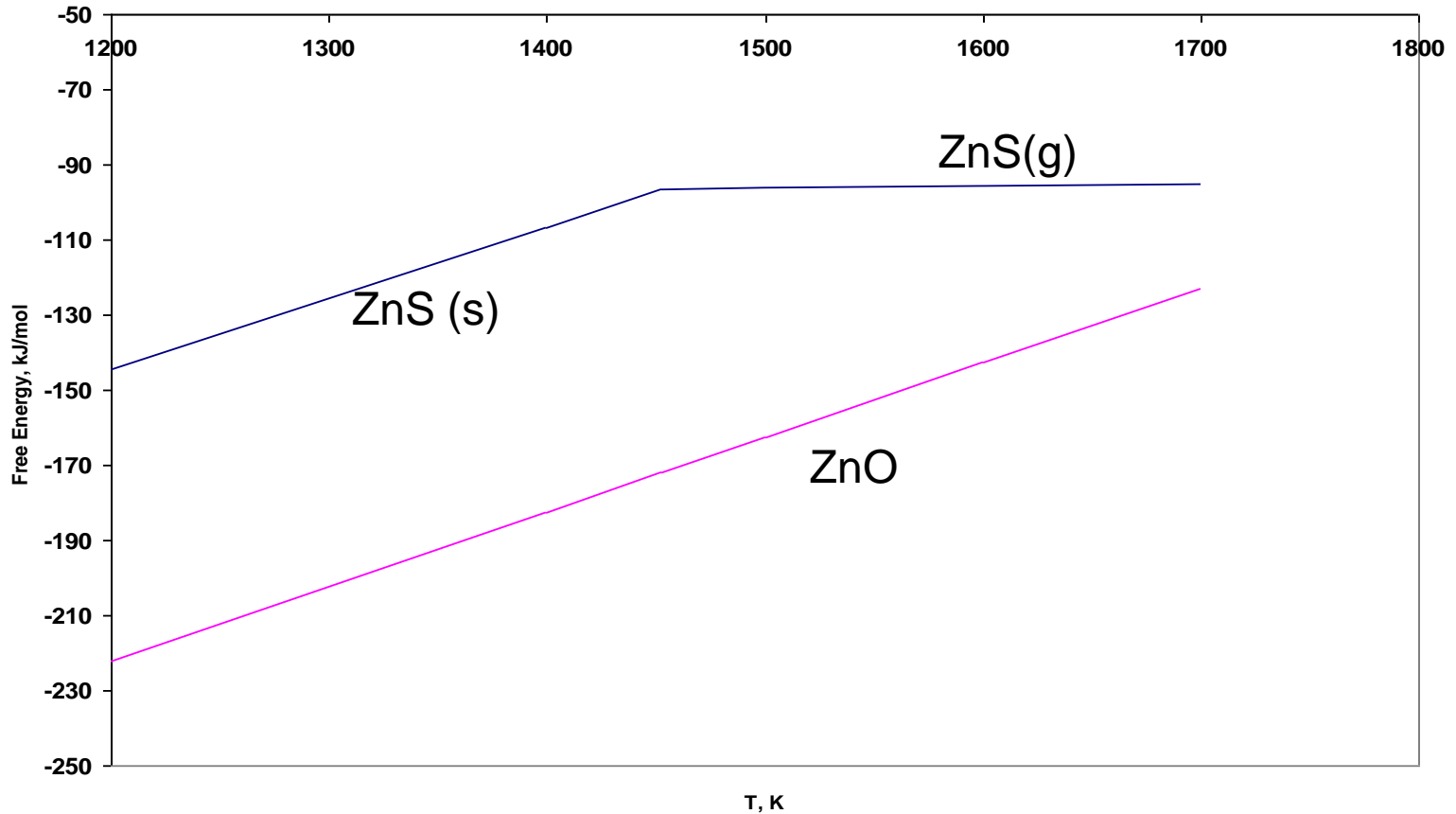
Standard Free Energy of Formation of ZnS

The standard free energy of formation for ZnS(s or g)



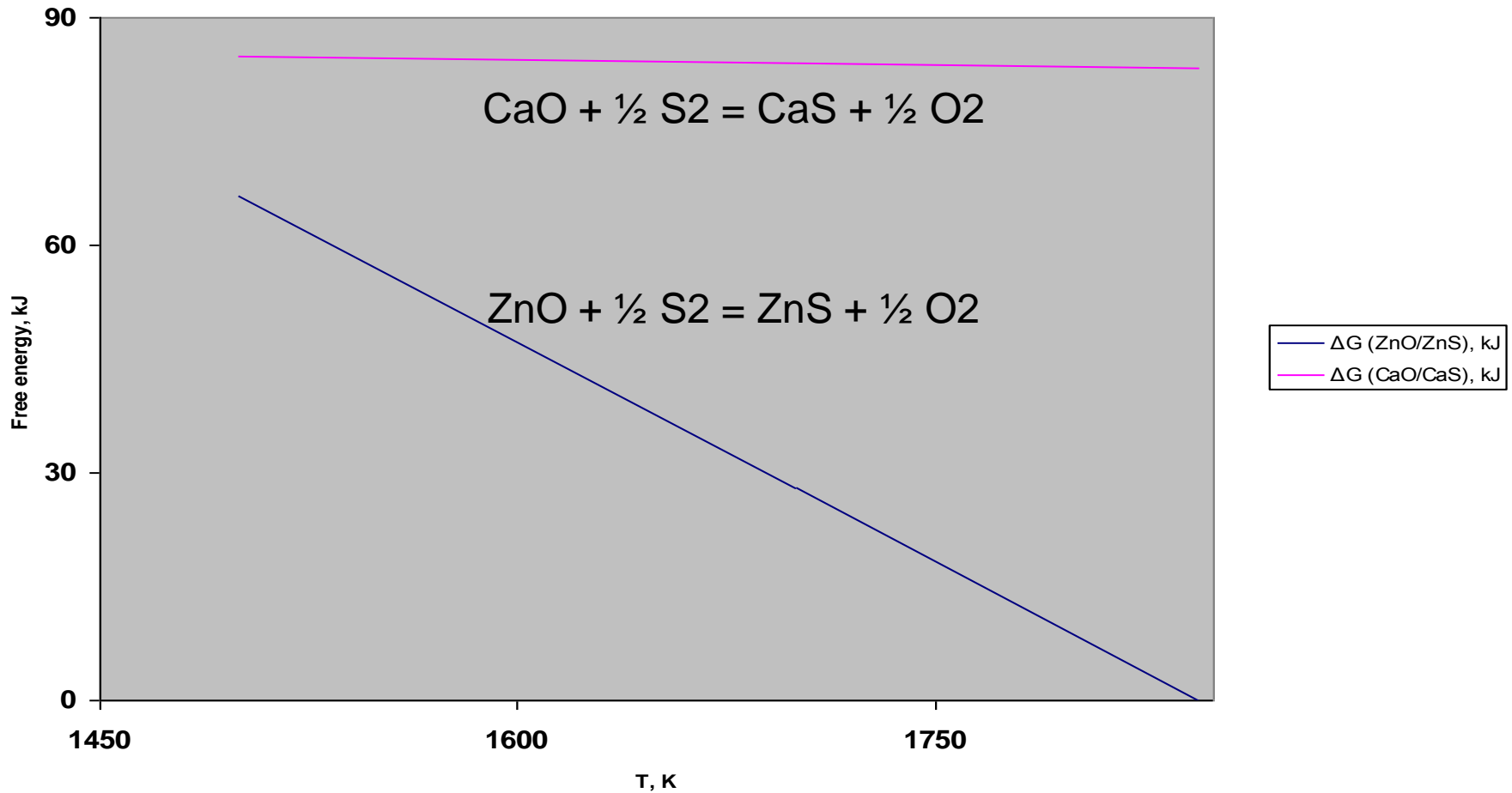
Standard Free Energy of Formation of ZnO and ZnS

The standard free energy of formation of ZnO and ZnS

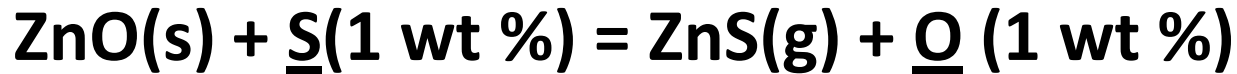


Desulphurization of CaO vs ZnO

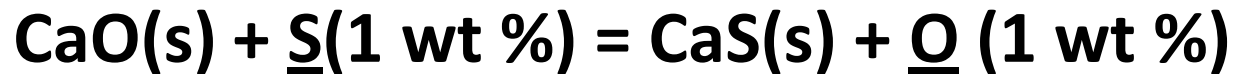
Free Energy of desulphurisation with CaO and ZnO



Desulphurisation

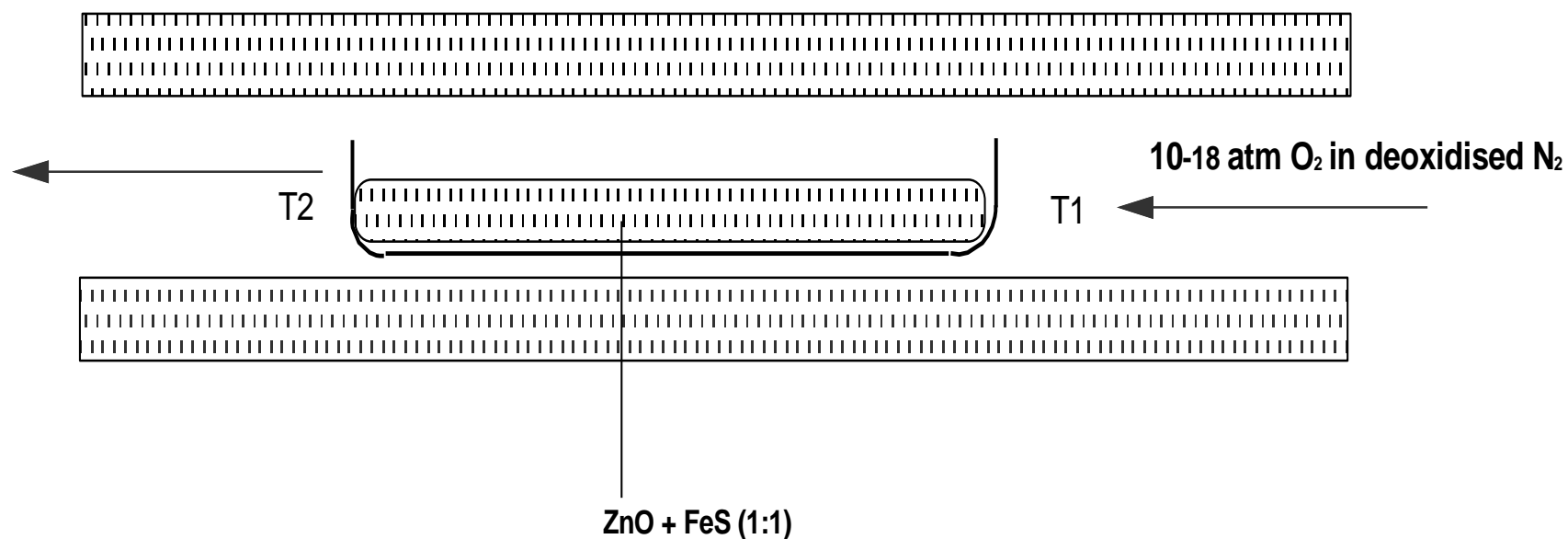


- ❖ At 1700K, $\Delta G^0 = -1685 \text{ J}$
- ❖ $\log h_s = \log h_o - 0.051$
- ❖ In a C-satd. Hot Metal, wt % S = 0.13 ppm

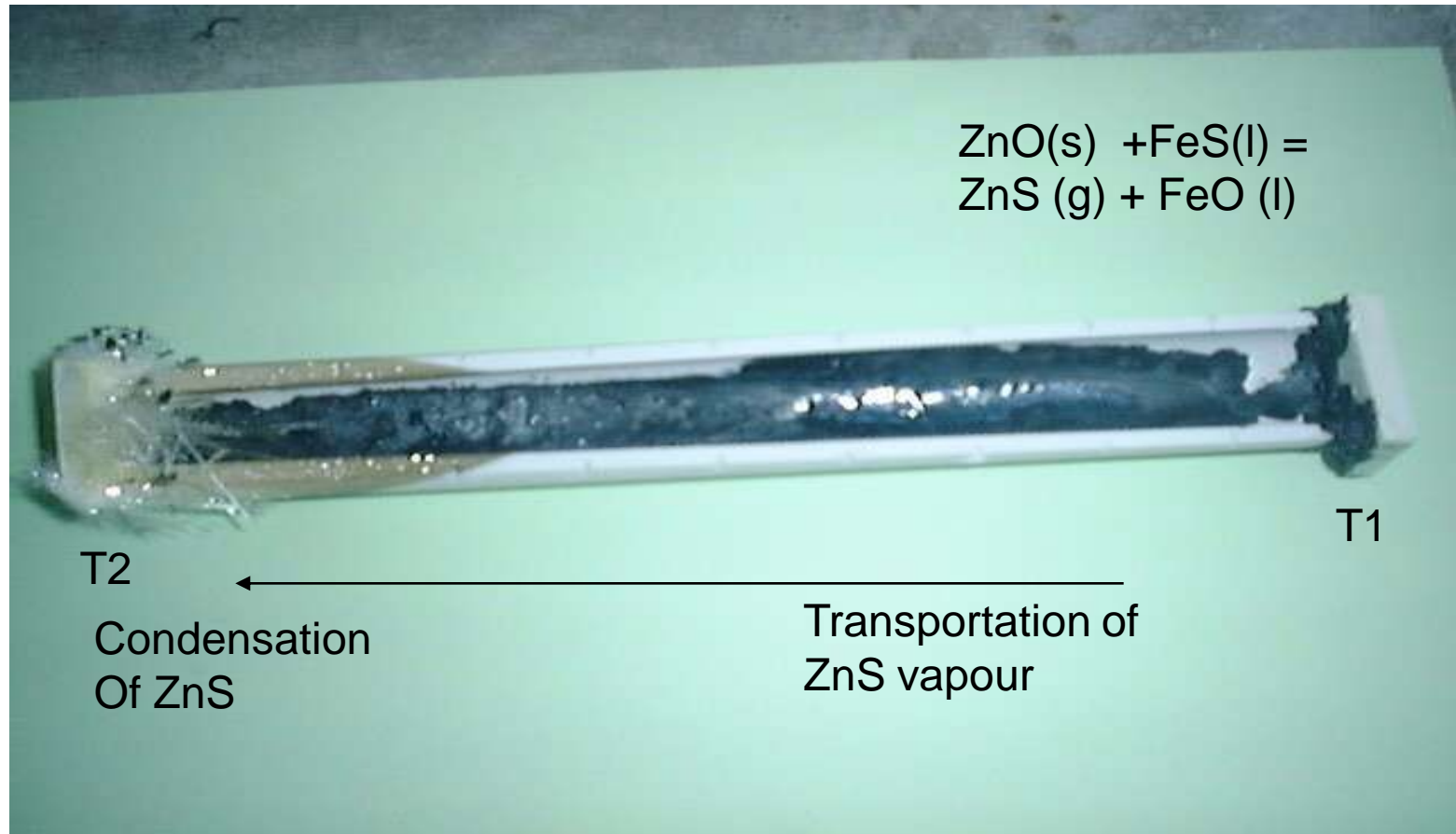


- ❖ At 1700K, $\Delta G^0 = 63,230 \text{ J}$
- ❖ $\log h_s = \log h_o + 2.06$
- ❖ In a C-satd. Hot Metal, wt % S = 13 ppm

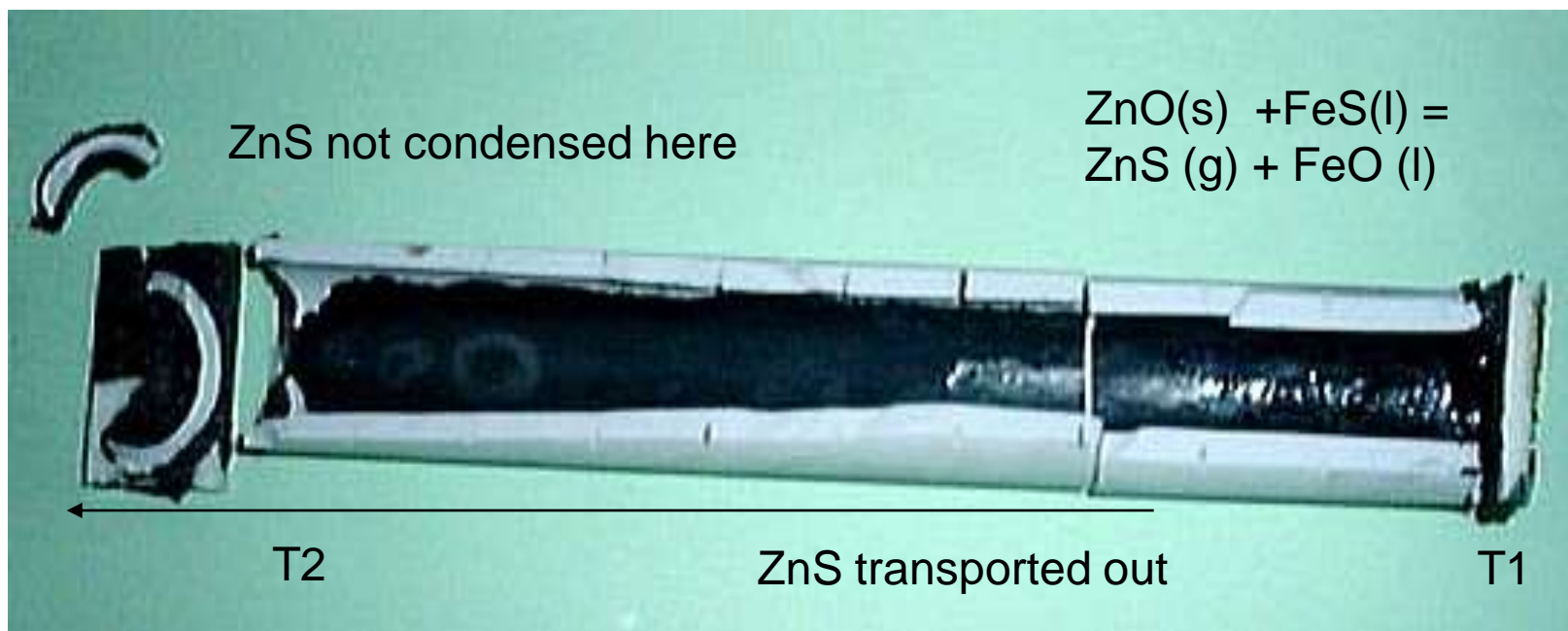
Demonstrate transport of S from the Fe-S phase as ZnS(g)



T1 >1653 K; T2 < 1453 K (ZnS formed at T1 and condensed at T2)



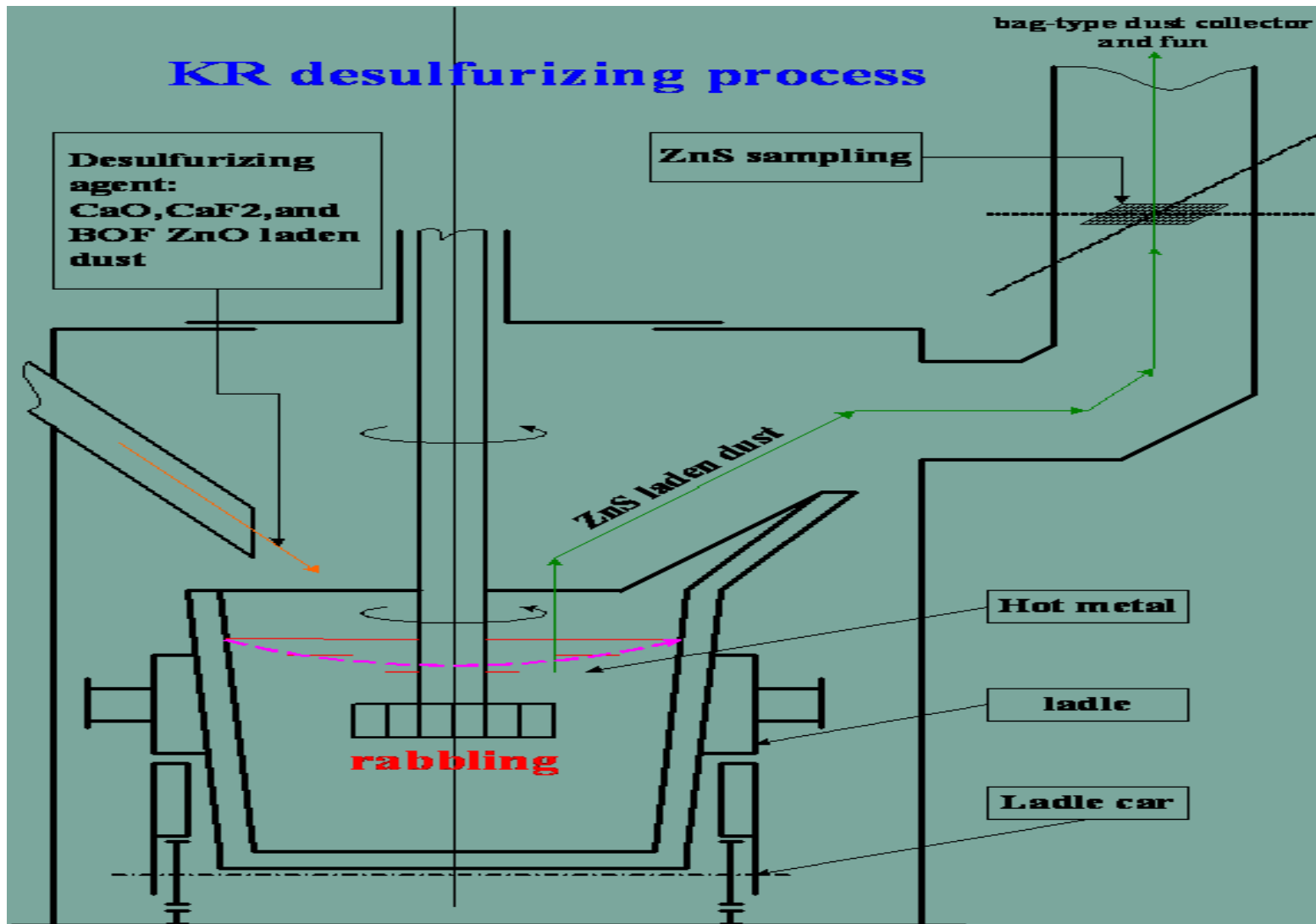
T1: 1473 K and T2: 1653 K; ZnS formed at T1, escaped from the ceramic boat at T2



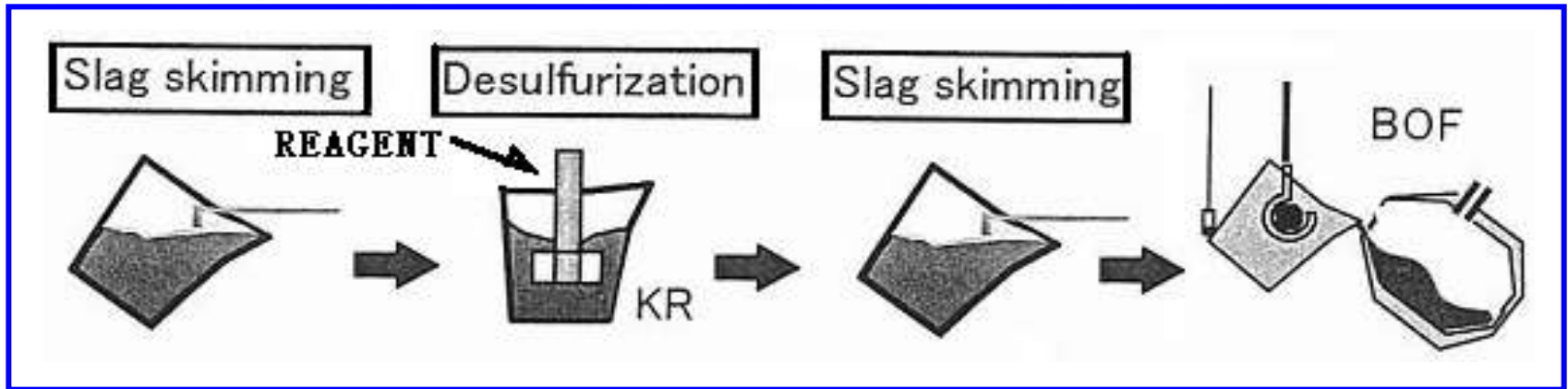
3000 kg scale industrial trial at Teeside Technology Centre: Steel cored wire with ZnO– 20 % S utilization



Desulfurizing Trials at Tang Shan Iron & Steel



The KR Process Steps



Slag Skimming before after de-S process

De-S agent addition with rabbling simultaneously

Desulfurizing Trials at Tang Shan Iron & Steel



Collection of ZnS Dust from Flue Gas



Trial using KR Process



Process Details

Amount of Hot Metal: 287 t containing 0.055 wt % S

Amount of initial carryover slag: 3.1 t

Slag left after 1st skimming: 345 Kg (1.05 wt % S)

**Amount of ZnO added: 200 Kg (@ 0.7 Kg / THM) –
corresponding to 47% of stoichiometric requirement**

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

Hot Metal Composition (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

Process Results

ZnO desulfurized both slag and hot metal, removing 2.35 Kg of S from the slag and 31.5 Kg from the hot metal, for a combined total of 34 Kg S removal, requiring 86 Kg of ZnO by stoichiometry

The calculated ZnO utilization is 43 %! The corresponding ZnO rate is 3.2 Kg / THM

A considerable violence accompanied the reaction

The captured dust (using sieve in the flue) showed 1.11 wt % ZnS, 68 % T-Fe (> 90 % iron oxides), remaining C, CaO, SiO₂, MnO

Benefits

- **Formation of ZnS(g) at $T > 1453$ K results in greater thermodynamic driving force with increasing temperature**
- **The product ZnS is eliminated from the hot metal resulting in the renewal of the reaction**
- **Reduction in slag skimming time due to removal of ZnS**
- **Minimum S reversion problems**
- **Utilization of ZnO from iron & steel dust**

Benefits

- **Formation of Zn vapour in-situ in the hot metal from ZnO is advantageous**
- **Exothermicity of ZnS formation tempered by ZnO reduction**
- **Low solubility of Zn in hot metal is beneficial to minimise desulphurisation fade**
- **Potential availability of concentrated ZnS in the exhaust dust – valuable by-product**
- **Savings in expensive Mg**

Conclusions

Pre-treatment of iron & steel dust generating enriched ZnO (plasma or Waelz-kiln processes) offers a new avenue, taking away the pressure to produce high spec ZnO

Potential availability of low-cost de-S agent from waste products as valuable reagent

Further trials are required to achieve the full potential of the new process

Acknowledgement

Thanks to Jianghua Liu (co-author) and very helpful staff at Tang Shan Iron & Steel for the trials

Papers:

- **R.V. Kumar and F. Tailoka, “On the possibility of utilizing zinc oxide for desulphurising hot metal”, On Waste Processing & Recycling in Mineral Metallurgical Industries, Conf. of Metallurgists, Canadian Inst. Of Metals, “Waste Processing V” ed. By Sr Rao et al, 667-74 (2004).**
- **R.V. Kumar and J. Liu, “Research for using iron and steel making zinc laden dust for desulphurizing hot metal” *Steel Res. Int.*, 81(9), 1-5 (2010).**
- **J Liu and RV Kumar, “Research for using Zn and/or ZnO for desulfurizing hot metal”, 1st UK-China Steel Forum, held at Leicester in July 2010**