## Lecture 25: Reduction smelting of zinc sulphide

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**Key words: imperial smelting process, zinc smelting, heat balance, material balance**

### Preamble

Technique of smelting and converting as applied for copper production is not applicable for production of $\mathrm{Zn}$ from sulphide ore since $\mathrm{ZnS}$ does not melt even at$1500°\mathrm{C}$. $\mathrm{ZnS}$ Concentrate is sinter roasted, that means sintering and roasting of sulphide concentrate occur simultaneously.

The burden Zinc sinter and coke is preheated to about $800°\mathrm{C}$ before it is charged into Imperial Smelting Furnace (here after ISF), which is very similar to the blast furnace. Preheated air is introduced at the tuyeres that reacts with coke to give CO and generates a temperature of about $1300°\mathrm{C}$. Rising CO within the shaft reacts with $\mathrm{ZnO}$ to produce a gas mixture of about $5\%\mathrm{Zn}$, $10\%\ \mathrm{CO_2}$ and $20\%\mathrm{CO}$ and $N_2$.

The hot gas mixture is shock cooled in a lead bath to about $500°\mathrm{C}$ . Zinc condenses and dissolves in lead without reoxidation.

### Materials and heat in balance imperial smelting process

In an imperial smelting blast furnace the sinter consists of $50\%\ \mathrm{ZnO}$, $20\%\ \mathrm{PbO}$, $20\%\ \mathrm{FeO}$ and $10\%\ \mathrm{SiO_2}$. The coke is regarded pure amorphous carbon. All $\mathrm{ZnO}$ is reduced to Zn vapor and $\mathrm{PbO}$ to liquid lead, whereas $\mathrm{FeO}$ and $\mathrm{SiO_2}$ form a molten slag. The gas composition after reduction is 7% $\mathrm{Zn}$ with $\mathrm{CO_2}/\mathrm{CO}$ ratio 0.5.

1. Make a mass balance and calculate wt. of carbon and volume of air and volume composition of top gas.
2. Make an overall heat balance when the raw materials are introduced at 1100K, liquid products are withdrawn at 1600K, and the top gas temperature is 1300K.

### Materials balance

Basis: 1000 kg sinter.

The reduction equations for $\mathrm{ZnO}$ and $\mathrm{PbO}$ can be written by using the moles of $\mathrm{ZnO}$ and $\mathrm{PbO}$ participating in the reaction and taking into account $\mathrm{CO}$: $\mathrm{CO_2}$ ratio in the exit gas is 2:1. This approach will directly give the moles of products. However, other approaches may also be used

| | Kg moles |
|---|---|
| Zn(v) = | 6.173 |
| Pb(l) = | 0.897 |
| $CO_2$ = | 7.070 |
| CO = | 14.140 |
| $N_2$ = | 39.875 |

The exit gas amount as determined from Zn vapour balance is 88.186 kg moles.

The amount of exit gas as determined from the stoichiometric reduction equation is equal to $67.258 \text{ kg moles}$

Difference $20.93 \text{ kg moles}$ is due to excess $O_2$ and excess $N_2$ in the flue gas. Thus the revised composition of exit gas is

| | Kg moles |
|---|---|
| Zn(v) = | 6.173 |
| $O_2$ | 4.40 |
| $CO_2$ = | 7.070 |
| CO = | 14.140 |
| $N_2$ = | 56.405 |

Liquid slag contains $FeO = 2.778 \text{ kg moles}$ and $SiO_2 = 1.667 \text{ kg moles}$

$\text{Amount of coke} = 254.52 \text{ kg}.$

$\text{Amount of air} = 71.40 \text{ kg moles}$

**Heat balance:**

Coke and Zn concentrate enter at 1100K, while air at 298K. The exit gas discharges at 1300K and liquid slag and lead exits at 1600K

Thermo chemical data

$-\Delta H^{\circ}_{ZnO} = 83500 \text{ kcal/kg mol}$

$-\Delta H^{\circ}_{PbO} = 52500 \text{ kcal/kg mol}$

Heat content in $\mathrm{kcal/kg\ mole}$

$\mathrm{H_{1100} - H_{298}|ZnO}$ 9500

$\mathrm{H_{1100} - H_{298}|PbO}$ 10800

$\mathrm{H_{1100} - H_{298}|FeO}$ 10280

$\mathrm{H_{1100} - H_{298}|SiO_2}$ 19940

$\mathrm{H_{1100} - H_{298}|C}$ 3320

$\mathrm{H_{1300} - H_{298}|Zn(V)}$ 36160

$\mathrm{H_{1300} - H_{298}|CO_2}$ 12010

$\mathrm{H_{1300} - H_{298}|CO}$ 7460

$\mathrm{H_{1300} - H_{298}|N_2}$ 7500

$\mathrm{H_{1300} - H_{298}|O_2}$ 7873

$\mathrm{H_{1600} - H_{298}|Pb}$ 10110

$\mathrm{H_{1600} - H_{298}|FeO}$ 11990

$\mathrm{H_{1600} - H_{298}|SiO_2}$ 21100

Heat of formation of $\mathrm{2FeO.SiO_2 = 153\ kcal/kg\ FeO}$

One can perform heat balance.

| Heat input | (kcal) | Heat output | (kcal) |
|---|---|---|---|
| Heat of reaction | 562539 | Exit gas | 871289 |
| Sensible heat | 200687 | Lead | 9069 |
| Heat of slag formation | 30602 | Slag | 68481 |
| Total | 793828 | Heat losses* | 79382 |
| | | | 1028221 |

* Heat losses are normally taken as $10\%$ of heat inputs if not mentioned in the problem.

We note there is heat deficit to the amount 234393 kcal. There are several ways to meet the heat deficit. One of the ways is to preheat the air. If average Cp of air is $7.5\ \mathrm{kcal\ kg\ mole^{-1}°C^{-1}}$ then Preheat air temperature is $463°\mathrm{C}$.

**Analysis of heat balance**

54.8% of the total heat is supplied through the heat of reaction. Preheating of air and the reactants bring 22.8% and 19.5% respectively of the total heat requirements. Heat supplied due to formation of slag is 2.9% of total requirement.

Heat carried by Zn vapor = 21.7%; vapors are shocked and heat recovery is within lead bath.

Amount of heat is carried away by gases $CO + CO_2 + N_2$ which is equal to 63.1%. Once the gases are shock cooled, temperature of gases $CO+CO_2+N_2$ must come down. Information on this temperature will help to consider waste heat recovery