

Appendix C – Energy balance in the preparation zone

This section presents the energy balance in the preparation zone (upper part of the blast furnace). In order to keep consistency with the rest of the methodology, we work with kcal/mol_{Fe} units (which are the units used by Rist in his original work). The energy balance follows Eq.(145), where p' is the heat removed by the staves, the term $q_{rwc}y_{rwc}$ is the heat consumed during the reduction of hematite to wüstite, the term $q_{rmc}y_{rmc}$ is the heat released by the reduction of hematite to magnetite, the term $q'_{\epsilon}y_{wgs}$ is the heat consumed by the reverse water-gas shift reaction, and the term $\sum q_{s,nr,i}y_{nr,i}$ stands for the sensible heat of the compounds that do not react.

$$0 = p' + q_{rwc}y_{rwc} + q_{rmc}y_{rmc} + q'_{\epsilon}y_{wgs} + \sum q_{s,nr,i}y_{nr,i} \quad (145)$$

The term p' is calculated in a similar way that p , but in this case the fraction of heat removed is $(1 - \theta_{st})$ instead of θ_{st} (Eq.(146)). A typical value for θ_{st} is around 0.7 [11], and the variable $n_{HM,Fe}$ is computed by Eq.(74).

$$p' = (1 - \theta_{st}) \cdot q_{st}/n_{HM,Fe} \quad (146)$$

The term $q_{rwc}y_{rwc}$ is calculated by Eq.(147) and Eq.(148). The former is the heat consumed by the reduction of hematite to wüstite by carbon monoxide (Eq.(1) plus Eq.(3)), including also the heat exchange between reactants that gives the final temperature of the products. This is given as a function of the temperature of the iron ore entering the blast furnace ($h_{Fe_2O_3}$ calculated at T_{IN}), the temperature of the reactant CO coming from the middle zone (h_{CO} calculated at T_R), the final temperature of the CO₂ exiting the top of the furnace (h_{CO_2} calculated at T_{BFG}) and the temperature of the wüstite descending to the elaboration zone (h_{FeO} calculated at $T_R - \Delta T_R$) (Eq.(147)). Regarding y_{rwc} , it represents the number of moles of FeO produced through this process. This is calculated as the difference between the moles of FeO in the thermal reserve zone and the moles of FeO that were already present in the burden since the beginning (Eq.(148)).

$$q_{rwc} = 0.5h_{Fe_2O_3} + 0.5h_{CO} - h_{FeO} - 0.5h_{CO_2} \quad (147)$$

$$y_{rwc} = (n_{R,FeO} - (n_{IO,FeO} + n_{K,FeO}))/n_{HM,Fe} \quad (148)$$

The term $q_{rmc}y_{rmc}$ is calculated by Eq.(149) and Eq.(150). The former is the heat released by the reduction of hematite to magnetite by carbon monoxide (Eq. (1)), including also the heat exchange between reactants and products at different temperature. This is given as a function of the temperature of the iron ore entering the blast furnace ($h_{Fe_2O_3}$ calculated at T_{IN}), the temperature of the reactant CO coming from the middle zone (h_{CO} calculated at T_R), the final temperature of the CO₂ exiting the top of the furnace (h_{CO_2} calculated at T_{BFG}) and the temperature of the magnetite descending to the elaboration zone ($h_{Fe_3O_4}$ calculated at $T_R - \Delta T_R$) (Eq.(149)). The term y_{rmc} is the number of moles of Fe₃O₄ produced through this process. This corresponds to the number of moles of Fe₃O₄ existing in the thermal reserve zone (point R), since no magnetite is originally in the burden.

$$q_{rmc} = 1.5h_{Fe_2O_3} + 0.5h_{CO} - h_{Fe_3O_4} - 0.5h_{CO_2} \quad (149)$$

$$y_{rmc} = n_{R,Fe_3O_4}/n_{HM,Fe} \quad (150)$$

The term $q'_{\epsilon}y_{wgs}$ is the heat consumed by the reverse water-gas shift reaction in the preparation zone. As occurred in the energy balance of the elaboration zone, the term related to this reaction is used to correct the calculation of the energy involved in the reduction of iron oxides, since it was assumed at first that it took place only by CO. Thanks to this term we consider that some part of the reduction takes place by hydrogen. In other words, Eq.(1) plus the reverse of Eq.(7) is equal to Eq.(2) for the reduction to magnetite, and the same occurs for the reduction to wüstite. Additionally, this term takes into account the H₂ converted to H₂O because of the water-gas shift reaction itself trying to reach equilibrium (i.e., iron oxide reduction is not the only responsible of the consumption of H₂). The variable q'_{ϵ} is calculated as Eq.(151), where the different temperature of reactants and products is taken into account (h_{CO_2} and h_{H_2} calculated at T_R , and h_{CO} and h_{H_2O} calculated at T_{BFG}). The variable y_{wgs} is the number of moles of H₂ reacting in the preparation zone. This is unknown because the water-gas shift reaction does not achieve equilibrium in this zone. We write it as a fraction of the H₂ available at point R. The percentage of H₂ consumed will be such that the energy balance is fulfilled, since p' is known.

$$q'_{\epsilon} = h_{CO_2} + h_{H_2} - h_{CO} - h_{H_2O} \quad (151)$$

$$y_{wgs} = \Phi n_{R,H_2}/n_{HM,Fe} \quad (152)$$

The summation $\sum q_{s,nr,i}y_{nr,i}$ stands for the sensible heat of the compounds that do not react. In the solid phase we are going to consider SiO₂, Al₂O₃, CaO, MgO, C, and the FeO entering with the burden at the beginning (we neglect other minor components). In the gas phase we have the N₂ and H₂O originally coming from the point R, and the non-consumed fractions of CO, CO₂ and H₂. The variables $y_{nr,i}$ are computed by Eq.(153) to Eq.(163).

$$y_{nr,SiO_2} = (n_{IO,SiO_2} + n_{K,SiO_2})/n_{HM,Fe} \quad (153)$$

$$y_{nr,Al_2O_3} = (n_{IO,Al_2O_3} + n_{K,Al_2O_3})/n_{HM,Fe} \quad (154)$$

$$y_{nr,CaO} = (n_{IO,CaO} + n_{K,CaO})/n_{HM,Fe} \quad (155)$$

$$y_{nr,MgO} = (n_{IO,MgO} + n_{K,MgO})/n_{HM,Fe} \quad (156)$$

$$y_{nr,C} = (n_{IO,C} + n_{K,C})/n_{HM,Fe} \quad (157)$$

$$y_{nr,FeO} = (n_{IO,FeO} + n_{K,FeO})/n_{HM,Fe} \quad (158)$$

$$y_{nr,N_2} = n_{R,N_2}/n_{HM,Fe} \quad (159)$$

$$y_{nr,CO_2} = n_{R,CO_2}/n_{HM,Fe} - y_{wgs} \quad (160)$$

$$y_{nr,CO} = n_{R,CO}/n_{HM,Fe} - 0.5y_{rwc} - 0.5y_{rmc} \quad (161)$$

$$y_{nr,H_2O} = n_{R,H_2O}/n_{HM,Fe} \quad (162)$$

$$y_{nr,H_2} = n_{R,H_2}/n_{HM,Fe} - y_{wgs} \quad (163)$$

The variables $q_{s,nr,i}$ are adjusted to Eq.(164) (T given in °C) and tabulated in **Table 9**. For solid phase, T_1 is T_{IN} and T_2 is $T_R - \Delta T_R$, while for gas phase T_1 is T_R and T_2 is T_{BFG} . Moreover, the enthalpies appearing in the different q terms of Eq.(147), Eq.(149) and Eq.(151) are adjusted to Eq.(165) (T given in °C), and the parameters are given in **Table 9**.

$$q_{s,nr,i} = a_0 + a_1(T_1 - T_2) + a_2(T_1^2 - T_2^2) + a_3(T_1^3 - T_2^3) + a_4(T_1^4 - T_2^4) + a_5(T_1^5 - T_2^5) \quad (164)$$

$$h = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 + a_5T^5 \quad (165)$$

Table 9. Parameters of Eq.(164) and Eq.(165) for the calculation of sensible heats, enthalpies and entropies. See units in the nomenclature list.

Term	Eq.	a_0	$a_1 \cdot 10^3$	$a_2 \cdot 10^6$	$a_3 \cdot 10^9$	$a_4 \cdot 10^{13}$	$a_5 \cdot 10^{16}$
h_{CO}	(165)	-26.590776	6.892443	0.351944	0.760803	-5.532971	1.161065
h_{CO_2}	(165)	-94.287539	8.891736	4.603344	-2.216655	6.571122	-0.900405
h_{FeO}	(165)	-65.318709	11.893590	1.896629	-0.129837	-2.104974	0.630635
$h_{Fe_2O_3}$	(165)	-197.685233	22.975743	27.962301	-25.909694	103.346475	-14.858752
$h_{Fe_3O_4}$	(165)	-267.705411	22.248252	92.414124	-113.039791	581.139433	-107.281713
h_{H_2}	(165)	-0.177166	7.013815	-0.220743	0.416396	-0.735801	-0.091152
h_{H_2O}	(165)	-58.019687	8.056125	0.593617	1.015110	-4.968145	0.737172
h_{N_2}	(165)	-0.173848	6.926795	0.077295	0.984240	-6.296343	1.254892
q_{s,nr,SiO_2}	(164)	0	15.732726	0.714133	0	0	0
q_{s,nr,Al_2O_3}	(164)	0	25.561357	2.478549	0	0	0
$q_{s,nr,CaO}$	(164)	0	11.584708	0.772859	0	0	0
$q_{s,nr,MgO}$	(164)	0	10.895662	0.762575	0	0	0
$q_{s,nr,C}$	(164)	0	1.892676	4.302515	-2.533624	7.781074	-0.945155
$q_{s,nr,FeO}$	(164)	0	11.893590	1.896629	-0.129837	-2.104974	0.630635
q_{s,nr,N_2}	(164)	0	6.926795	0.077295	0.984240	-6.296343	1.254892
q_{s,nr,CO_2}	(164)	0	8.891736	4.603344	-2.216655	6.571122	-0.900405
$q_{s,nr,CO}$	(164)	0	6.892443	0.351944	0.760803	-5.532971	1.161065
q_{s,nr,H_2O}	(164)	0	8.056125	0.593617	1.015110	-4.968145	0.737172
q_{s,nr,H_2}	(164)	0	7.013815	-0.220743	0.416396	-0.735801	-0.091152
s_{CO}	(165)	0.021170	0.018098	0.009241	0.002166	0	0
s_{CO_2}	(165)	0.000277	0.026154	0.011729	0.002557	0	0
s_{H_2}	(165)	-0.000143	0.017941	0.009841	0.002405	0	0
s_{H_2O}	(165)	-0.010844	0.021117	0.010258	0.002450	0	0

When trying to solve this energy balance, we found 8 additional unknown variables related to the mole streams at point R (solids streams $n_{R,FeO}$, n_{R,Fe_3O_4} , gas streams n_{R,N_2} , n_{R,CO_2} , $n_{R,CO}$, n_{R,H_2O} , n_{R,H_2} , and the fraction of H_2 consumed, Φ). The solid streams of FeO and Fe_3O_4 at point R can be found through a balance of Fe in the upper zone (Eq.(166)) and the ordinate Y_R of the operating line (Eq.(167)). The gas streams are calculated through the mass balances of Eq.(168) to Eq.(172) (it must be noted that the variables n_{BFG} do not add additional unknown variables, since they appear in the mole balances of the individual elements mentioned in the section 4.3.3 Blast furnace gas composition). The last equation is the relation between CO, CO_2 , H_2 , and H_2O in the thermal reserve zone (at point R), where the water-gas shift reaction is at equilibrium (Eq.(173)).

$$0.947(n_{IO,FeO} + n_{K,FeO}) + 2(n_{IO,Fe_2O_3} + n_{K,Fe_2O_3}) = 0.947n_{R,FeO} + 3n_{R,Fe_3O_4} \quad (166)$$

$$Y_R = (4n_{R,Fe_3O_4} + n_{R,FeO})/(3n_{R,Fe_3O_4} + 0.947n_{R,FeO}) \quad (167)$$

$$n_{BFG,N_2} = n_{R,N_2} \quad (168)$$

$$n_{BFG,CO_2} = n_{R,CO_2} + 0.5(n_{R,FeO} - (n_{IO,FeO} + n_{K,FeO})) + 0.5n_{R,Fe_3O_4} - \Phi n_{R,H_2} \quad (169)$$

$$n_{BFG,CO} = n_{R,CO} - 0.5(n_{R,FeO} - (n_{IO,FeO} + n_{K,FeO})) - 0.5n_{R,Fe_3O_4} + \Phi n_{R,H_2} \quad (170)$$

$$n_{BFG,H_2O} = n_{R,H_2O} + \Phi n_{R,H_2} \quad (171)$$

$$n_{BFG,H_2} = n_{R,H_2}(1 - \Phi) \quad (172)$$

$$K_{eq} = (n_{R,CO_2}n_{R,H_2})/(n_{R,CO}n_{R,H_2O}) \quad (173)$$

In order to calculate the equilibrium constant K_{eq} , the Eq.(174) to Eq.(176) are used, with the temperature in K. The ideal gas constant is $R = 0.001987207$ kcal/(mol K). The equilibrium constant K_{eq} has to be calculated at T_R .

$$K_{\text{eq}} = \exp\left(-\frac{\Delta G}{RT}\right) \quad (174)$$

$$\Delta G = g_{\text{CO}_2} + g_{\text{H}_2} - g_{\text{CO}} - g_{\text{H}_2\text{O}} \quad (175)$$

$$g_i = h_i - Ts_i \quad (176)$$

The enthalpies and entropies are adjusted to Eq. (165) and tabulated in **Table 9**.