

MATHEMATICAL MODELLING OF SHAFT BASED DIRECT REDUCTION PROCESSES OF IRON MANUFACTURE WITH RECIRCULATION OF MOISTURE FREE FLUE GASES

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Introduction

Shaft furnaces account for over 80 percent of the world production of the directly reduced iron that is fed to an electric arc furnace as an alternative to the blast furnace - basic oxygen steelmaking route. The process is characterised by high rates of production as well as high degrees of metallisation of the product for its economic melting in the electric arc furnace for its survival in the present day competitive world. This is best done by keeping the amount of hot reducing gases such as CO and H₂ well above the theoretical minimum as the same would tend to ensure rapid preheating of the incoming uniformly sized burden materials and the accompanying high rates of iron ore reduction. The unutilised portions of CO and H₂ in the flue gases are partly recycled back to the furnace through a reformer where CO₂ in flue gases is used to convert the natural gas into CO and H₂ at around 1000C, and partly used as fuel to meet the energy requirements of the reformer. As the flue gases are to be cooled to get rid of the dust particles, most of the water vapours, present in the gases as a result of reduction of iron ore by hydrogen in the shaft, are removed by condensation. A simple flow sheet of the process is shown schematically in Fig. 1 while the reactions occurring in various stages of the process are summarised in Table 1. Nomenclature used in the text is explained at the end of the paper. The appropriate thermodynamic and enthalpy data of species of interest are given in Table 2.

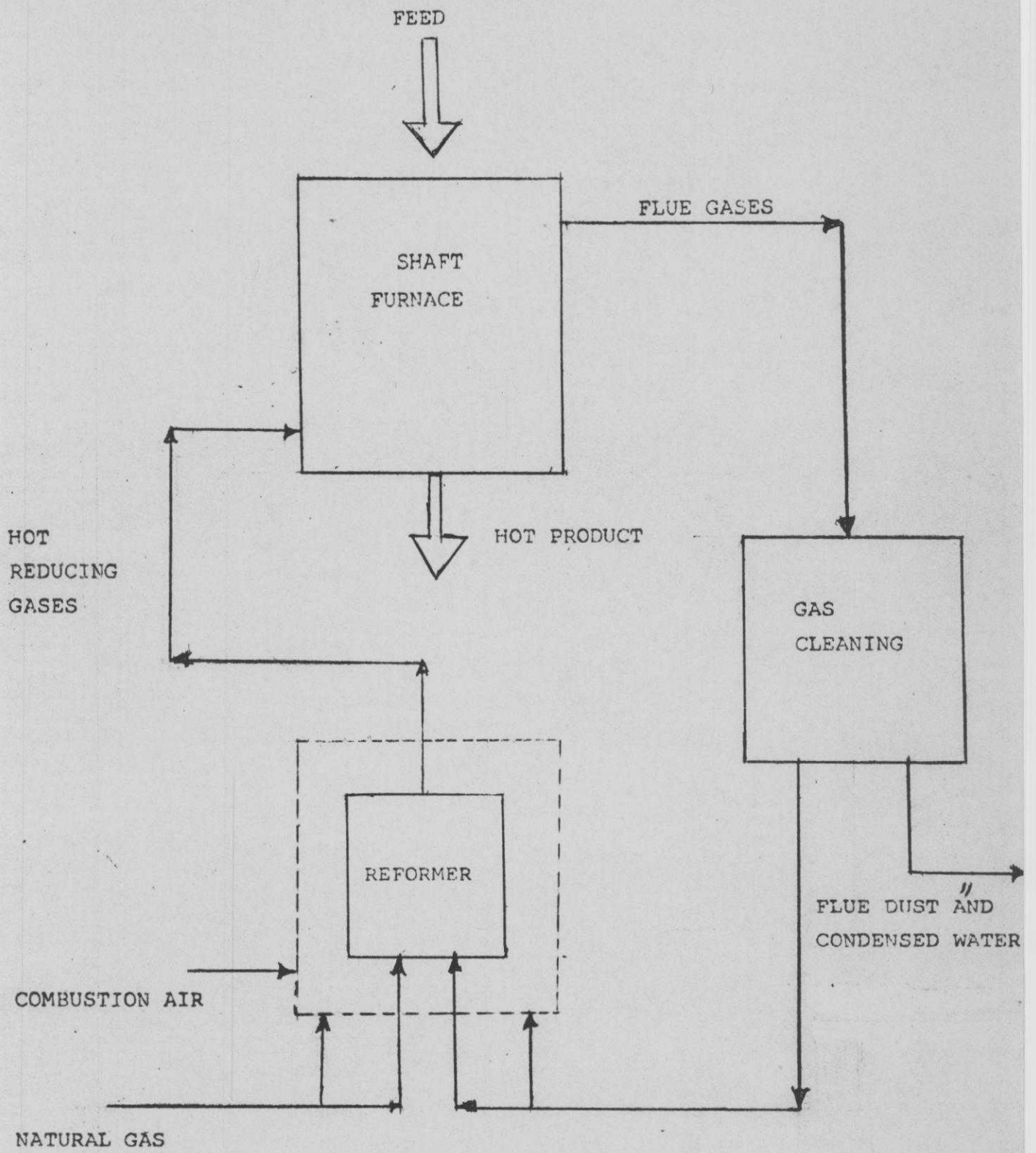


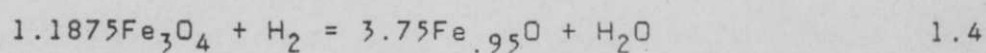
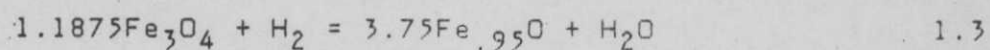
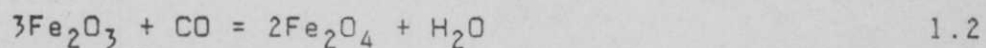
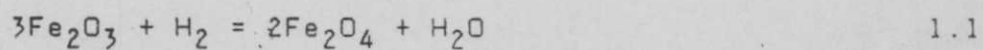
FIG.1 Schematic of the Flow Sheet of a Shaft Based Direct Reduction Process with Recirculation of Moisture Free Flue Gases.

TABLE 1

Chemical Reactions Occurring in the Direct Reduction Process of
Iron Manufacture

Shaft

Pre reduction of Iron ore



Primary Reduction



Water Gas Shift Reaction



Reformer Reaction



Water Condensation

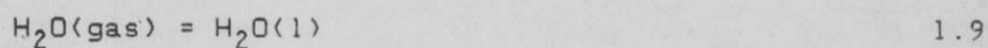


TABLE 2

Thermodynamic and Enthalpy data of Species of Interest

$$C_p = a + bt/1000 - C \times 10^5/T^2 \text{ Kcal/Kmole}^\circ \text{ K}$$

Specy	Free energies of formation Kcal/Kmole ^o	Heat of formation at 298K (-KCal/mole)	Sp. Heat capacit		
			a	b	c
H ₂	-	-	6.52	0.78	-.12
H ₂ O	-56850 + 13.12T	57.8	7.30	2.46	-
CO	-26760 - 20.98T	26.42	6.79	0.98	0.11
CO ₂	-94260 - 0.27T'	94.05	10.57	2.10	2.06
CH ₄	-21550 + 26.16T	17.89	5.67	11.44	0.46
Fe(25-760C)	-	-	3.04	7.58	-.60
760-910C			11.113	-	-
910-1400C			5.80	1.98	-
Fe ₉₅ O	-63200 + 15.47T	63.5	11.66	2.00	0.67
Fe ₃ O ₄ (25-600C)	-265660 + 76.81T	266.8	21.88	48.2	-
(600-1537C)	-261200 + 71.36T		48.0	-	-
Fe ₂ O ₃ (25-677)	-195450 + 61.38T	196.2	23.49	18.6	3.55
677-777			36.00	-	-
777-1537	-192500 + 58.30T		31.71	1.76	-

Ref: Making, Shaping and Treating of Steel 9th edition, editor HE McGani
U.S. Steel 1971

Mathematical Model

Any mathematical analysis of the process would entail the following:

- (1) reduction of iron ore in the shaft
- (2) Enthalpy balance in the shaft
- (3) reforming of natural gas
- (4) Energy balance for the reformer

Assuming that there are no undecomposed hydrocarbons left in the freshly generated reducing gases from the reformer, no carbon deposition in the shaft, all water vapours in flue gases are removed by condensation, and there are no volatiles or free moisture present in the burden materials; carbon, hydrogen and oxygen atom balances for the overall system give the following:

$$X = (1 - F) (b_3 + b_4) n \quad (1)$$

$$2X = [b_2 + (1 - F)b_1] n \quad (2)$$

$$Y = [(b_2 + (1 - F) (b_3 + 2b_4))] n \quad (3)$$

n is the amount of reducing gases being passed, X natural gas fed to the reformer, Y the amount of oxygen atoms removed, all expressed per Kg-mole of iron in the system, and b_1 , b_2 , b_3 and b_4 are mole fractions of H_2 , H_2O , CO and CO_2 in the flue gases of the shaft. If the weight fractions of iron in the product and burden are known, value of Y may be determined as follows:

$$Y = 56 \left[\frac{1}{f_b} - \frac{1}{f_p} \right] / 16 \quad (4)$$

The degree of metallisation of the product, may be found as follows:

$$M = 1.0 - (1.5 - Y) \times 0.95 \quad (5)$$

It is assumed that there is no other oxide present other than Fe_2O_3 which is reduced by H_2 or CO in the shaft, and any

unreduced iron in the product is present as $Fe_{.95}O$ phase.

The two additional equations which are needed to solve for b_1 to b_4 and n in terms of known or assumed parameters such as X , Y and F may be obtained as follows:

$$b_1 + b_2 + b_3 + b_4 = 1 \quad (6)$$

$$b_1/b_2 = \beta b_3/b_4 \quad (7)$$

Value of β depends upon the extent to which iron ore reduction occurs by CO or H_2 gas in the upper parts of the shaft where the water gas shift reaction may not be reaching equilibrium. Hydrogen being a smaller molecule than CO gas may take part in the reduction reaction more easily but the water gas shift reaction being exothermic in nature is favoured at low temperatures. For these reasons, the value of β may be taken to be equal or less than the theoretical value determined by assuming that the water gas shift reaction equilibrium prevails in the flue gases. The theoretical values of β as a function of temperature are summarised in Table 3. Values of b_1 to b_4 and n as calculated from the above model equations must satisfy the following:

$$(b_2 + b_4)n \geq Y \quad (8)$$

$$Fb_4n \geq X \quad (9)$$

The composition of reducing gases passed to the shaft is calculated by making the material balances for the shaft alone i.e.

$$a_1 + a_2 = b_1 + b_2 \quad (10)$$

$$a_3 + a_4 = b_3 + b_4 \quad (11)$$

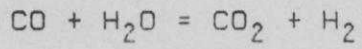
$$a_1 + a_3 = b_1 + b_3 + Y/n \quad (12)$$

and

$$a_1/a_2 = k a_3/a_4 \quad (13)$$

TABLE 3

Equilibrium Constant for the Water Gas Shift Reaction



$$\log k_{\text{wgsr}} = -1.66 + 1890/T$$

$$k_{\text{wgsr}} = [\text{PH}_2/\text{PH}_2\text{O}] / [\text{PCO}/\text{PCO}_2]$$

T		k_{wgsr}
$^{\circ}\text{C}$	$^{\circ}\text{K}$	
400	673	14.0
500	773	6.10
600	873	3.20
700	973	1.92
800	1073	1.26
900	1173	0.89
1000	1273	0.67

Value of k may be taken to be same as the value of the water gas shift reaction equilibrium constant (Table 3).

The calculated amount of the reducing gases passed for a given set of X , F , Y and B values must not be below the theoretical minimum value determined from the thermodynamic considerations i.e.

$$n \geq \frac{M}{\frac{(a_1/k_1 - a_2)}{1 + k_1} + \frac{(a_3/k_2 - a_4)}{1 + k_2}} \quad (13)$$

Values of k_1 and k_2 correspond to the equilibrium constants for the reduction of $Fe_{.95}O$ phase by H_2 and CO respectively at around 1200K in the shaft i.e.

$$\log K_1 = -952/T + .514 \quad (14)$$

$$\log K_2 = 941/T - 1.15 \quad (15)$$

After determining the amount and composition of both the flue gases and reducing gases, one may carry out a heat balance for the shaft to determine the temperature of flue gases. Details of the model and equations developed are given in Table 4. Any additional amount of natural gas that is required for combustion purposes to supply heat in addition to the heat supplied by combustion of CO and H_2 of the left over flue gases may be obtained by considering a heat balance for the reformer if the thermal efficiency of the same is known. Details are included in Table 5. The profiles of the gas temperature, solid temperature and composition of the gas in the shaft may be determined next by developing the differential models based on the materials and enthalpy balances in the shaft which would entail the following:

- (1) rate of oxygen removal from the ore as a function of the degree of reduction achieved, gas composition, temperature, nature of the ore etc.

TABLE 4

Details of Heat Balance in the Shaft.

Base : 1 Kmole Fe (Total)

Heat Supply

Sensible heat of reducing gases

$$H_{rg} = n \sum_{i=1}^{i=4} \int_{298}^{t_{rg}+273} a_i C_{pi} dT \quad 4.1$$

Heat of Reactions

$$H_R = n [(b_2 - a_2) \times 57800 + (b_3 - a_3) 26420 + (b_4 - a_4) 94050] + \frac{M}{.95} 63500 - 98100 \quad 4.2$$

Heat Demand

Sensible Heat of Product

$$H_{pr} = \int_{298}^{t_p+273} [MC_p(\text{Fe}) + [(1-M)/.95] C_p(\text{FeO})] dT + 56[1/f_p - 1/.7] \times .22[t_p - 25] \quad 4.3$$

Sensible Heat of Flue gases

$$H_{fg} = \sum_{i=1}^{i=4} n \int_{298}^{t_{fg}+273} b_i C_{pi} dT = n \bar{C}_{pg} (t_{fg} - 25) \quad 4.4$$

Heat Losses

$$H_L = \int_0^H L \pi D (t_g - 25) dz \quad 4.5$$

Heat Balance

$$H_{fg} = H_{rg} + H_R - H_{pr} - H_L \quad 4.6$$

TABLE 5

Details of Heat Balance in the Reformer

Sensible Heat of reducing gases = H_{rg}

Heat of combustion of CO in flue gases = $67630b_3 n(1 - F)$ 5.1

Heat of combustion of H_2 in flue gases = $57800 b_1 n [1 - F]$ 5.2

Heat of combustion of additional natural gas = $191000 X_1$ 5.3

Heat of reformer reactions = $59100 X + 9860 a_2 n$ 5.4

Heat Balance

$$\eta 191000X_1 = H_{rg} + 59100 X + 9860 a_2 n - \eta [n(1-F)[57800b_1 + 67630b_3]] \quad 5.5$$

Value of H_{rg} is same as determined in Table 4.

η = Thermal efficiency of the reformer.

= Heat utilised/Heat Supplied

Total amount of natural gas consumed

$$X_T = X + X_1 \quad 5.6$$

- (2) gas to solid heat exchange rate at any cross section of the shaft.
- (3) velocity of the burden movement or dwell time of the solid particles in the shaft.

The model equations are further complicated by the existence of a temperature gradient within a solid particles, uneven flow of the gas as well as that of solid particles at any cross-section of the bed, and lack of the reliable kinetic data. The complete details of the model may lie outside the scope of present write-up and will be described elsewhere.

Results and Discussions

The results of the computer calculations based on the model equations developed in this paper are summarised in Table 6. It may be noted that steady state solutions under many cases such as values of F less than 0.9 for $X = 0.5$, 0.70 for $X = .55$, 0.75 for $X = 0.6$ and less than 0.80 for $X = 0.65$ were not possible to be attained. Similarly no solutions could be obtained for all values of F for X less than 0.45 or greater than 0.70. The range of the steady state operation is increased if the value of B is increased a bit or external moisture is added to the reformer or water vapours are not completely removed during wet cleaning of the gases. Model equations may be suitably modified to take into account such variations.

In general the amount of hot reducing gases generated by the reformer must increase with either increase in the amount of natural gas fed to the reformer or by increasing the degree of recirculation of flue gases. The temperature of outgoing flue gases is closely linked to the amount of hot reducing gases passed, as the sensible heat of the production, heat losses and

TABLE 6

Summary of Results of the Model Calculations under Steady State Conditions

Base : 1 Kmole Iron

$T_{rg} = 1000.$

$k = .67$

$z = 10.0$

$B \leq 2.0$

$f_b = 0.65$

$f_p = 0.90$

$M = .996$

$Y = 1.496$

$\eta = 0.80$

Natural Gas to reformer X Kmole	Degree Recycled F	Amount of Reducing gases		Flue gas temp. t_{ofg} °C	Total natural gas used X_T Kmole
		Actual n Kmole	Theoretical minimum n^* Kmole		
0.5	0.9	7.6	6.0	784	.922
0.55	0.70	3.92	3.50	481	.718
0.55	0.75	4.52	3.80	565	.752
0.55	0.80	5.40	4.20	653	.800
0.55	0.85	6.71	4.30	725	.865
0.55	0.90	9.20	4.20	798	.979
0.60	0.75	5.2	3.4	606	.782
0.60	0.80	6.25	3.7	685	.837
0.60	0.85	7.80	3.7	743	.907
0.60	0.90	10.85	3.6	815	1.040
0.65	0.80	7.1	3.3	706	.87
0.65	0.85	8.9	3.3	762	.95
0.65	0.90	12.6	3.3	832	1.12

the heat of reactions are not affected by varying the amount of the reducing gases. If the amount of hot reducing gases and hence the temperature of flue gases are increased to the required level as to cause rapid heating of the incoming burden materials by increasing the degree of recirculation, the followings may occur:

- (1) There would be more of unreacted CO_2 in reducing gases.
- (2) Presence of unreacted CO_2 in gases will result in greater formation of H_2O by the reverse of water gas shift reaction as to increase the overall heat requirements of the reformer.
- (3) Presence of H_2O and CO_2 in hot reducing gases retard the rate of iron ore reduction, increase the theoretical minimum amount of hot reducing gases and may result in lesser degree of metallisation of the product.

The best results may be obtained by keeping the amount of natural gas fed to reformer around 0.55 or 0.60 kmole/kmole Fe with 75-80 pct as the degree of recirculation of flue gases as to obtain the flue gas temperature of around 600C, total amount of reducing gases as 5 kmoles/kmole Fe and the overall natural gas requirement as 0.8 kmole/kmole Fe or around 300 Nm^3 /ton of the product. This is equivalent to using of about 2.5Gcal of energy in producing one ton of the directly reduced iron, which may be one of the lowest for any direct reduction process. The presence of free moistures, carbonates, extra gangue etc in the iron ore, incomplete dissociation of hydrocarbons in the reformer and lowered thermal efficiency of the reformer etc all result in increasing the overall energy requirements of the process. The model equations described in the paper may thus be very helpful

in optimising the process parameters as well as in evaluating the performance of an existing unit.

Conclusions

Model equations have been developed to determine the composition and amount of hot reducing gases, composition and temperature of the flue gases and the overall energy requirements of the process as a function of process parameters such as the degree of flue gases recycled to the reformer, amount of natural gas fed to the reformer, the approach to the water-gas shift reaction equilibrium in the shaft, thermal efficiency of the reformer etc. Model equations can be suitably modified if the water vapours are either not completely removed before recirculation or added separately to the reformer as to increase the range of steady state operations of the shaft. A flue gas temperature of around 600C may be achieved to ensure rapid heating of burden materials, rapid reduction of iron ore, high degree of metallisation of the product and high productivity of the shaft by recirculating 75 to 80 pct of the moisture free flue gas with consumption of as little as 2.5 Gcal of the energy in producing one ton of the directly reduced iron.

Nomenclature

a_1	mole fraction of H_2 in reducing gases
a_2	mole fraction of H_2O in reducing gases
a_3	mole fraction of CO in reducing gases
a_4	mole fraction of CO_2 in reducing gases
b_1	mole fraction of H_2 in flue gases
b_2	mole fraction of H_2O in flue gases
b_3	mole fraction of CO in flue gases
b_4	mole fraction of CO_2 in flue gases
$C_{pi}, C_p(i)$	Specific heat of i th specy, Kcal/Kmole ^{°K}
C_{pg}	Average specific heat of flue gases, Kcal/Kmole ^{°K}
D	dia of shaft, m
F	degree of dry flue gases recirculated
H	height of shaft, m
H_{fg}	sensible heat of flue gases, Kcal/Kmole Iron
H_L	Heat losses, Kcal/Kmole Iron
H_{pr}	Sensible heat of the product Kcal/Kmole Iron
H_{rg}	Sensible heat of reducing gases Kcal/Kmole Iron
H_R	Heat of reactions in the shaft, Kcal/Kmole Iron
K_{wgrs}	Water gas shift reaction equilibrium constant
M	degree of metallisation of the product
n	Amount of reducing gases passed to the shaft, Kmole/Kmole Iron
n^*	Theoretical minimum amount of reducing gases, Kmole/Kmole Iron
t_{fg}	temperature of flue gases, C
t_g	temperature of the gas phase C
t_p	temperature of the product C
t_{rg}	temperature of reducing gases C
T	temperature in K

- X amount of natural gas fed to reformer, Kmole/Kmole Fe
X₁ amount of natural gas for combustion, Kmole/Kmole Fe
X_T Total amount of natural gas used, Kmole/Kmole Fe
Y Oxygen removed from Iron Ore, Kgatom/Kmole Fe.
z vertical distance in the shaft, m
 β H₂/H₂O to CO/CO₂ ratio in flue gases
 η Thermal efficiency of the reformer
 L Wall heat transfer coefficient, Kcal/m²hrK