J. Chem. Soc. Pak., Vol. 35, No.3, 2013

Determination of Kinetic Constants from Tests of Reducibility and their Application for Modelling in Metallurgy

[1]PAVLINA PUSTEJOVSKA*, [2]SIMONA JURSOVA AND [3]BROZOVA SILVIE
[1] VSB - Technical University of Ostrava, Research Centre ENET, Department of Metallurgy, 17. listopadu 15/2172, 70833 Ostrava-Poruba, Czech Republic.
[2] VSB–Technical University of Ostrava, Research Centre ENET, 17. listopadu 15/2172, 70833 Ostrava -Poruba, Czech Republic.
[3]VSB-Technical University of Ostrava, Department of Non-ferrous Metals, Refining Processes and Materials Recycling, 17. listopadu 15/2172, 70833 Ostrava - Poruba, Czech Republic.
pavlina.pustejovska@vsb.cz*

(Received on 24th May 2012, accepted in revised form 12th November 2012)

Summary: The paper analyses details for renewal of the research in blast furnace process within Research Centre ENET at VŠB – Technical University of Ostrava. A newly established laboratory for reducibility testing is an impuls to overcome the former limits and renew a research in its coherence after years. The paper deals with the possibilities of optimization of blast furnace operation. In the introduction, it sums up different approaches how to model blast furnace operation. It discusses the variety of optimal operation for different kinds of iron making technologies. It evaluates reduction course and reducing gas consumption in the stack of reduction aggregate. In the experimental, it creates kinetics model of blast furnace operating using Matlab mathematical library. It determines kinetic and heat limits of carbon consumption for different process conditions.

Keywords: heat balance, kinetic model, carbon consumption, reducibility.

Introduction

Heat balance of blast furnace operation has been for many years based on heat supply and heat consumption in the heart of furnace. It is necessary for calculation to determine the composition of top gas or prerequisite of chemical equilibrium between composition of reductive gas and iron ore charge. The procedure of calculation is described in Czech literature in a favourite text book of Professor Broz. [1].

The theory of counter flow reactors meant a fundamental turning point in chemical engineering. Their application excepting blast furnace process was designed by professor Rist. So called Rist‘s diagram presents a graphic dependence of oxidation grade of the charge on oxidation grade of the reductive gas. As it results from the principle of matter conservation, this dependence is described by operative line that location is determined by equilibrium state between iron oxides and reductive gas. The stationary model of oxygen circulation between the charge and the reductive gas was designed by [2].

The knowledge was followed in former Czechoslovakia by further research activities. The variant for the shaft related to numerical solving the differential equations, while differential equations for reducibility tests were written in formulas. The experimental data were provided by Dr. Honza. It was possible to count a kinetic constant of each reduction grade of iron oxides according to the matter depletion in time. Prof. Tuma [3, 4] interconnected both model of indirect reduction and Rist‘s model. The established procedure for calculation enabled to predicate coke consumption for pig iron production according to laboratory tests of blast furnace raw without the advanced defined top gas composition. The model was not necessary to reflect the creation of chemical equilibrium, so endless keeping of charge in the furnace top, either. Modelling of the reduction in reductive aggregate COREX was evaluated by prof. Bilik at VSB – Technical University [5, 6].

Results and Discussion

Mathematic model based on the indirect reduction describes well the reduction course in the area of the blast furnace where speed of Boudouard´s reaction is small. But this model can also be successfully applied at simulation of reduction process of so called direct iron production (Fig. 1) where coke is not used or for estimation of proportion of direct/indirect reduction with processes of melting reduction, Fig. 2.

---

*To whom all correspondence should be addressed.

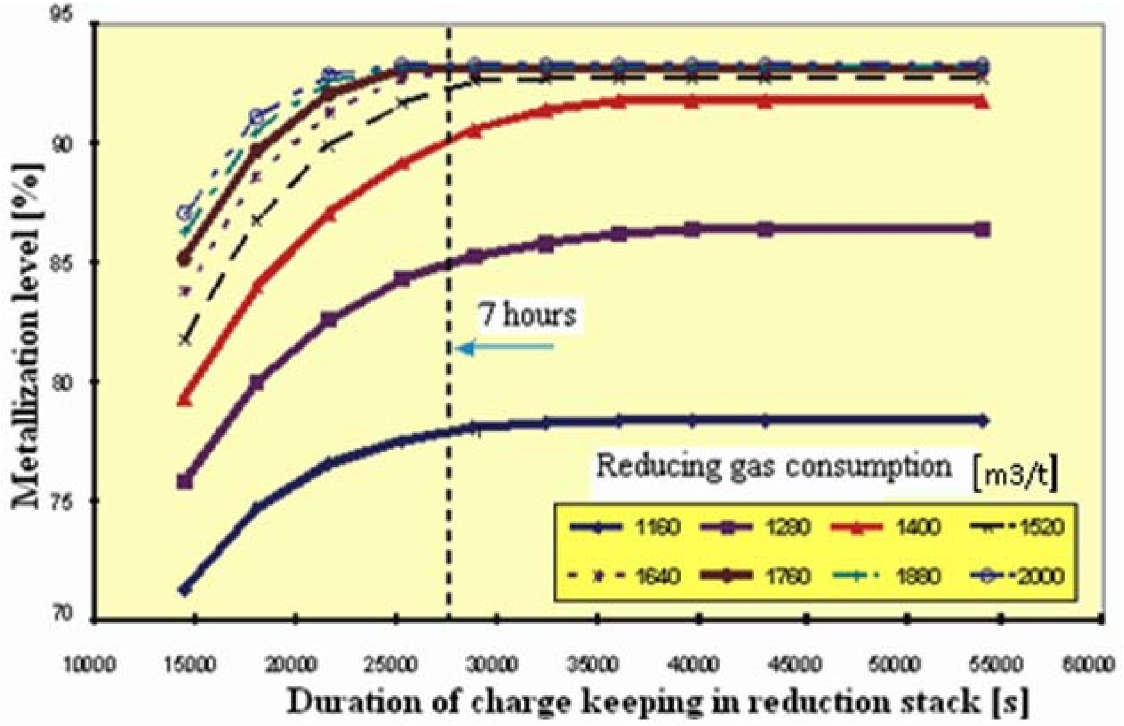


Fig. 1: Reduction course and reducing gas consumption in the stack of reduction aggregate.

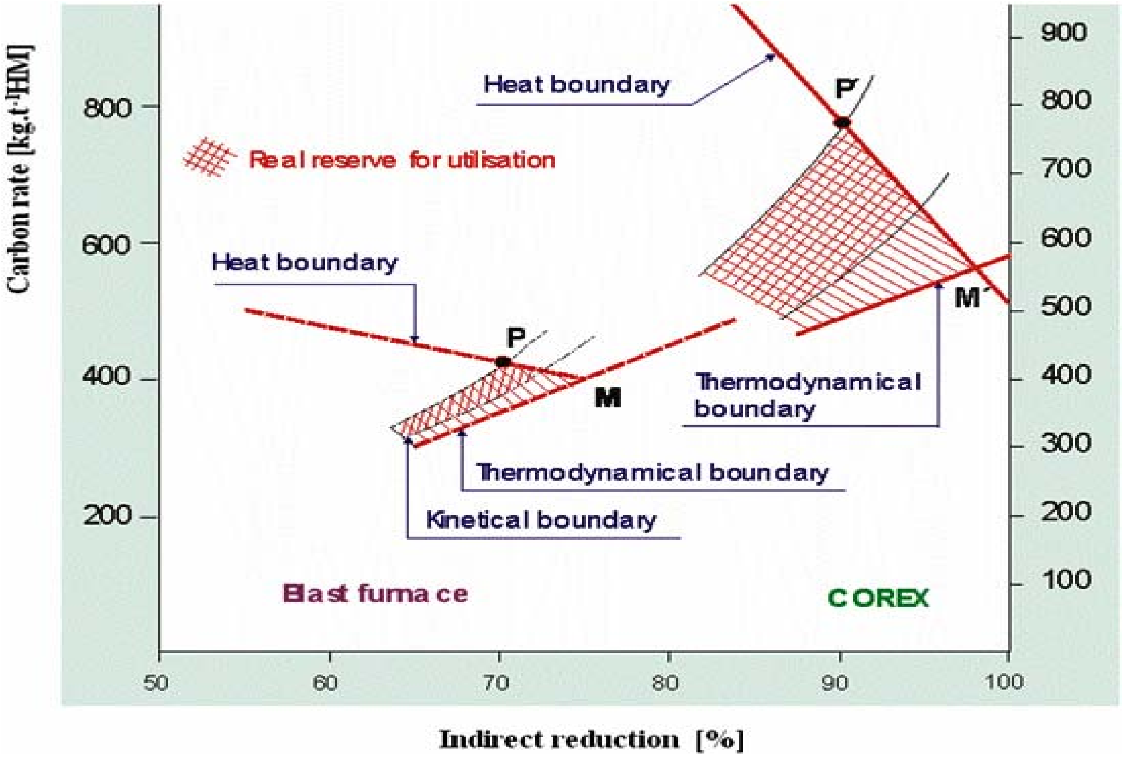


Fig. 2: Evaluation of proportions of both reduction forms and schematic determination of technological reserve during blast-furnace process and process of COREX – FINEX melting reduction.

First of all the level of ore charge metallization reached at the charge exit from the reduction stack in its bottom part is important for the evaluation of simulation results of these alternative processes.

Calculation of concentration profiles can be carried out for different specific consumptions of reduction gas. Calculations then enable prediction of metallization level (pre-reduction) for various kinds of charges (ore, pellets, agglomerates) coming into question. As model also enables simulation of different reduction duration and/or speed of charge decline in the stack the application practicability of various charge kinds can also be evaluated from the point of view of aggregate productivity [7, 8].

Fig. 1 represents relations among quality of sprayed metal product (metallization level), aggregate productivity (duration of charge keeping in reduction stack) and specific consumption of deoxidizing agent. From the indicated example of graphic review follows that for reviewed ore it can be reached a high level of metallization (above 90 %) when it is kept in the reactor for the period of approx. 7 hours with the consumption of gaseous deoxidizing agent of approx. 1800 m^3 per ton of the product.

Next Fig. 2 shows comparison of alternative technology of COREX (FINEX) heat reduction with classic blast furnace with an application of analytic CDR diagram. Figure illustrates diagram area with a high proportion of indirect reduction. In case of blast furnace deoxidizing agent (coke) consumption on provision of reducing gas generation declines with decreasing proportion of indirect reduction because direct reduction does not require surplus of deoxidizing agent. This trend remains retained up to the proportion of indirect reduction of iron oxides of approx. 75 %, in point M then function of fuel consumption begins to be limiting for total coke consumption, mainly provision of heat demands of endothermic direct reduction. [9] But carbon consumption for indirect reduction during actual process is rather higher and it is characterized by working point P. The total hatched surface represents then existing reserve in comparison with thermodynamic minimum. Kinetic model enables further specification of actual possibilities of partial run out of this reserve up to practically reachable minimum of deoxidizing agent consumption. Model takes into account actual reducibility of used ore charge (two-side hatched area) during this determination.

Situation with COREX (FINEX) process is slightly different in comparison with the blast furnace. Lines of theoretic and practical limiting consumptions of deoxidizing agent intersect in the immediate vicinity of 100 % proportion of indirect reduction (point M′ and P′) and in case of no pre-reduction of ore charge to needed level (approx. 90 %) considerable increase of coal specific consumption occurs in the result of explosive heat demands of the process.

This much steeper increase of heat limit has the cause in technological conception of the process, which enables to use only a small part of heat from the total energetic input of this alternative technology to cover direct reduction demands. Prognosis of the reduction course and results by kinetic model can therefore have considerable signification for evaluation of deoxidizing agent/fuel consumption and thereby also for the prognosis of energetic efficiency of the new technology. [10, 11]. In blast furnace department the decrease of total costs of production is possible mainly by decrease of the costs of fuel. [12].

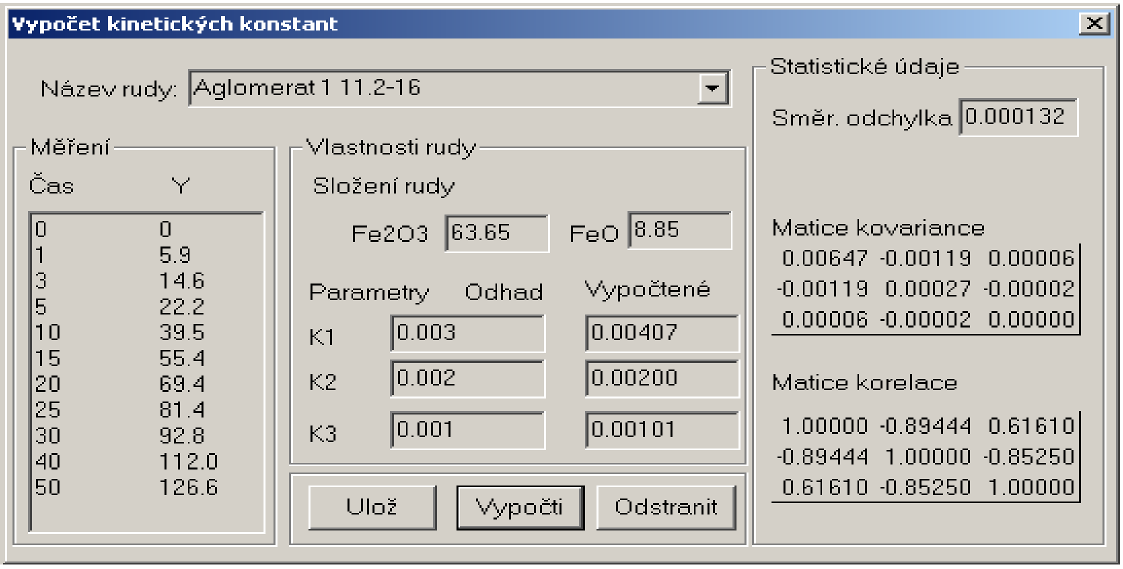
Experimental

Parameters of measurement are indicated in table 1. Lenveberg-Marquart′s method was used for optimization of function $F(k_1,k_2,k_3) = \Sigma(Y_j-Y(t_j))^2$. Optimization was programmed using MATLAB mathematical library. Calculations were made for different initial estimations of effective kinetic constants and convergence occurred in all cases. Supplementary statistic data such as matrices of covariance and correlation of these constants are also results of calculation. Calculated kinetic constants are an important starting parameter during simulation of reduction processes of iron oxides in the stack of blast furnace. Fig. 3 shows an example of entering inputs for calculation of kinetic constants, including results of model calculation.

Table-1 Characteristics of reducibility measurement.

Sample weight	1000 g
Temperature of measurement	900°C
Composition of reducing gas	40% CO, 60% N_2
Equilibrium gas concentrations	$X_{r,1}$ =0.01 ; $X_{r,2}$=0.198; $X_{r,3}$=0.675

Results of reducibility test were used for simulation of different model options of indirect reduction of iron oxides. Proportion of direct reduction on total reduction range – direct reduction level r_d forms an output of this simulation. Proportion of direct/indirect reduction ideally represents proportion of wüstit in reduced charge when area relative height of indirect reduction is zero. Bellow it Boudouard′s reaction already starts. [13 - 15].



Vypočet kinetických konstant

Název rudy: Aglomerat 1 11.2-16

Měření

Čas	Y
0	0
1	5.9
3	14.6
5	22.2
10	39.5
15	55.4
20	69.4
25	81.4
30	92.8
40	112.0
50	126.6

Vlastnosti rudy

Složení rudy

Fe2O3 63.65 FeO 8.85

Parametry	Odhad	Vypočtené
K1	0.003	0.00407
K2	0.002	0.00200
K3	0.001	0.00101

Statistické údaje

Směr. odchylka 0.000132

Matice kovariance

0.00647	-0.00119	0.00006
-0.00119	0.00027	-0.00002
0.00006	-0.00002	0.00000

Matice korelace

1.00000	-0.89444	0.61610
-0.89444	1.00000	-0.85250
0.61610	-0.85250	1.00000

Fig. 3: Example of the dialog box for calculation of kinetic constants from the reducibility test used in the Czech version of the model.

First of all kinetic model of reduction of iron oxides can be particularly applied during simulation of the reduction course in the blast furnace. Using approaches applied by Rist during graphic analysis of reduction and heat operation of a blast furnace the results of kinetic model were transformed into CDR where a new limiting curve acquired in this way characterizes actually reachable "kinetic limit", carbon/fuel consumption taking into account real current reducibility of blast-furnace ore charge (Fig. 4). From the point of view of enthalpy balance it is also necessary to provide that heat developed during carbon gasification to reducing gas will cover also necessary heat needs of the process. Carbon needed for heat (heat limit) also depends significantly on the level of direct reduction.

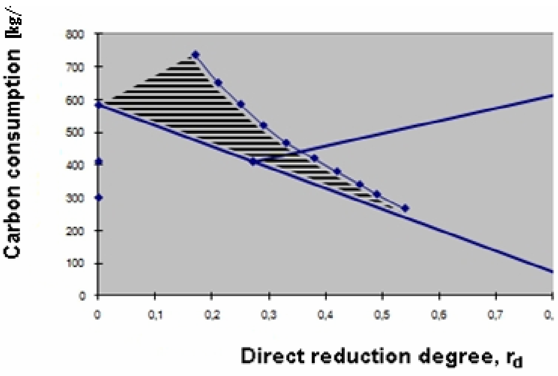


Fig. 4: Determination of kinetic and heat limits of carbon consumption for different process conditions (modified CDR-diagram).

In comparison with the original form of CDR – diagram in Fig. 4 shows not only theoretic but rather actual limits of minimum specific consumption of reduction gas that take into account actual charge reducibility and that can be reached only through better use of reduction gas.

Conclusion

As it follows from present trends of metallurgy development in the Czech Republic as well as in Europe we can expect that blast-furnace technology for preparation of input charge for steelworks will play decisive role in next two decades further on. To increase level of control of energetically extra demanding blast-furnace process VŠB – Technical University of Ostrava has developed system of models where approaches of chemical engineering were applied in wider extend, mainly thermodynamic and kinetic reduction model of ore charge. Practical application of models enables to determine particular limits specified with heat conditions and kinetics of reduction. This also enables more objective assessment of impact of prepared innovations in the sphere of iron production.

But it is also necessary to state that impossibility of model description of reduction processes during which Boudouard´s reaction is applied in greater extend is weak point of presented approach. Therefore now more complex model for more precise prognosis of proportion of direct and indirect reduction is developed in VŠB – Technical University of Ostrava.

Acknowledgement

Article has been done in connection with project Energy Units for Utilization of non Traditional Energy Sources, re. No. CZ.1.05/2.1.00/03.0069 supported by Research and Development for Innovations Operational Programme financed by Structural Founds of Europe Union and from the means of state budget of the Czech Republic.

References

1. L. Broz, *Theoretical Basics of Ironmaking*. SNTL/ALFA, Praha, p. 464.
2. C. L. Corre, Modele Mathematique de la Reduction a contre / courant des oxydes de fer contenus dans les agglomeres. *C.I.T.*, **34**, 3 (1977).
3. J. Tůma, J. Drabina, O. Honza,V. Stanek, P. Moravec, *Hutnické Listy,* **43**, 228 (1988).
4. Rist, N. Meysson, Recherche Graphique de la mise on mille minimale du haut fourneau a faible temperature du vent. *Rev. de Metall.* **2**, 121 (1964).
5. J. Bilík, W. Schűtzenhőfer. Smelting reduction of fine grained ores and coal. *Hutnické listy,* **LIV**, 10 (1999).
6. J. Bilík, W. Schützenhofer, H. Hiebler, Einsatz der mathematischen Modellierung in der Reduktionsmetallurgie.*Berg-und üttenmännische Monatshefte*, **143**, 166 (1988).
7. J. Kozaczka, P. Kolat, Exergy and Its Applications. TANT Publisher, Tarnow, p. 133 (2010).
8. J. Bilík, Kinetics of wüstite reduction together with coke gasification by Bourdouard´s reaction for operational results prediction. *Iron and Steelmaking*, 64 (1999).
9. J. Tuma, M. Prouza and M. Pokorny, Control of blast furnace operation. *Hutnické aktuality*, **27**, 57 (1986).
10. V. Roubíček and J. Buchtele, *Coal – Resources, Processes, Utilization*. Montanex. Ostrava, p. 173 (2002).
11. E. Back and J. Bilík, Smelting reduction as an alternative of blast furnace. *Hutnické listy,* **12**, 3 (1977).
12. E. Kardas, M. Konstanciak, M. Prusak and R. Budzik, *Acta metallurgica Slovaca*, **13**, 497 (2007).
13. V. N. Andronov. *Extraction of Ferrous Metals from Natural and Secondary Resources*, St. Petersburg, SPbGTU, p. 72 (2007).
14. A. Babich, D. Senk, H. W. Gudenau and K. Th. Mavrommatis. *Ironmaking*, Textbook, Verlagshaus Mainz GmbH Aachen, p. 402 (2008).
15. R. Jeschar, H. G. Bittner, A theoretical model coupling kinetics of ore reduction and coke gasification in blast furnaces. *1st. EIC* 1986.