

PROCESS OPTIMISATION MODEL FOR FeMn AND SiMn PRODUCTION

Elena Jipnang, Peter Monheim, Harmen Oterdoom

SMS SIEMAG AG, Eduard Schloemann-Strasse 4, 40237 Duesseldorf, Germany  
e-mails: Elena.Jipnang@sms-siemag.com, Harmen.Oterdoom@sms-siemag.com

**ABSTRACT**

*In its' history, SMS Siemag has designed several ferromanganese (FeMn) and silicomanganese (SiMn) submerged arc furnaces (SAFs) around the world. A number of projects involve a combined FeMn/SiMn process, at which the slag from the FeMn production is used as a charge to the SiMn process. The combined process strategy requires a numerical model, helping to select the optimum process route for both process steps. For this reason a FeMn/SiMn-process optimization model was developed. This determines a raw material mix by optimizing a target function, such as for example, the total operating costs, energy consumption, Mn recovery, amount of slag, alumina content in slag, etc. The optimization procedure considers the user-defined amount of Mn bearing materials, reducing agents, slag formers (quartz, dolomite, limestone) and Fe sources. The developed model is based on the mass and energy balances, solved in Matlab as a non-linear system of equations. The energy balance is calculated via a FactSage® thermodynamic database. This way, more efficient calculations can be carried out to optimise the operation when confronted with changing raw material or final product specifications.*

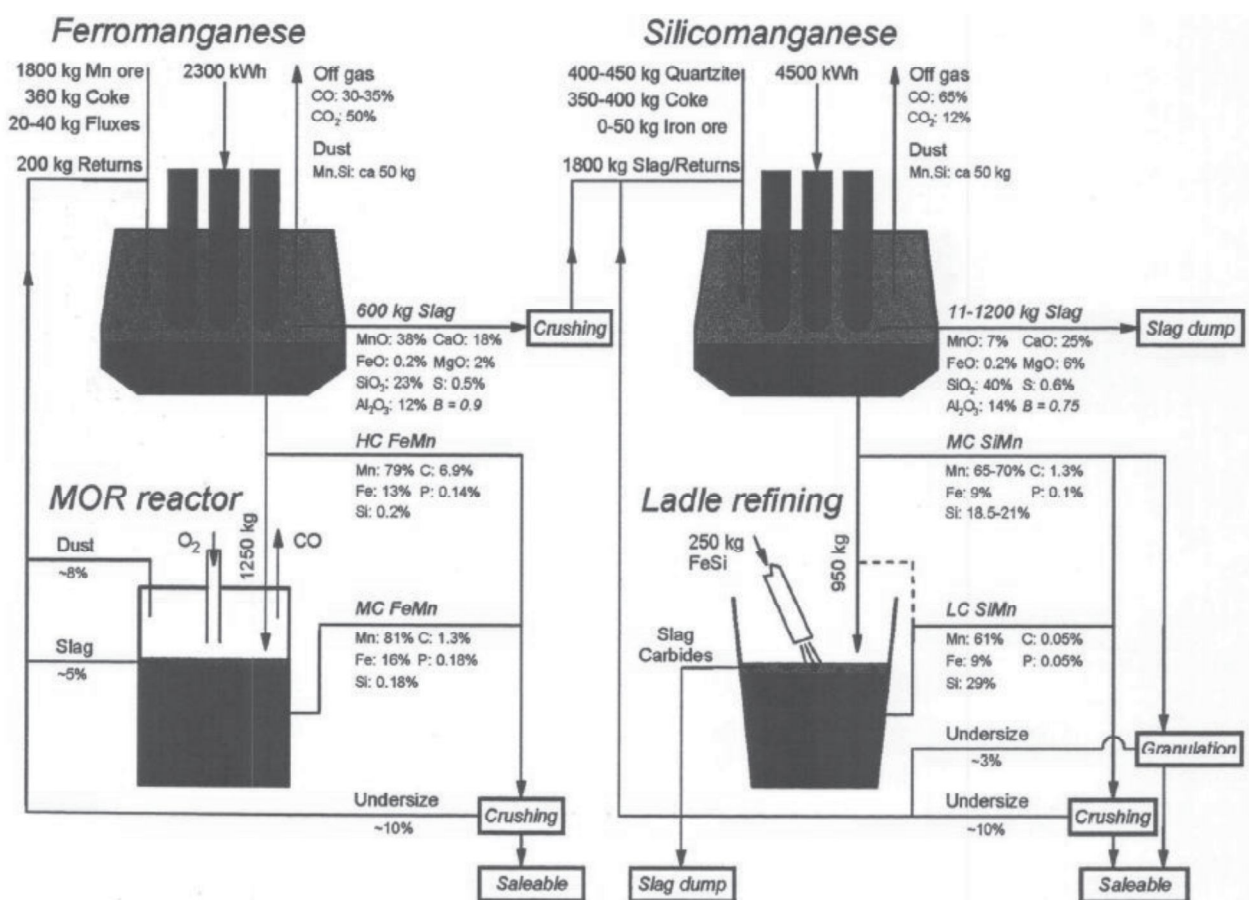
**KEYWORDS:** Ferromanganese, FeMn, silicomanganese, SiMn, SAF, model, mass balance, energy balance, optimisation, SimuSage.

For more than 100 years it has been business and tradition of SMS Siemag to work out solutions in the field of submerged-arc furnaces and electric smelters. SMS Siemag is a leading company in the supply of furnaces for the ferroalloy industries. References from all over the world demonstrate the economic success which is achieved through stable and safe operation. SMS Siemag designs and builds complete state-of-the-art submerged-arc furnaces, as well as integrated plants and components. A number of projects involve the production of both FeMn and SiMn, where the slag from the FeMn production is used in the production of SiMn. FeMn/SiMn furnaces constructed by SMS Siemag are located at RDME in France, Tulcea in Rumania, Zunyi in China, Gulf Ferro Alloys Comp. in Saudi Arabia.

**PRODUCTION OF FeMn AND SiMn IN SUBMERGED ARC FURNACE**

FeMn is usually available on the market as high-carbon (6 to 8% C), medium-carbon (1 to 4% C) and low-carbon (<0.4% C) products. Alloys with high Si contents (15 to 20%) are known as SiMn. High-carbon FeMn and SiMn are produced in open or closed SAFs with a stationary shell by carbothermic reduction of manganese ores. In SAF the heat requirement is supplied as electrical energy and the coke is both a reducing agent and electrical resistance element. The relative costs of production of the two processes depend mainly on the price of electricity and coke. Compared to the blast furnace, the electric furnace offers several advantages such as higher overall yield of Mn from the ores, less carbon consumption, lower quality of reducing agents, and greater flexibility in its ability to produce different grades of alloys. In addition, the furnaces can be utilized both for production of HC FeMn as well as for the production of SiMn, according to requirement.

In FeMn production two chemical practices can be distinguished. The first is the discard slag practice, in which a low MnO slag is produced. The second is the high MnO slag practice, where the slag is used for further processing in duplex production of HC FeMn and SiMn, figure 1. In the discard slag practice, high slag basicity is needed to achieve a MnO content in the slag as low as 15-20% and a Mn-recovery in tapped metal up to 80%. Such operation involves high consumption of carbon and electricity. For the high MnO slag practice, high slag basicity is not needed. Therefore very limited amounts or no fluxes at all are added to the charge materials. By selection of raw materials (e.g. ores from different mines), the melting point and chemistry of the slag can still be controlled to some extent to about 1400-1500°C and 30-50% MnO. Because not all MnO has to be reduced, the amount of carbon that needs to be added is also lower than that of the discard slag practice. By further processing of the high MnO slag the MnO content can be reduced to ca.5%, and an overall manganese recovery of 85-90% Mn can be achieved.



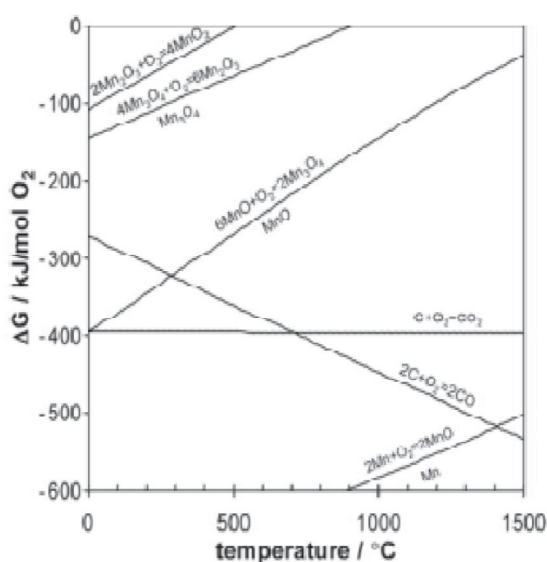
**Figure 1:** Duplex production of HC FeMn and SiMn, with refining processes [1]

## THERMODYNAMICS OF MANGANESE REDUCTION

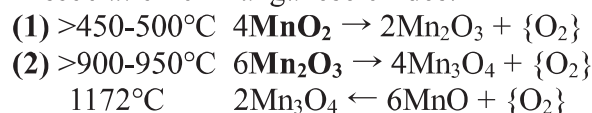
The reduction of the highest manganese oxide MnO<sub>2</sub> occurs in four steps. The Ellingham diagram for the Mn-O-C system in figure 2 indicates that the first reduction step from MnO<sub>2</sub> to Mn<sub>2</sub>O<sub>3</sub> is reached at a temperature of >450-500°C and the second step Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub> at >900-950°C and that both can be realised without reducing agent only by thermal decomposition alone. Both steps in the thermal decomposition show the range of the manganese oxide's stability. The reduction of Mn<sub>3</sub>O<sub>4</sub> to MnO is only possible by CO gas or solid carbon. The reduction of MnO by carbon at atm. pressure is only feasible at temperatures > 1410°C [2,3,4]. To achieve full reduction

the temperature needs to be even higher. The problem here is the high vapour pressure of manganese and its resulting strong evaporation. In the case of the Mn production process with its various reduction steps, MnO first dissolves in the slag phase from which Mn is reduced by solid carbon and moves into the metal phase. Here the non-ideal solutions of slag and alloy are of great importance. Up-to-date thermodynamic methods are to be used to determine phases and the energy balance based on the mass balance.

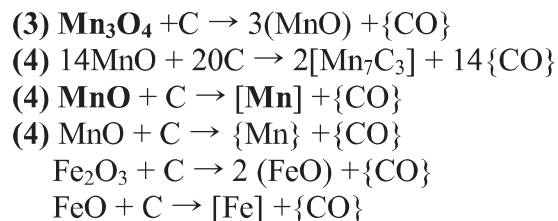
The factors influencing the manganese recovery beside temperature are slag basicity ( $\text{CaO}+\text{MgO}/\text{SiO}_2$ ), the  $\text{CaO}/\text{MgO}$  ratio and the  $\text{Al}_2\text{O}_3$  content in the slag. Increasing temperature favours the endothermic reduction reaction both thermodynamically and kinetically. The effect of slag chemistry on manganese oxide reduction is more complex. The manganese recovery is higher for the basic slag, due to higher MnO activity coefficients in the basic slag. The addition of lime to the raw material mix decreases the MnO saturation concentration and increases the MnO activity in the slag for the same MnO content. The result is a decreasing equilibrium MnO concentration in the slag and an increasing rate of reduction. An increase in the slag basicity above 1.1 has a less significant effect on the manganese recovery. Much higher CaO and MgO contents result in higher slag viscosity which impairs the reduction of manganese.  $\text{Al}_2\text{O}_3$  as well increases the slag viscosity; this can slow down the reduction reaction of manganese. To keep the slag well flowable, the concentration of  $\text{Al}_2\text{O}_3$  in the slag should not exceed 20%.



Dissociation of manganese oxides:



Carbothermic reactions:



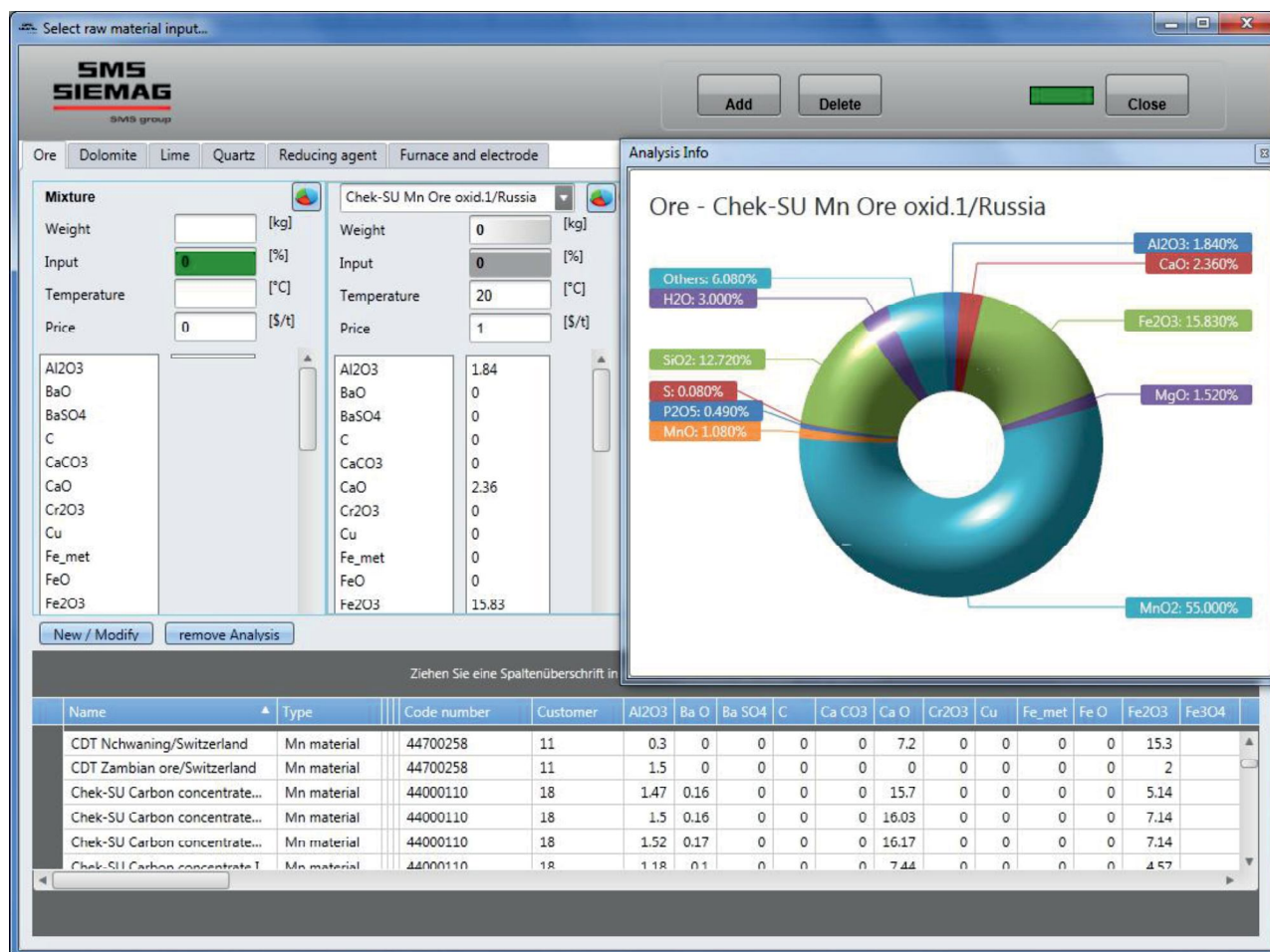
**Figure 2:** Ellingham diagram for the Mn-O-C system at 1 atm total pressure [5] with dissociation/carbothermic reactions

## PROCESS OPTIMISATION MODEL

Calculating manganese alloys is not an easy task due to the number of variables involved. The aim of the process optimisation model for FeMn/SiMn production presented in this paper is to find the raw material mix which optimises a target function such as costs per ton of product, energy consumed per ton of product, slag produced per ton of product, Mn recovery etc. The model is capable to optimise any amounts of manganese bearing materials, reducing agents, slag formers (lime/limestone, dolomite, quartz) and iron sources. Each material can be selected/deselected by the



button “Add”/”Delete” in “Raw materials selection screen”, figure 3. For better control the analysis can be presented as a diagram. Additionally it is possible to modify/remove existing analysis or generate new one.

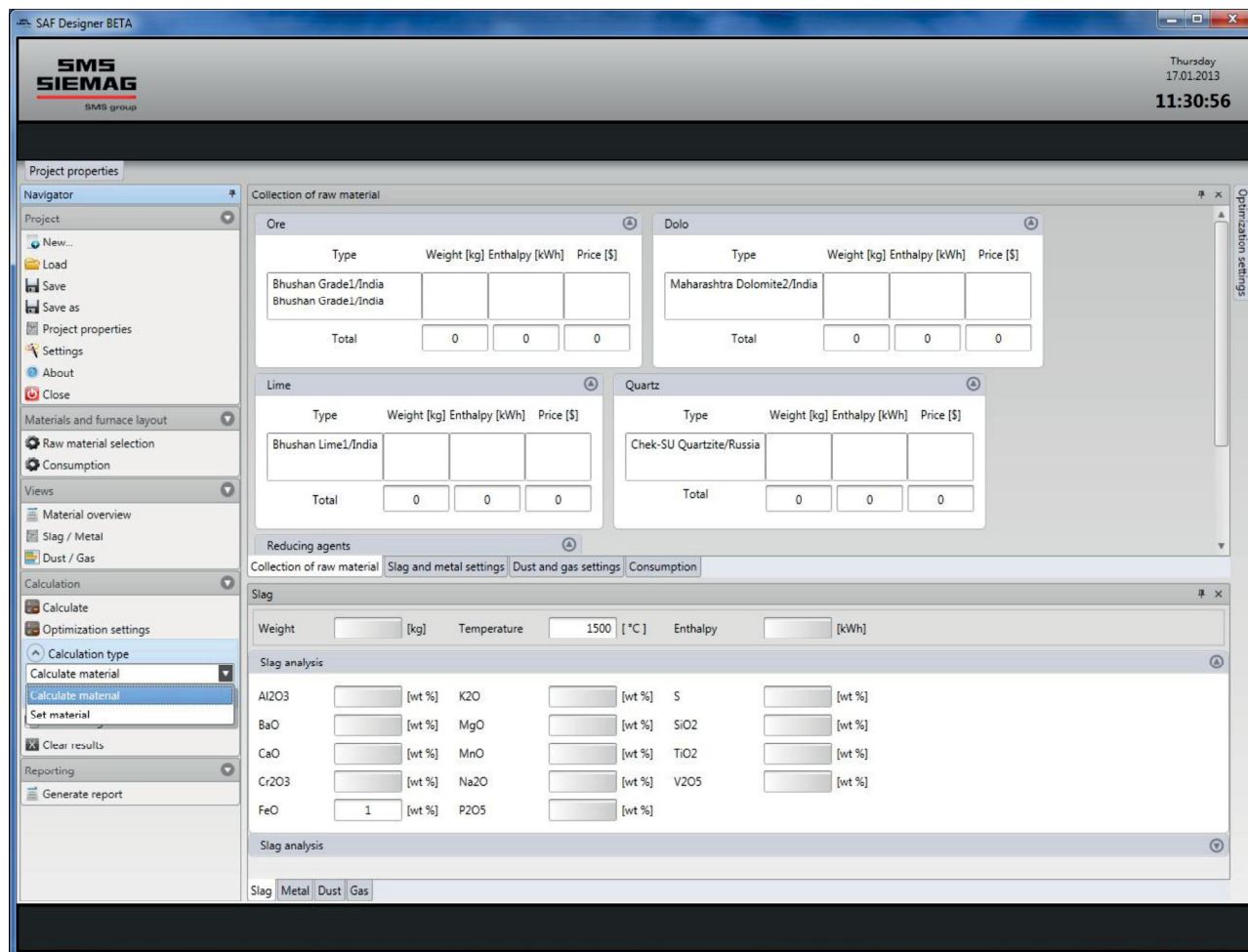


**Figure 3:** Raw materials selection screen of FeMn/SiMn model

The model is designed as a targets/constraints optimisation model. Targets and constraints are the values that have to be achieved, with more or less flexibility. These include product specification and process parameters. The product specifications are the composition of alloy to be produced (carbon and silicon content in case of FeMn), tapping weight, and temperature of the melt; slag has to be  $\geq x\%$  liquid and within a certain composition (slag basicity, FeO and  $Al_2O_3$  content, CaO to MgO relation), tapping weight and temperature range. The process parameters are reduction degrees (Cr, P, Pb, S), Mn distribution between metal and slag, slag to metal ratio, evaporation factors (Ba, K, Mn, Na, Pb, Si, S), mechanical dust loss of raw materials and electrode consumption. Optimisation is performed using the MATLAB<sup>®</sup> Optimisation Toolbox. Criteria for optimisation are costs per ton of product, energy consumed per ton of product, slag produced per ton of product, Mn recovery etc.

The possibility to change variables to constants and vice versa is provided by a special algorithm which allows both the determination of the necessary raw materials input for predefined targets/constraints and calculation of the output for the predefined input. In the first case, calculation type named “calculate material”, the calculation is carried out in the opposite direction to the material flow, see Navigator in figure 4. As calculation input serve the product specification,

process parameters and raw materials analysis. As calculation output the weight of charged raw materials, the weight and the composition of metal, slag, dust and off gas are obtained. In the case of “set material” calculation type the weight and the composition of metal, slag, dust and off gas can be calculated without defined product specifications. Here the weights and analysis of raw materials as well as process parameters are used as calculation input.



**Figure 4:** Main screen of FeMn/SiMn model

The model contains two parts for FeMn and SiMn as separate items. However it has to be mentioned that in a later project a model will be developed further as a linked FeMn/SiMn optimisation model.

## MASS BALANCE

The mass balance is calculated in MATLAB<sup>®</sup> as a nonlinear system of equation. This gives the flexibility to set variables and constants in the system of equations, so that the mass balance can be solved in the direction of material flow as well in opposite direction. The system of equations has, of course, to be determined, that is that the number of variables has to be matched by the corresponding number of independent relationships. Solving a system of equations by a numerical algorithm instead of analytical methods has great advantages to the maintenance and further development of the model because single equations or whole section can be replaced in a modular way. The elements with their compounds considered in the balances are Al, Ba, C, Ca, Cr, Cu, Fe,

H, K, Mg, Mn, N, Na, Ni, O, P, Pb, S, Si, Ti, V. Every element is balanced by respectively reactions.

In ores the manganese is presented mostly as oxides such as  $MnO_2$ ,  $MnO_2 \cdot H_2O$ ,  $MnO \cdot MnO_2 \cdot H_2O$ ,  $Mn_2O_3$ ,  $Mn_3O_4$ ,  $MnO$  or as carbonate  $MnCO_3$ . For the  $MnO_2$  and  $Mn_2O_3$  oxides a thermal decomposition is assumed, so that the total input of  $Mn_3O_4$  through  $MnO_2$  and  $Mn_2O_3$  input can be calculated:

$$m_{MnO_2 \text{ in}} = (< MnO_2 >_{ors} + < MnO_2 \cdot H_2O >_{ors} \cdot \frac{\mu_{MnO_2}}{\mu_{MnO_2 \cdot H_2O}} + < MnOMnO_2 \cdot H_2O >_{ors} \cdot \frac{\mu_{MnO_2}}{\mu_{MnOMnO_2 \cdot H_2O}}) \cdot m_{ors} \cdot (1 - l_{ors}) \quad (1)$$

$$m_{Mn_2O_3 \text{ in}} = < Mn_2O_3 >_{ors} \cdot m_{ors} \cdot (1 - l_{ors}) + m_{MnO_2 \text{ in}} \cdot \frac{\mu_{Mn_2O_3}}{2 \cdot \mu_{MnO_2}} \quad (2)$$

$$m_{Mn_3O_4 \text{ in}} = < Mn_3O_4 >_{ors} \cdot m_{ors} \cdot (1 - l_{ors}) + m_{Mn_2O_3 \text{ in}} \cdot \frac{2 \cdot \mu_{Mn_3O_4}}{3 \cdot \mu_{Mn_2O_3}} \quad (3)$$

The carbothermic reduction of  $Mn_3O_4$  determines the weight of  $MnO$  entering the slag. The rest of manganese oxides  $MnO_2$ ,  $Mn_2O_3$ ,  $Mn_3O_4$ ,  $MnO$ , not accounted for  $MnO$  entering the slag goes to the dust. The balance between the  $MnO$  input,  $MnO$  in slag,  $Mn$  in metal and  $Mn$  in off gas can be presented by the following equation:

$$m_{MnO \text{ in}} = m_{(MnO)} + m_{[Mn]} \cdot \frac{\mu_{MnO}}{\mu_{Mn}} + m_{(Mn)} \cdot \frac{\mu_{MnO}}{\mu_{Mn}} \quad (4)$$

The balancing structure is preserved also for the iron balance. Iron goes to dust as  $Fe_2O_3$  and  $Fe_3O_4$ , to slag as  $FeO$  and to metal as metallic  $Fe$ . Nearly all of iron is found in the metal. Similar to manganese balance, firstly the total input of  $FeO$  into the slag is calculated:

$$m_{FeO \text{ in}} = (< Fe_2O_3 >_{ors} \cdot m_{ors} \cdot (1 - l_{ors}) + < Fe_2O_3 >_{lime} \cdot m_{lime} \cdot (1 - l_{lime}) + < Fe_2O_3 >_{dolomite} \cdot m_{dolomite} \cdot (1 - l_{dolomite}) + < Fe_2O_3 >_{quartz} \cdot m_{quartz} \cdot (1 - l_{quartz}) + < Fe_2O_3 >_{coal} \cdot m_{coal} \cdot (1 - l_{coal})) \cdot \frac{2 \cdot \mu_{FeO}}{\mu_{Fe_2O_3}} + < Fe_3O_4 >_{ors} \cdot m_{ors} \cdot (1 - l_{ors}) \cdot \frac{3 \cdot \mu_{FeO}}{\mu_{Fe_3O_4}} + < FeO >_{ors} \cdot m_{ors} \cdot (1 - l_{ors}) \quad (5)$$

The balance between  $FeO$  input,  $FeO$  in slag and  $Fe$  in melt is following:

$$m_{FeO \text{ in}} = m_{(FeO)} + m_{[Fe]} \cdot \frac{\mu_{FeO}}{\mu_{Fe}} \quad (6)$$

The silicon balance is simpler as balances of manganese and iron, due to single silicon oxide, but it is written in a similar manner. Firstly the total  $SiO_2$  input from raw material is defined:

$$m_{SiO_2 \text{ in}} = < SiO_2 >_{ors} \cdot m_{ors} \cdot (1 - l_{ors}) + < SiO_2 >_{lime} \cdot m_{lime} \cdot (1 - l_{lime}) + < SiO_2 >_{dolomite} \cdot m_{dolomite} \cdot (1 - l_{dolomite}) + < SiO_2 >_{quartz} \cdot m_{quartz} \cdot (1 - l_{quartz}) + < SiO_2 >_{coal} \cdot m_{coal} \cdot (1 - l_{coal}) \quad (7)$$

The balance between the  $SiO_2$  input,  $SiO_2$  in slag,  $Si$  in metal and  $SiO$  in off gas can be presented by the following equation:

$$m_{SiO_2in} = m_{(SiO_2)} + m_{[Si]} \cdot \frac{\mu_{SiO_2}}{\mu_{Si}} + m_{[SiO]} \cdot \frac{\mu_{SiO_2}}{\mu_{SiO}} \quad (8)$$

Carbon is balanced in the way that only solid carbon from reducing agents and electrodes contributes to the reduction of oxides. Proper handling of solid fuels in a mass/energy balance requires the following: the resulting flue gas must be fully consistent with the ultimate analysis, the energy balance of the complete combustion with a final temperature of combustion products must be based on the reaction enthalpy of combustion or calorific value, the amount of solid carbon for the reduction shall not exceed the total carbon. For such reduction processes, it is important to know the percentage of carbon, which does not escape with the volatile fraction. A corrected value for the so called fixed carbon is used so that the total carbon content of the coal is not exceeded. Before calculating the mass balance, the standard coal analyses were converted to a material analysis on an as supplied basis to 100%: total carbon, fixed carbon  $C_{fix}$  as solid carbon, moisture, hydrogen without moisture, oxygen excluding oxygen in ash, nitrogen, total sulphur and ash components.

The enthalpy of coal was calculated as well. Due to the fact that the enthalpy of a compound at 25°C corresponds the formation energy of the pure substances in their naturally occurring form, the calorific value of coal corresponds the enthalpy of reaction at 25°C:

$$Calorific\ value_{coal} = H_{combproduct}^0 - H_{coal}^0 - H_{air}^0 \quad (9)$$

Combustion products and their enthalpy at 25°C can be calculated from ultimate analysis, ash content and ash analysis. The enthalpy of air at 25°C is zero. So the enthalpy of coal is equal to the enthalpy of combustion products minus calorific value.

Carbon charged with reducing agents and electrodes as well with carbonates can be found in metal and gas. Fixed carbon  $C_{fix}$  from reducing agents, which is still available in solid form at high temperatures, and carbon from electrodes is counted as process input for the direct reduction of oxides and for metal phase. The gas composition is determined by post processing before the calculation of the energy balance. Sulphur in the off gas is converted to  $SO_2$  by the oxygen in the gas stream. Further oxygen is consumed by the oxidation of evaporated material in the dust. It is sufficient to consider the fraction of this which enters dust. After these amounts of oxygen have been subtracted from the oxygen in gas, the equilibrium between the remaining oxygen in gas, carbon and hydrogen in gas is calculated to determine the composition of the gas stream.

## ENERGY BALANCES

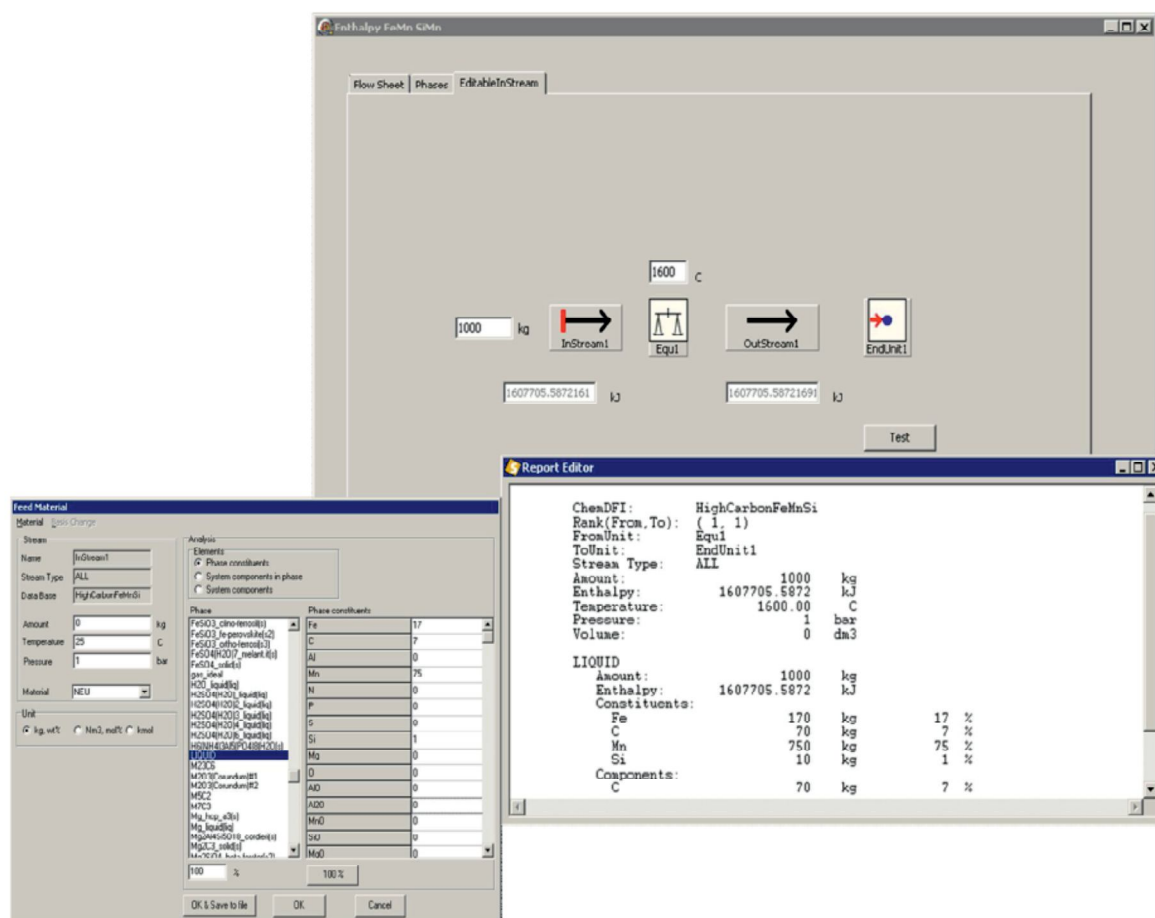
The energy balances is solved using a SimuSage-DLL, constructed on the basis of FactSage® databases, figure 5. The main goal in solving the energy balance by thermodynamic databases is the inclusion of the enthalpies of the strongly non-ideal solutions metal and slag into the energy balance on a thermodynamically sound basis. The fraction of solids accompanying the slag phase is determined to ensure manageability.

SimuSage-Dll provides 5 functions/ procedures:

- Function that calculates the enthalpy of a material stream with given composition and temperature. There is a possibility to choose between equilibrium and non-equilibrium of the input substances.
- Procedure that calculates both the enthalpy and the liquid fraction for metal and slag by the given temperature at equilibrium.
- Procedure that prepares a linearized enthalpy function for a reference temperature and a reference composition. It can be selected whether the equilibrium has to be calculated or not. The absolute total weight plays no role in choosing the reference composition.



- Function that calculates the linearized enthalpy prepared by the previous procedure.
- Procedure that removes all projects generated by the SimuSage-DLL.



**Figure 5:** Test user interface of SimuSage-DLL for energy balance with “Feed Material” and “Report Editor” windows

For each material stream a separate instance for the enthalpy calculation is created. In this way the previous linearization will be not overwritten. So for example, it is not meaningful to calculate metal and slag with the same linearization. A uniform structure of SimuSage-DLL means that also non-linearized Enthalpy calculations using the methods of stream objects can be carried out within the same frame work.

## CONCLUSIONS

A new FeMn/SiMn process optimisation model has been built based on mass and energy balance. Optimisation routines for optimal raw materials mix with the targets such as price, energy consumption, manganese recovery, etc. are implemented as well. It is already capable to calculate the process for FeMn and SiMn as separate items. In progress is the work to connect two models in one to have a possibility to calculate different process strategy: discard slag practise by FeMn production as well as high MnO slag practise by FeMn production connected to SiMn production.



Incorporating SimuSage/FactSage® thermodynamical features by the model helped to improve the metallurgical accuracy.

## SYMBOLS

|                         |                                  |
|-------------------------|----------------------------------|
| $m$                     | - mass, kg                       |
| $\langle \dots \rangle$ | - fraction in a raw material, -  |
| $\mu$                   | - molar mass, g/mole             |
| $l$                     | - mechanical dust loss factor, - |
| $H$                     | - enthalpy                       |

## INDEXES

|               |                               |
|---------------|-------------------------------|
| in            | - charge input to the process |
| $\{ \dots \}$ | - gas phase                   |
| $( \dots )$   | - slag phase                  |
| $[ \dots ]$   | - metal phase                 |

## REFERENCE

- [1] S.E Olsen, M. Tangstad, T. Lindstad, “Commercial Production of Manganese Ferroalloys”, Production of Manganese Ferroalloys“, ©SINTEF and Tapir Academic Press, Trondheim 2007, pp. 43-44.
- [2] G.J.W. Kor , “The Thermal Decomposition of  $Mn_2O_3$  and the Reduction of  $Mn_3O_4$  by C and CO”, Metallurgical Transactions B, Process Metallurgy and Materials Processing Science B, Vol. 9B, June 1978, pp. 307-311.
- [3] N.J. Welham, “Activation of the Carbothermic Reduction of Manganese Ore,” Int. J. Miner. Process, Vol. 67, 2002, pp. 187-198.
- [4] M. Yastreboff, O. Ostrovski, S. Ganguly, “Effect of Gas Composition on the Carbothermic Reduction of Manganese Oxide”, ISIJ Internat., Vol. 43, No. 2, 2003, pp. 161-165.
- [5] K. de Melo Martins, E. Gorbunova, D. Senk, H.W. Gudenau: “Process of Carbothermic Reduction of Iron and Manganese Ore Bearing Briquettes”, Proc. of 5th European Oxygen Steelmaking Conference, Aachen, 2006, pp. 595-598.

