THERMOCHEMICAL COMPUTATIONS IN CARBOTHERMIC AND METALLOTHERMIC FERROALLOY PROCESSES

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ABSTRACT

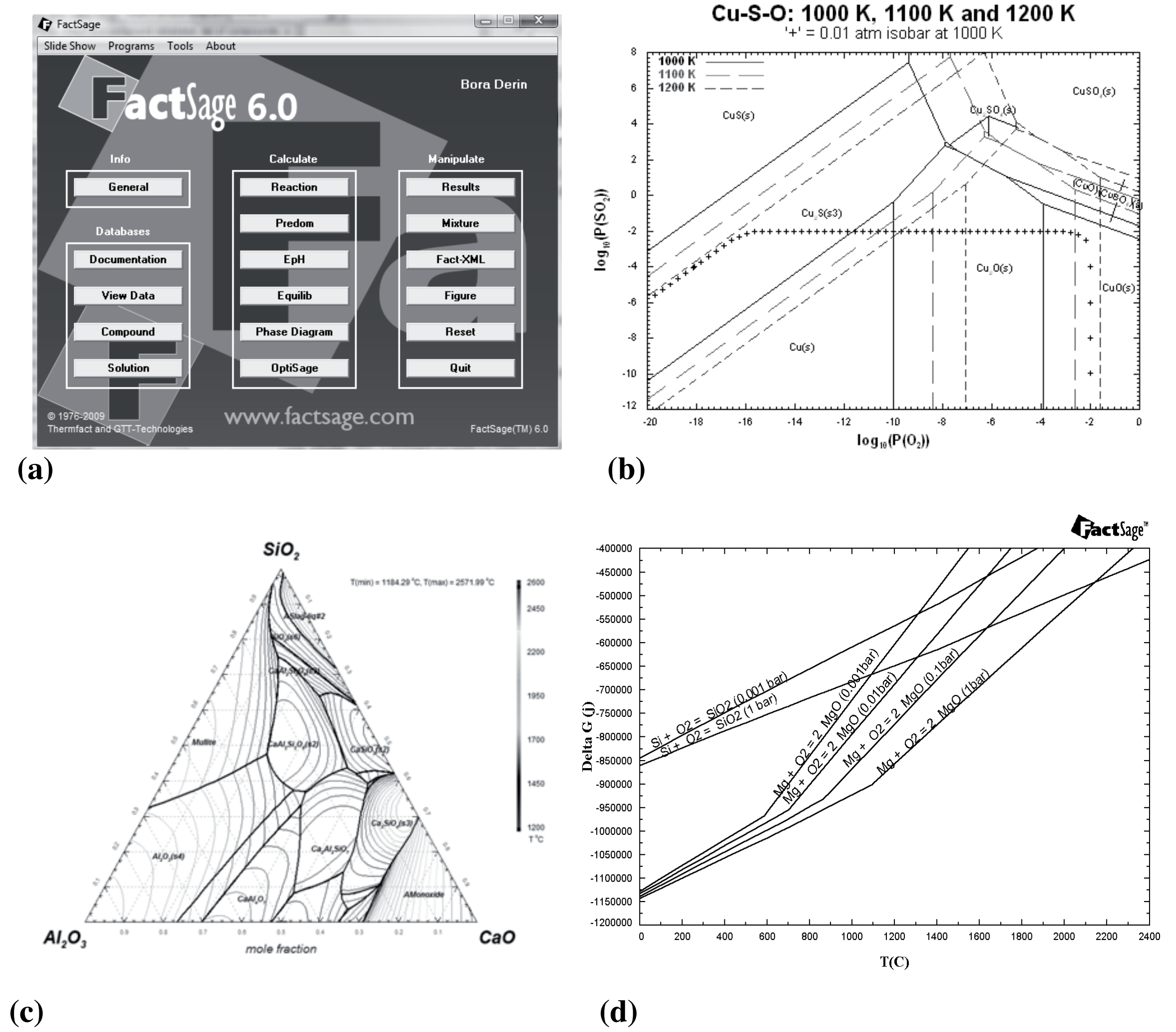
Computational thermochemistry has been increasingly used in both metallurgical science and industry. Recent developments in this area made the performance of complex reaction calculations much easier and more accurate. In the present study, some introductory examples on ferroalloy production processes carried out by both carbothermic and metallothermic methods are given by using "Equilib" module of the FactSage 6.0 thermochemistry software. In the case examples, the interactions and effects of both oxygen and CaO on phosphorus and silicon removals during the second refining stage of crude ferronickel, the optimum quantity of intermediate Fe-Si-Cr alloy needed to reduce the molten rich slag in the Perrin process, the effect of temperature on the carbothermic reduction of SiMn production, and the effect of raw materials on the metallothermic production of FeMo were simulated and the results are tabulated and/or presented as graphs.

1 INTRODUCTION

Recent enhancements in computational thermochemistry made the performance of complex reaction calculations much easier and more accurate. Successful results of thermochemical simulations have increased the attention of both the academic and industrial sector. One of the advanced thermochemistry software, "FactSage" is an integrated thermodynamic databank system (ITDS) which contains databases for hundreds of solutions of metals, liquid and solid oxides, mattes, salt, as well as aqueous solutions. Thanks to its easy-to-use thermochemical application modules, one can easily calculate the thermodynamic properties of isothermal and non-isothermal stoichiometric reactions, free and constrained complex equilibrium states, and all types of classical phase diagrams and Pourbaix diagrams. Results are available in extensive tabulations and also as user defined two-dimensional plots [1,2]. The main menu and some graphical output using different modules of FactSage are shown in Figure 1.

Briefly, in FactSage, the "Reaction" module calculates changes in extensive thermochemical properties (H, G, V, S, Cp, A) for a single species or for a chemical reaction. The "Predom" module is capable of calculating and plotting isothermal predominance area diagrams for one-, two or three-metal systems with two non-metallic components using data from compound databases. With the "EpH" module, one can generate Eh vs pH (Pourbaix) diagrams for one-, two or three-metal systems, again using data from compound databases. The aqueous phase is treated as an ideal mixture of infinitely dilute species. As the "work horse" of the FactSage, the "Equilib" module is the general tool for complex equilibrium calculations based on Gibbs energy minimization. It calculates from a given set of input amounts of specified elements or compounds and for predefined values of temperature and pressure, the amounts of the equilibrium phases, and the concentrations of chemical species, if these phases are solutions. Besides, this module can also handle calculations for reactions with predefined changes in extensive properties, e.g. heat balances, or predefined occurrence of phases, so-called phase target calculations. "Phase Diagram" is a generalized module that permits one to calculate, plot and edit unary, binary, ternary and multicomponent phase diagram sections where the axes can be various combinations of T, P, V, composition, activity, chemical potential, etc.

In the present paper, some introductory simulation examples are given for scientists and engineers who want to take a closer look at thermochemical phenomena in the ferroalloy processes. The case studies have been executed using the Equilib module of FactSage.



(a) (b)

(c) (d)

Figure 1: a) FactSage Main Menu b) Superimposed “Predom” diagrams for Cu-$SO_{2(g)}$-$O_{2(g)}$ at 1000, 1100 and 1200 K c) Polythermal projection on CaO-Al_2O_3-SiO_2 Phase Diagram d) “Reaction” module used for superimposed ΔG-T diagrams of silicothermic reduction of MgO under different pressures.

2 MODELLING STUDIES

2.1 Case One - Reaction of crude FeNi with variable amounts of CaO and O2

The first refining stage of crude ferronickel (FeNi) is the elimination of sulfur under reducing conditions by adding soda ash, lime or calcium carbide to the molten alloy in a ladle furnace. In the second refining stage, removal of carbon, silicon, and phosphorus is generally carried out in an oxygen-blown converter or an oxygen lanced ladle. Whereas the carbon elimination is easily done by only blowing the melt with oxygen, the silicon is removed by simultaneous oxidation and fluxing with lime and fluorspar. Phosphorus can be oxidized with oxygen, addition of iron ore and/or fluxing the P_2O_5 with lime [3].

In the present calculations, the interactions and effects of both oxygen and CaO on phosphorus and silicon removal during the second refining stage of the crude ferronickel were investigated by using the “Equilib” module of FactSage 6.0. The liquid phases occurring in the reaction process were selected as Fe-liquid (FSstel database, includes Fe,Ni,Si,C,O,P,Ca etc.) and as ASlag-liq (FToxid database, includes CaO, FeO, Fe_2O_3, NiO, SiO_2, dissolved P etc.), whereas all gas and stoichiometric solid phases were selected from the Fact53 database. In order to simulate the reactions, 100 g of crude FeNi (containing 24 wt %Ni, 2.5 wt % C, 0.15 wt % P, and 0.02 %S) was equilibrated with a variable amount <A> of CaO and <10 g - A> amount of oxygen at 1600 °C setting the total pressure to 1 atm. The value range of <A> was selected between 0 and 10 g. The result of the calculations is shown in Figure 2. It can be seen that phosphorus removal is possible in form of $Ca_3(PO_4)$ only when both CaO and oxygen are present. The degree of removal reaches its optimum lwith additions of 3-3.5 g of CaO and 6.5-7 g of oxygen respectively. The oxygen injection to the system oxidizes both carbon and silicon in the molten alloy as CO (gas phase) and SiO_2 (slag phase), respectively. The CaO addition provides slag formation with SiO_2, FeO, and Fe_2O_3. However, higher CaO amount (>4.5 g) results in solid calcium silicate formations, if the temperature of the bath is kept constant during the process. It should be noted that a higher amount of oxygen additions also results in oxygen dissolution in the liquid Fe-phase and furthermore to transfer of iron from the liquid metal to the slag phase in both FeO and Fe_2O_3 forms.

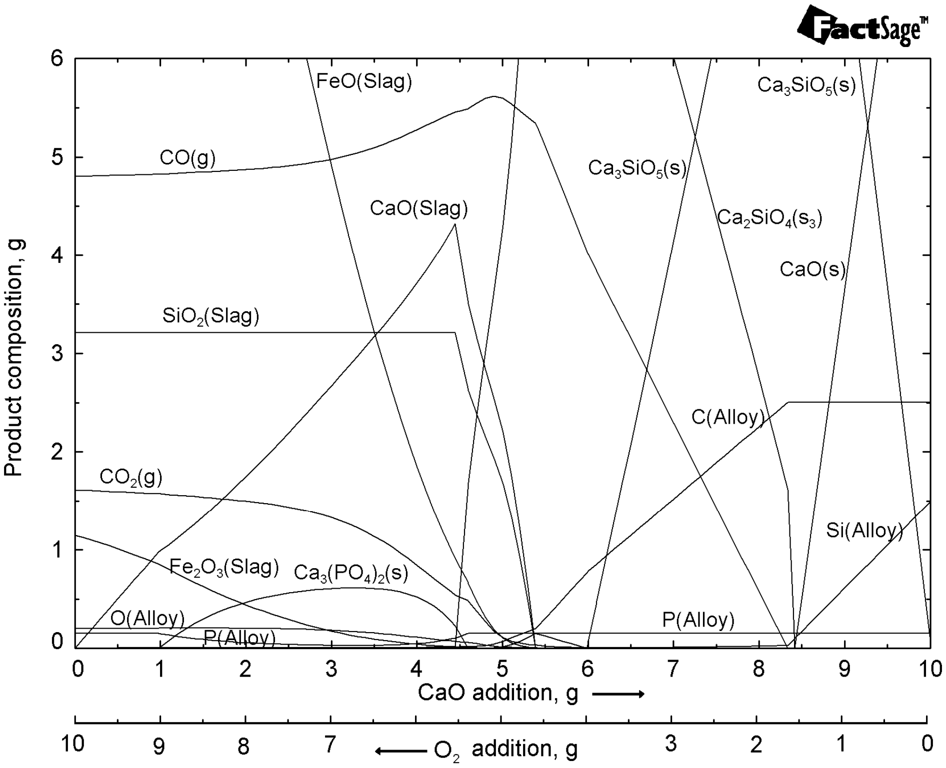


Figure 2: Simulation result of interactions and effects of both oxygen and CaO on phosphorus removal during the second refining stage of the crude ferronickel at 1600 °C and P_{tot}=1 atm.

2.2 Case Two - Production of Ferrochromium by the Perrin Process

One of the most important processes for the production of LC ferrochromium is the Perrin Process based on a silicothermic reduction of a chrome ore-lime melt (rich slag) with a ferrosilicon-chromium (Fe-Si-Cr) alloy by using two ladle steps. In the first step, basically, the Fe-Si-Cr alloy produced in a submerged arc furnace is cast into a ladle and reacted with a molten intermediate slag taken from the second ladle to produce intermediate alloy and waste slag. Meanwhile, in the second step, the rich slag produced in an open arc furnace is cast into a basic-lined ladle together with crushed intermediate Fe-Si-Cr alloy taken from the first ladle to form LC ferrochromium and intermediate slag [3,4].

In the present calculation, the optimum quantity of intermediate Fe-Si-Cr alloy (60 wt% Cr, 20 wt %Si, 19.95 wt% Fe and 0.05 wt% C) to reduce 100 g of molten rich slag (27 wt% Cr_2O_3, 48 wt% CaO, 10 wt% FeO, 6 wt% MgO, 6 wt% Al_2O_3, and 3 wt% SiO_2) was estimated simulating the process conditions of the second ladle with "Equilib" module of FactSage 6.0. The liquid phases occurring in the reaction process were selected as Fe-liquid (FSstel database, includes Fe, C, Cr, Al Si, Mg and O) and as ASlag-liq (FTOxid database, includes Al_2O_3, SiO_2, CaO, FeO, Fe_2O_3, MgO, CrO,Cr_2O_3), whereas all gas and stoichiometric solid phases were taken from the Fact53 database.

The reaction of the process was assumed as adiabatic ($\Delta H=0$) and the initial reaction temperature was selected as 1700 °C. The adiabatic condition was searched for using the temperature while adding a variable amount <A> of Fe-Si-Cr with <A> in the range between 0 and 100 g. Figure 3 shows that as the quantity of intermediate Fe-Si-Cr alloy added to the molten rich slag increases, the degree of simultaneous reduction of Cr^{3+} to Cr^{2+} in the slag and a subsequent transfer of Cr° to the alloy phase increases. As the amounts of CaO and Al_2O_3 remain unchanged in the slag, SiO_2 content increases with increasing intermediate Fe-Si-Cr addition due to the oxidation of silicon. It should be noted that the addition of the intermediate Fe-Cr-Si to the molten rich slag should be limited to a level that does not increase the Si content in the molten LC FeCr alloy higher than that of desirable specification limits (<1.5 wt%Si). For example, the results of the calculation showed that in order to obtain an alloy with %70 Cr content, the amount of intermediate Fe-Si-Cr should be selected as 31.25 g and the adiabatic temperature of the process then was found to be 2395 °C. The product composition of the process is shown in Table 1.

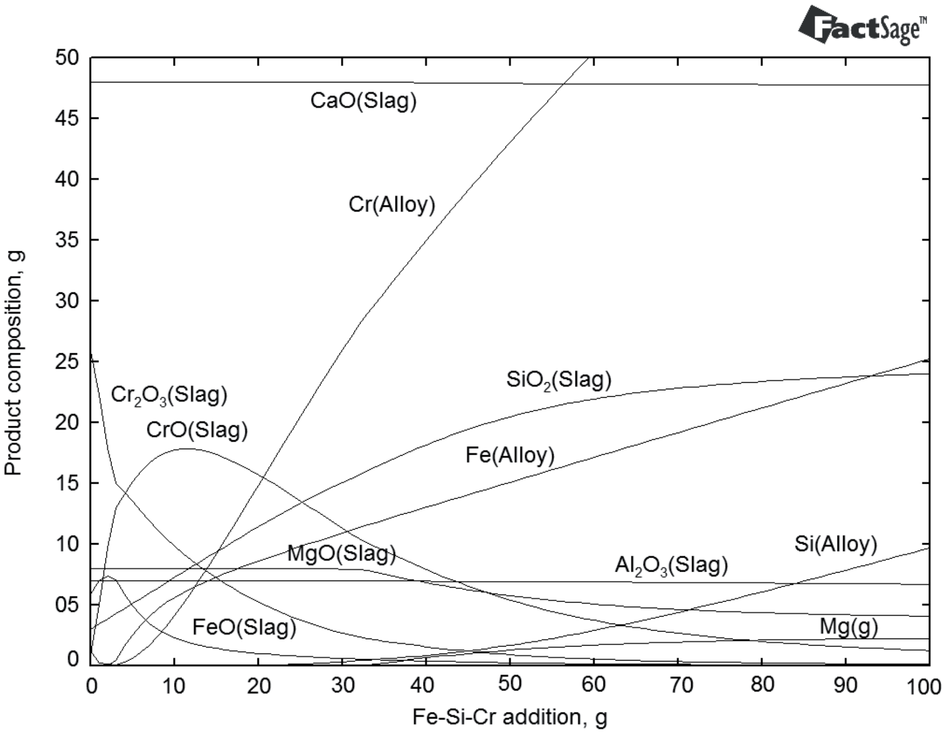


Figure 3: Simulation result of effect of intermediate Fe-Si-Cr alloy on perrin process for the production of LC ferrochromium

Table 1: The output substances of calculated LC FeCr alloy with 70% Cr

Alloy			Slag		
Comp.	wt, g	wt%	Comp.	Wt, g	wt%
Cr	27.26	70.00	CaO	48.00	52.01
Fe	11.21	28.79	SiO_2	15.48	16.78
Si	0.4088	1.050	CrO	10.79	11.69
Mg	0.0282	0.0723	MgO	7.953	8.619
C	0.0156	0.0401	Al_2O_3	6.979	7.563
O	0.0096	0.0246	Cr_2O_3	2.487	2.696
Al	0.01102	0.0283	FeO	0.5863	0.6354

2.3 Case Three - SiMn production

Silicomangenese (SiMn), which is produced in electric submerged arc furnaces, is not only used as substitute for ferromanganese and ferrosilicon in steelmaking but also as a raw material for the production of MC or LC FeMn and industrial Mn metal [3]. Even though the same type of furnace is used for HC FeMn production, in case of SiMn production, a higher operation temperature is needed in order to obtain an alloy within desired specifications. Silicomangenese with a composition of 18-20 % Si and 70 % Mn is generally produced from a mixture composed of a MnO-rich slag from the HC FeMn process (~35-45% MnO), manganese ores, quartzite, FeSi remelts or off-grade qualities, and coke.

In order to get better furnace operations approximately one-quarter of manganese is added to the charge mixture as ore. MgO-containing fluxing materials (e.g. dolomite or olivine) are sometimes added in minor amounts [5].

In this case study, a thermochemical simulation of the effect of temperature on the carbothermic reduction of SiMn was carried out in order to obtain the desired FeMn alloy composition. The liquid phases occurring in the reaction process were selected as Fe-liquid (FSstel database, includes Fe, C, Mn, P, Si, Mg, O etc.) and as ASlag-liq (FTOxid database, includes Al_2O_3, SiO_2, CaO, FeO, Fe_2O_3, MgO, MnO, Mn_2O_3), whereas all gases and stoichiometric solid phases were taken from the Fact53 database. The initial charge composition close to industrial practice is given in Table 2. The calculated result of the process is shown graphically in Figure 4.

Table 2: The amounts of input substances for the simulation of SiMn production.

Input, kg.	MnO_2	MnO	Mn	Fe	Fe_2O_3	Si	SiO_2	Al_2O_3	CaO	MgO	P	Fix C
Mn-ore	316				57		16	1	23	2	0.16	
HC-slag		546					308	156	181	82		
Metal in slag			174	33								7
Quartz					4		399	14	7	7		
Coke mixture					3		15	10	1		0.14	264
Dolomite								3	29	17		
Si-met.sculls				4		79	36	7	7			1
Total	316	546	174	37	64	79	774	191	248	108	0.30	272
Sum of mixture	2809	kg										

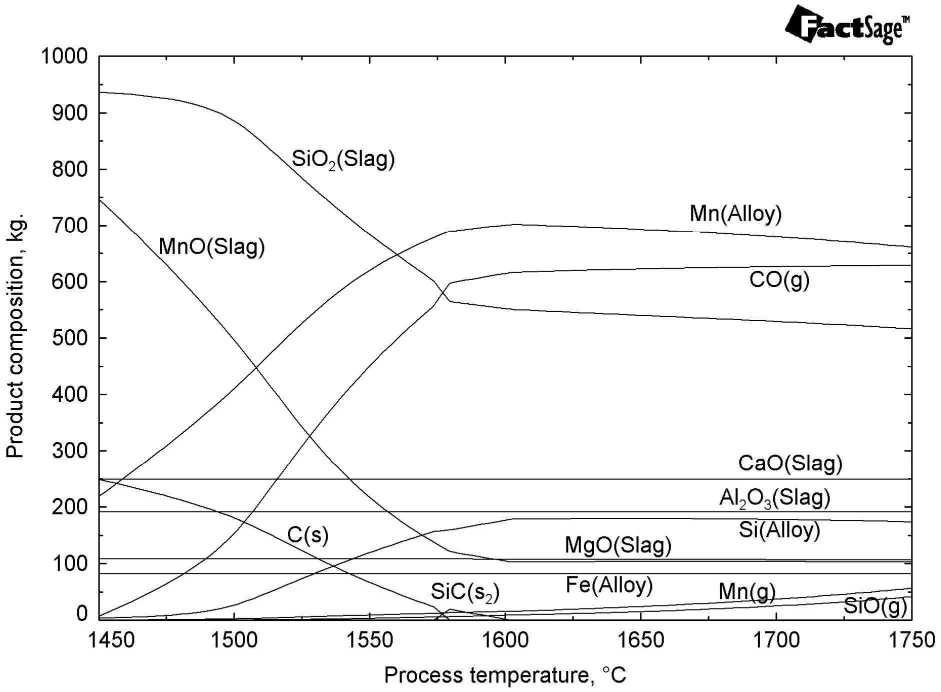


Figure 4: Simulation result of effect of temperature on carbothermic FeMn process

As can be seen from the figure, Mn and Si recoveries increase with increasing process temperature and reach their peak values at around 1600 °C. It should be noted that in the liquid Fe-phase the carbon content decreases with increasing silicon. A small amount of silicon carbide occurs between 1575-1600 °C. Higher reaction temperatures result in losses of Mn and Si to the gas phase. The product composition from the calculation result shows that it is possible to obtain SiMn at 1600 °C within desired specifications with a high amount of slag containing approximately 8.7 wt % MnO (Table 3).

Table 3: The output substances of simulated result for FeMn production at 1600 °C

Alloy	wt. kg	wt.%	Slag	wt. kg	wt.%	Gas	wt. kg	wt.%
Mn	700.5	72.46	SiO_2	551.7	45.88	CO	614.1	96.20
Si	176.2	18.22	CaO	248.0	20.62	Mn	15.28	2.394
Fe	81.76	8.457	MgO	190.9	15.88	SiO	8.562	1.341
C	8.101	0.8380	Al_2O_3	107.5	8.938	Mg	0.3121	0.0489
P	0.1205	0.0125	MnO	104.3	8.677	CO_2	0.0545	0.0085

2.4 Case Four - Metallothermic production of Ferromolybdenum

Ferromolybdenum (FeMo) is commonly produced by a metallothermic method in which silicon or aluminum is used to reduce the molybdenum three oxide (MoO_3). The advantages of the metallothermic method for FeMo production are basic equipment and single-step process requirements resulting in an alloy within expected specifications and a low molybdenum containing slag. The large Gibbs energy difference between Si (or Al) and MoO_3 provides almost a complete molybdenum recovery in the process [3].

In this case study, the effect of addition of ferrosilicon as reducing material to the termit mixture to produce FeMo was investigated regarding the product composition and adiabatic temperature change. The composition and weight of the termite mixture used in the calculation were selected close to the industrial practice and are given in Table 4. The liquid phases occurring in the reaction process were selected as Fe-liquid (FSstel database, includes Fe, Al, Mo, Si, O etc.) and as HSlag-liq (FTOxid database, includes FeO, SiO_2, CaO, Al_2O_3, FeO, Fe_2O_3, CaF_2, and FeF_2), whereas all gases and stoichiometric solid phases were taken from the Fact53 database. Since the reaction was assumed to be adiabatic, ∆H was set to zero. Furthermore, the temperature of the input substances was set to 25 ° C.

Table 4: The amounts of input substances for the simulation of FeMo production.

Input, kg.	MoO_3	Fe_2O_3	Fe	Si	SiO_2	CuO	Al	CaO	CaF_2
Roasted Mo Conc.	85	3			8	0.7			
Iron Ore		27							
Ferrosilicon, 50%Si			10-35	10-35					
Al							5		
Lime								7	
Fluorspar									2

The product composition change and adiabatic temperature change with FeSi addition are shown in Figure 5 and 6, respectively. Figure 5 shows that in order to obtain FeMo with 60-75 %Mo, FeSi addition should be between approximately 20-28 kg. Silicon in the alloy formation together with gaseous SiO occurs after 20 kg FeSi addition. Adiabatic temperature value is important for obtaining combustion products (alloy and slag) which are in liquid-phase state (Figure 6). Thus, the melting temperature difference clearly will result in a very good separation of the multi-phase alloy and the slag phase. Adiabatic temperature of the total reaction increases with increasing FeSi up to 25 kg FeSi addition (~2470 °C). Beyond that point excess FeSi additions clearly result in a decrease of temperature.

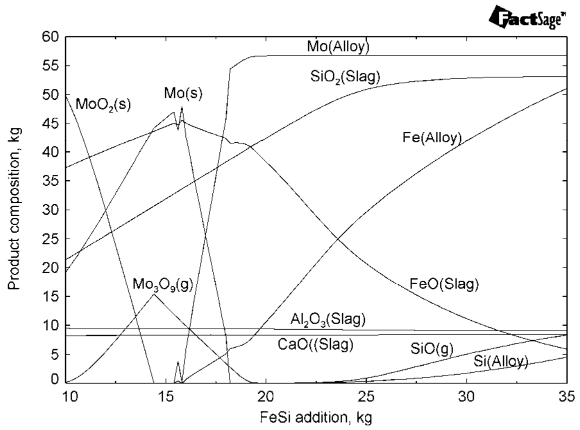


Figure 5: The composition change with FeSi addition

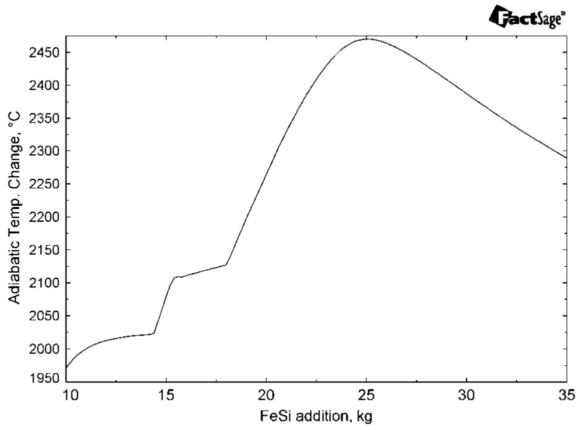


Figure 6: The adiabatic temperature change with FeSi addition

3 CONCLUSION

The “Equilib” module of FactSage proved to be an ideal tool for simulating the reactions occuring in ferroalloy processes of practical importance. In all cases, the practical findings could be very well explained by the results of the calculations. It can be concluded that FactSage is an invaluable tool for academic and industrial researchers who work on the understanding and optimization of existing processes and also the development of new processes in metallurgical and materials sciences.

4 REFERENCES

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