FREDRIKSSON, P. and SEETHARAMAN, S. Thermodynamic studies of FeO-containing slags and their impact on ladle refining process. *VII International Conference on Molten Slags Fluxes and Salts,* The South African Institute of Mining and Metallurgy, 2004.

Thermodynamic studies of FeO-containing slags and their impact on ladle refining process

P. FREDRIKSSON and S. SEETHARAMAN
Department of Materials Science and Engineering, Division of Metallurgy, Royal Institute of Technology, Sweden

In the ladle refining process, the 'FeO'-content of the ladle slag is of great importance in the chemistry as well as the energetics of the process. An optimization of the process requires an accurate knowledge of the thermodynamic activities of 'FeO' in the ladle slags. Due to the discrepancies in the existing data, renewed attempts are being made at the Royal Institute of Technology to generate reliable data for binary, ternary and multicomponent slags containing 'FeO' at steelmaking temperatures.

In order to measure the activities of 'FeO' in the slags, a gas equilibration technique was employed in the present work. The slags, kept in Pt-crucibles, were equilibrated with a CO-CO_2-Ar gas mixture and quenched after equilibration. The chemical composition of the slag was analyszed. From a knowledge of the thermodynamics of Fe-Pt system, the 'FeO' activities in the slag could be evaluated.

The results of the present studies, together with other literature values, were optimized in the slag software, THERMOSLAG® developed in the Royal Institute of Technology, Sweden. The results of the optimization are presented.

Model calculations were performed with the KTH slag software, THERMOSLAG®, by using plant data from OVAKO Steel, Hofors, Sweden. It was found that oxygen estimations in the metal from the 'FeO' analyses of slags, obtained by conventional sampling and analysis methods, where less reliable. Estimation of the oxygen levels utilizing the sulphur partition between the slag and the metal were carried out using the THERMOSLAG® software. Reasonable estimations of the oxygen contents in the metal confirmed that this could be a very useful tool for the plant operator.

Keywords: ladle, thermodynamics, slags, 'FeO', experimentation, modelling, sulphur partition

Introduction

An optimization of unit processes in steel production and quality control of the products presupposes a fundamental understanding of the thermodynamics of the metallic and slag systems. Further, during plant operations, it is necessary to have the chemical compositions of these phases by well-planned sampling and quick chemical analysis. However, due to the uncertainties involved in sampling and analysis, contradictory information of the process status could be created.

In order to sort this out, it is necessary to have a complete understanding of the thermodynamics involving slag-metal reactions. This, however, requires an access to reliable and accurate estimations of the thermodynamic properties of the metallic and slag systems.

A number of thermodynamic software, like Thermo-Calc®, enables relatively accurate estimations of the thermodynamic properties of the metal bath. Even in the case of slag systems, some thermodynamic models and software based on them are available. The common ones are (1) the IRSID® model that has been incorporated in Thermo-Calc®, (2) F*A*C*T®, based on the Pelton-Blander model and (3) THERMOSLAG® based on the KTH-model. The last-named was developed in the Division of Theoretical Metallurgy, Royal Institute of Technology, Stockholm, Sweden. The present paper illustrates the application of the THERMOSLAG® software in solving a puzzle in the chemistry of the ladle refining process at OVAKO Steel, Hofors, Sweden.

A thermodynamic slag model was developed at KTH, which has the feature to, not only, estimate the thermodynamic activities, but also sulphide capacities as well as viscosities of higher order systems from the experimental data for lower order systems. The literature results[1–17] were assessed and complemented by experiments carried out in the present laboratory in optimizing the computations of the THERMOSLAG® software. In the present work, the software was used in estimating the oxygen levels in the bath as the chemical analysis results were often uncertain due to sampling and analysis difficulties.

Ovako steel ladle refining practice

Ovako Steel, situated in Hofors, Sweden, is the world's leading manufacturer of steels for rolling bearings and a major producer of other special engineering steels such as seamless tubes, bars, rings, surface removed wire and low-alloyed speciality steels for highly stressed applications. The annual production capacity in 2002 was 525 000 tonnes of special engineering steel.

The scrap is melted in a 100-tonne, bottom-tapped electric arc furnace. Tapping into a ladle furnace is accompanied by pre-deoxidation after adjusting the steel to the desired, carbon, phosphorous and temperature levels. After removal of the EAF slag by raking, the molten metal is transported to the ASEA-SKF furnace station, which is equipped with graphite electrodes for heating, a vacuum chamber for degassing, wire injection, an electromagnetic stirrer and porous plugs, located at the bottom, for argon stirring.

The refining process is divided into three main operations. Initially (step 1), during alloying, deoxidation and melting of the synthetic top slag, induction stirring is used. Secondly (step 2), during the vacuum degassing step, argon gas is injected during electromagnetic stirring in order to enhance the removal of the dissolved sulphur and hydrogen. Finally (step 3), the ladle is returned to the heating and induction stirring position for temperature adjustments and inclusion separations from the steel before casting into 24 ingots (capacity 4.2 tonnes each) by up-hill teeming. This process sequence is illustrated in Figure 1.

Sampling, accompanied by on-line chemical analysis of the total oxygen content in the steel, is today becoming quite common in order to control the non-metallic inclusion content and thereby, the quality of the steel. In the present work, 23 heats of high-carbon chromium bearing steel grade of 1 weight per cent C and around 1.4 weight per cent Cr were studied. Steel and slag samples were taken at the end of step 1, immediately after step 2 and in the end of step 3 respectively.

Plant data from OVAKO Steel, Hofors, Sweden, taken during the vacuum degassing operation in the ladle refining process, focused on samples taken directly after the second step, were used in the present work. The liquid steel samples were taken by an automatic sampling system at a depth of 300 mm below the slag/metal interface. At this stage of the refining process, the liquid steel has good mixing conditions and a uniform temperature distribution. These samples, however, lacked oxygen analysis. The slag samples were manually collected by a spoon and subjected to chemical analysis. The top slag was completely molten.

In the present paper, solution to some of the inconsistencies in the plant data was attempted by means of thermodynamic calculations using the software developed in the Division of Theoretical Metallurgy, KTH.

Problem definition

The chemical analysis of the liquid steel (1 weight per cent C and 1.4 weight per cent Cr) and the slag samples respectively are taken immediately after the vacuum degassing operation are presented in Table I. By regarding the accuracy of the chemical analysis of the metal and slag phases, the resulting calculations of the dissolved oxygen in the metal phase, as well as the calculated activity of ‘FeO’ in the slag phase, were given a scatter of ± 13 per cent.

As mentioned earlier, the oxygen analyses of the steel samples were not available. A logical method to estimate the oxygen levels in the steel bath could be to estimate the activities of ‘FeO’ in the slag from ‘FeO’ contents obtained by sampling and chemical analysis, and use these to estimate the oxygen potential in the steel bath, assuming slag/metal equilibrium.

$$\begin{aligned} &\text{‘}FeO\text{’}_{(Slag)} = Fe_{(Steel)} + \underline{O}_{(Steel)} \\ &\Delta°G_1 = 116147 - 48.8T^{18}(J/mol) \end{aligned} \qquad [1]$$

$$K_1 = \frac{a_{Fe} \cdot a_{\underline{O}}}{a_{\text{‘}FeO\text{’}}} \qquad [2]$$

where K_1 is the equilibrium constant of reaction [1], a_{Fe} is the activity of iron in the steel, which is considered as unity, $a_{\underline{O}}$ is the activity of oxygen dissolved in steel (Henrian standard state in weight per cent) and $a_{\text{‘}\underline{FeO}\text{’}}$ is the activity of ‘FeO’ in the slag with liquid stoichiometric FeO as the standard state. The activity of ‘FeO’ in the slag could be estimated by the THERMOSLAG® software. Thus, if the slag sampling and the ‘FeO’ analysis values are consistent, it should be possible to estimate the amount of dissolved oxygen in the steel under equilibrium conditions.

The results of such estimations of the oxygen contents of the steel, obtained from slag analyses, are illustrated in Figure 2 where the oxygen content is shown for the various heats. Other commercial software gave somewhat similar results. The oxygen levels are at least one order of magnitude higher than the expected oxygen levels in steel and exhibit a wide scatter. Thus, it can clearly be seen that this method of estimating the oxygen content in the steel bath is less reliable due the uncertainties in slag sampling and analysis. The present paper illustrates the effective use of the slag software, THERMOSLAG®, in approaching the problem through the sulphur partition between the steel bath and the slag.

THERMOSLAG® software

This software has been developed on the basis of a unified description of the slag in order to extrapolate the

Figure 1. Deoxidation and alloying (step 1), vacuum degassing (step 2), and heating and stirring (step 3)

Table I

Steel and normalized slag analysis in weight percentage for a 1% C and 1.4% Cr grade

Heat	T(C)	Slag analysis (wt%)							Steel analysis (wt%)			
		Al_2O_3	CaO	'FeO'	MgO	MnO	SiO_2	S	Al	Mn	Si	S
1	1536	25.9	55.8	0.5	6.0	0.1	11.7	2.00	0.015	0.22	0.28	0.009
2	1622	30.5	52.9	1.0	8.6	0.0	7.0	3.19	0.033	0.28	0.29	0.004
3	1508	34.3	48.9	0.6	9.0	0.1	7.1	2.43	0.040	0.28	0.27	0.005
4	1509	31.9	55.1	0.7	8.1	0.0	4.3	3.16	0.039	0.13	0.28	0.006
5	1509	32.5	47.7	1.8	10.8	0.1	7.1	2.51	0.032	0.26	0.28	0.007
6	1534	32.6	50.8	1.6	8.8	0.1	6.1	2.90	0.035	0.30	0.28	0.008
7	1543	33.3	47.0	1.2	11.5	0.1	6.9	2.20	0.035	0.26	0.29	0.007
8	1545	32.7	49.2	0.8	9.8	0.1	7.4	2.00	0.038	0.10	0.28	0.009
9	1537	31.1	48.9	1.7	9.5	0.1	8.7	2.42	0.038	0.26	0.29	0.010
10	1623	35.7	40.8	0.7	11.7	0.2	10.9	1.16	0.021	0.24	0.27	0.013
11	1507	40.0	45.7	1.3	8.5	0.1	4.5	2.15	0.026	0.13	0.27	0.005
12	1516	43.6	41.6	0.5	7.0	0.1	7.2	1.31	0.047	0.29	0.28	0.014
13	1497	41.7	42.0	1.0	8.1	0.2	7.0	1.58	0.044	0.28	0.33	0.013
14	1552	41.9	43.7	0.5	7.7	0.1	6.1	1.00	0.024	0.28	0.29	0.009
15	1535	43.1	41.6	0.3	7.7	0.1	7.3	1.55	0.022	0.25	0.26	0.013
16	1526	35.4	40.5	0.8	20.7	0.0	2.6	1.21	0.050	0.28	0.35	0.009
17	1515	28.2	58.0	1.0	6.0	0.1	6.7	2.03	0.044	0.30	0.27	0.014
18	1594	31.6	53.5	1.0	7.0	0.0	6.9	2.56	0.042	0.26	0.27	0.009
19	1530	29.9	50.3	0.9	9.3	0.2	9.4	2.02	0.038	0.25	0.27	0.008
20	1528	43.2	45.1	2.0	5.0	0.1	4.7	2.67	0.038	0.25	0.27	0.009
21	1514	38.3	40.9	1.8	12.8	0.1	6.1	2.05	0.044	0.26	0.28	0.011
22	1534	40.6	39.4	0.5	16.0	0.0	3.5	1.61	0.051	0.29	0.27	0.007
23	1520	42.1	40.9	1.1	9.3	0.1	6.6	1.70	0.045	0.29	0.28	0.012

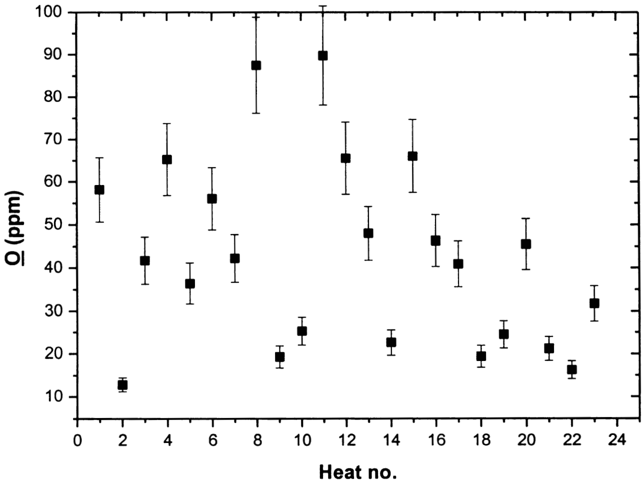


Figure 2. Calculated oxygen level in the liquid steel for various heats based on slag/metal equilibria involving 'FeO' in the slag (Equation [2])

thermophysical and thermochemical properties of slags as functions of temperature and composition. Presently, the software is capable of estimating the thermodynamic activities of slag components, sulphide capacities and viscosities. A brief description of the same is presented below:

A generic composition description19

According to this model, a system containing *m* different oxides, $C1_{c1}O_{a}1$, $C2_{c2}O_{a}2$,.... $Ci_{ci}O_{ai}$,.... $C_{cm}O_{am}$ can be represented as

$$\left(C1^{v1},C2^{v2},...Ci^{vi},..,Cm^{vm}\right)_p\left(O^{2-}\right)_q \qquad [3]$$

where *p* and *q* are stoichiometric numbers, Ci^{i} stands for cations, the superscript _*i* represents the electrical charge. The presence of basic cations such as Ca^{2+}, Fe^{2+}, Mg^{2+} and Mn^{2+} along with Si^{4+} will distort the oxygen matrix and determine the configuration of the ionic melt as well as the bond energies between different ions. The configuration of the ions and the bond energies will be functions of composition and temperature. While there are mutual effects between the cations and oxygen ions, the thermodynamic properties of the solution can be formulated by the consideration of the next-nearest neighbour interactions, namely the interactions between the cations when oxygen ions are present.

The models for sulphide capacity and activity estimations are presented in the following section. The viscosity model, which is widely used by a number of steel industries around the world is not taken up in the present paper. The module for the estimation of molar volumes is being introduced shortly. One of the salient features of this software is the establishment of mutual compatibilities between the various properties for a given slag composition.

Sulphide capacity model[20]

The sulphide capacity can be expressed as follows:

$$C_s = \exp\left(\frac{-\Delta^\circ G}{RT}\right)\frac{a_{o^{2-}}}{f_{s^{2-}}} \qquad [4]$$

where ΔG^o stands for the Gibbs energy change for the reaction:

$$\underline{S} + O^{2-} = \underline{O} + S^{2-} \qquad [5]$$

The ratio of the activity of O^{2-} to the activity coefficient of S^{2-} is expressed as:

$$\frac{a_{o^{2-}}}{f_{s^{2-}}} = \exp\left(\frac{-\xi}{RT}\right) \qquad [6]$$

In the present model, pure stoichiometric 'FeO' was chosen as standard for which the above ratio is taken as unity. In the case of unary systems, ξ is described as

$$\xi = {}^1L + {}^2L \cdot T \qquad [7]$$

On the other hand, ξ in a multicomponent system is a function of both temperature and composition and is expressed as:

$$\xi = \sum X_i \xi_i + \xi_{Mix} \qquad [8]$$

The term ξ_{Mix} represents the mutual interaction between different species.

Activity model[21–24]

The present description of silicate melts necessitates the assumption that the silicate network is completely dissociated into Si^{4+} and O^{2-} ions and even any aluminate complex to Al^{3+} and O^{2-} ions. The integral Gibbs energy of a solution can be expressed as:

$$G_m = \sum_i x_{Ci\,ci\,O\,ai}\,{}^{\circ}G_{Ci\,ci\,O\,ai} + RTp\sum_i y_{ci}\ln\left(y_{ci}\right) + {}^{E}G \qquad [9]$$

where R is the gas constant, T is the temperature and p is a stoichiometric number. The second term in Equation [9] corresponds to Temkin's[25] ideal mixing and the ${}^{E}G$, the excess Gibbs energy of the solution. In all the three cases, the term ξ_{Mix} (in the case of sulphide capacities), as well as ${}^{E}G$ (in the case of activities), is represented by Redlich-Kister polynomials. The model calculations were carried out assuming that 'FeO' is stoichiometric.

In the case of slag systems with relatively low amounts of 'FeO', it was found that the experimental data available in literature are often scarce and somewhat contradictory. The thermodynamic activities of 'FeO' were determined experimentally in these cases. A brief description of the technique adopted is presented below.

The principles, the preparation of material and their purities, the purification route for the gases involved, the experimental assembly, as well as the procedure, are described in detail in previous investigations[26–27]. The principle employed is based upon the equilibria between the molten slag in a platinum crucible and the partial pressure of oxygen defined by an Ar-CO-CO_2 gas mixture. The reaction at equilibrium can be represented as

$$Fe(Pt) + \frac{1}{2}O_2(g) = \text{'}FeO\text{'}(slag) \qquad [10]$$

$$\Delta^{\circ}G = -244433 + 47.2T^{28}\,(J/mol)$$

The activities of 'FeO' were calculated by using chemical analysis coupled with the thermodynamic information of the binary Fe-Pt system[29–31]. The partial pressures of the different components in the gas mixture were calculated by using the Thermo-Calc® software.

THERMOSLAG® calculations for 'FeO'-containing slags

In Figure 3, the results from the present optimization of the 'FeO' and SiO_2 activities with THERMOSLAG® along with model calculations by Thermo-Calc® at 1673 K and 1873 K, and with the F*A*C*T® software at 1873 K are presented. No experimental data are shown for the sake of clarity. The standard states are pure liquid 'FeO' and pure solid SiO_2. The present calculations are in agreement with the Thermo-Calc® calculations. F*A*C*T® shows a slight deviation for the 'FeO' activity. It can be observed from the present calculations that the activity of 'FeO' becomes more ideal with increased temperature. The activity of SiO_2 approaches unity as the temperature increases. A slight temperature effect on both activites was observed in the present calculations. This was also seen in the experimental measurements of this system. In short, the Thermo-Calc® and the THERMOSLAG® describe the activities throughout the liquidus composition range for a given temperature and composition without any significant difference.

An example of the calculated iso-activity lines of 'FeO' in the Al_2O_3-'FeO'-SiO_2 system at 1873 K (which is relevant to the ladle slags) by THERMOSLAG® is illustrated in Figure 4, along with the results of the gas equilibration measurements carried out by the present authors. It can be seen that the model predictions agree well with the experimental data. From the laboratory work, it was concluded that the temperature coefficient was negligible for the activities of 'FeO' in this system. It was also noted that the activities of 'FeO' show a negative

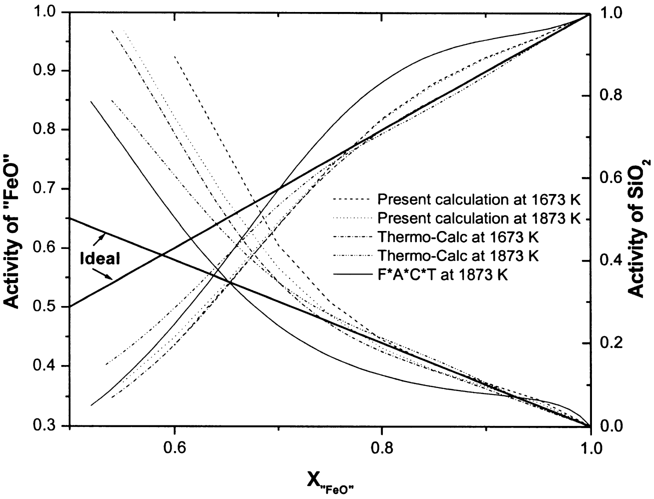


Figure 3. Calculated activities of 'FeO' and SiO_2 in the 'FeO'-SiO_2 system

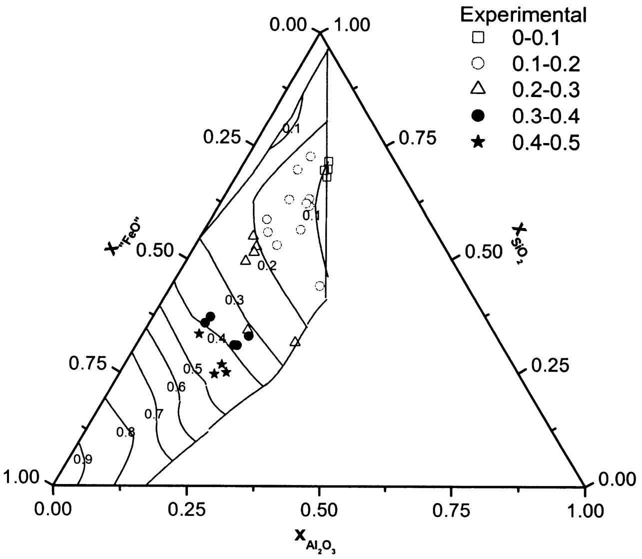


Figure 4. Calculated and experimentally determined activities of 'FeO' in the Al_2O_3-'FeO'-SiO_2 system at 1873 K

deviation from Raoult's law at low 'FeO' contents in the slag. Similar results were also shown by Yamanaka *et al.*[12] when measuring the liquid 'FeO' activity in this slag system in equilibrium with pure solid iron at 1673 K.

In Figure 5, some examples of the application of the THERMOSLAG® software for iron- and steelmaking slags is presented. In this figure, the variation of the activity of Al_2O_3 for some typical slags in the EAF, BF and LF processes used by the Swedish steel industry are shown. Figure 6 shows an overview of the running software when calculating the sulphide capacity for the Al_2O_3-CaO-SiO_2 system.

It would be interesting to utilize the capabilities of the THERMOSLAG® software to compute the impact of the slag basicity on the sulphide capacities as well as the activities of 'FeO'. In order to carry out this, both the activity as well as the sulphide capacity modules from the software were utilized for fictitious slags in the composition ranges of the slag samples reported in Table I. Three different ranges of slag compositions were selected at 1873 K. In these composition ranges, the Al_2O_3 content was varied between 30 and 40 weight per cent, the 'FeO' content between 0.5 and 2 weight per cent, and the MnO content between 0.1 and 0.2 weight per cent. Figure 7 illustrates the variations of the activity of 'FeO' thus computed and sulphide capacity of the slags as functions of the basicities in the range of the OVAKO Steel refining practice. It can be seen that the activity of 'FeO' increases with increasing 'FeO' content in the slag and with decreasing basicity in the selected basicity region of the slag under investigation. The calculations also show an increasing sulphide capacity with increasing basicity. The trends are in conformity with the general observations.

Application of THERMOSLAG® software to sulphur partition

An alternative strategy to estimate the oxygen content in steel would be to follow the partition of sulphur between the slag and the steel bath. This is due to the fact that the sulphur analyses in the slag are generally known with better certainty. Further, the sulphur content in the slag is not easily affected by the errors in the sampling procedure. The strategy used in the present work to estimate the oxygen levels in the steel bath was to exploit the link between the

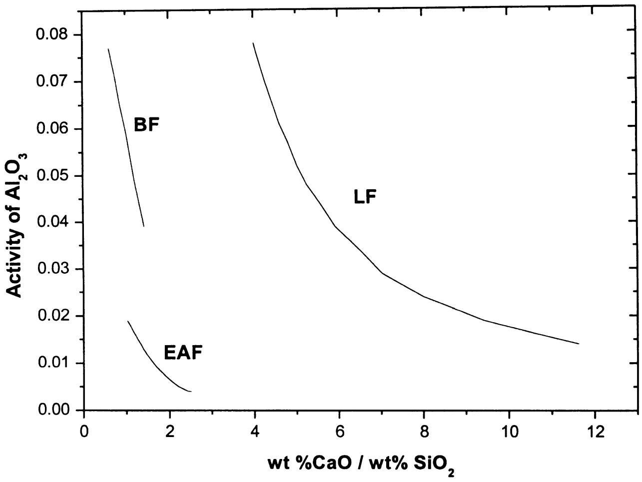
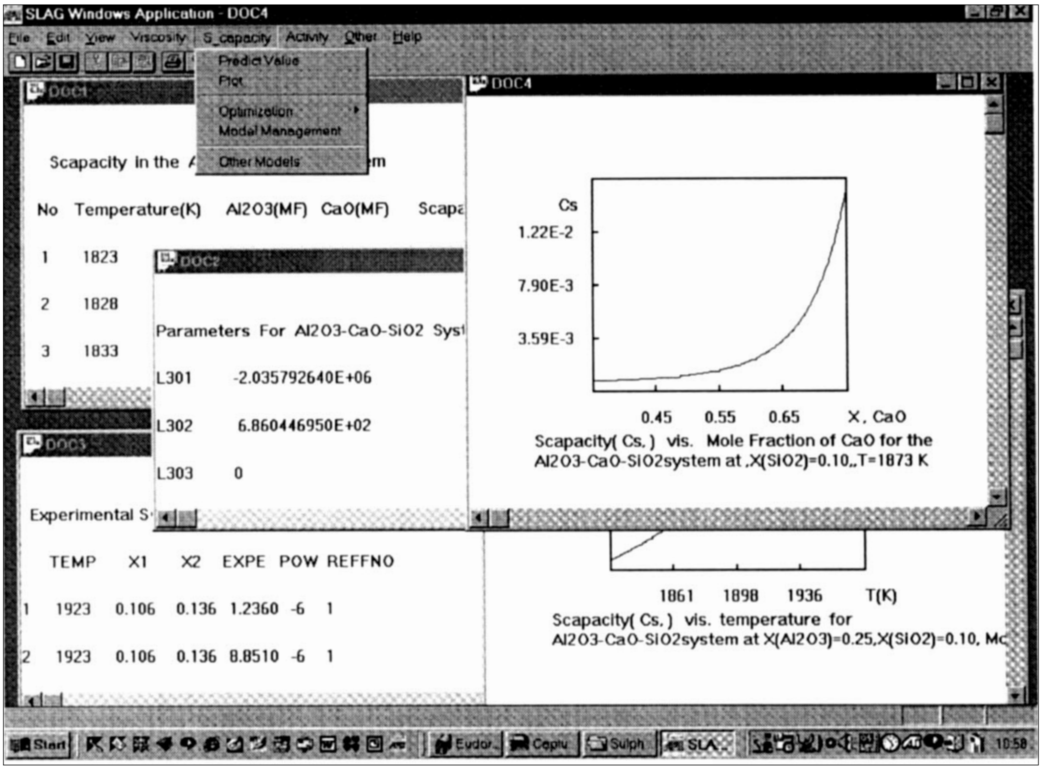


Figure 5. The activity of Al_2O_3 in some EAF, BF and LF slags as a function of the amount of CaO and Sio_2 present in the slag



```
Scapacity in the A                    m

No  Temperature(K)   Al2O3(MF)  CaO(MF)   Scapa

1    1823

2    1828

3    1833
```

```
Parameters For Al2O3-CaO-SiO2 Syst

L301      -2.035792640E+06

L302       6.860446950E+02

L303      0
```

```
Experimental S

   TEMP    X1     X2    EXPE   POW  REFFNO

1  1923   0.106  0.136  1.2360  -6   1

2  1923   0.106  0.136  8.8510  -6   1
```

Scapacity(Cs.) vis. Mole Fraction of CaO for the Al2O3-CaO-SiO2system at ,X(SiO2)=0.10,,T=1873 K

Scapacity(Cs.) vis. temperature for Al2O3-CaO-SiO2system at X(Al2O3)=0.25,X(SiO2)=0.10, Mc

Figure 6. An overview of the running THERMOSLAG® software

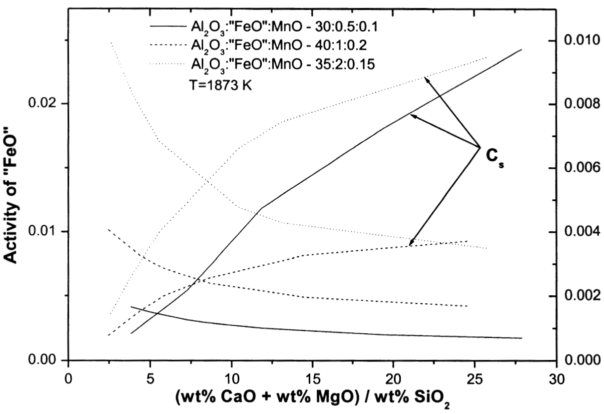


Figure 7. The calculated activity of 'FeO' and sulphide capacity at various compositions as a function of the basicity at 1873 K

sulphur content in the slag and oxygen in the metal in order to estimate the oxygen content in the liquid steel bath. In this approach, the equilibrium relationship between sulphur and oxygen in the metal, as shown in Equation [5], may be described as follows

$$\underline{S}_{(Steel)} + [O]_{(Slag)} = \underline{O}_{(Steel)} + [S]_{(Slag)}$$
$$\Delta°G_{11} = 17908 - 26.31T^{32}(J/mol) \qquad [11]$$

The equilibrium constant for Equation [11] is

$$K_{11} = \frac{a_o}{a_s}\cdot\frac{[S]}{[O]} = \frac{\%\underline{O}}{\%\underline{S}}\cdot\frac{[S]}{[O]} \qquad [12]$$

Assuming equilibrium conditions and constant activities of sulphur and oxygen (in the slag of high basicity with very small amounts of sulphur) during this stage of the plant operations, the above equation shows that an increase of sulphur in the molten metal will show a corresponding increase of oxygen in the same phase. The oxygen content in the metal phase may then be calculated by using the following relationship

$$L_s = \frac{(wt\%S)_{slag}}{[wt\%S]_{metal}} = K_{11}C_S\frac{f_{\underline{s}}}{wt\%\underline{O}\cdot\gamma_{\underline{o}}} \qquad [13]$$

where L_s is the sulphur distribution ratio, C_S the sulphide capacity, calculated by using the Sulphide capacity model[20], $f_{\underline{S}}$ is the sulphur activity coefficient and $\gamma_{\underline{O}}$ is the Henrian activity coefficient of the dissolved oxygen in the molten metal on the weight per cent basis.

Using Equation [13], the weight per cent (wt%) $\underline{O}$ in molten steel could be estimated. The terms $f_{\underline{S}}$ and $\gamma_{\underline{O}}$ could be estimated using the classical Wagner's equation. The weight per cent $\underline{O}$ in the metal could be estimated by iterative computation.

In an effort to see how the oxygen content in the metal computed by means of the sulphur partition affects the 'FeO' activities in the slag, the values of $a_{\text{'FeO'}}$ in the slag were 'back-calculated' using the estimated weight per cent $\underline{O}$ from Equation [13]. In Figure 8, the dissolved oxygen in the steel bath is shown as a function of the calculated activites of 'FeO' in the slag. The oxygen content was calculated by employing Equations [11]–[13] along with the steel and slag analysis presented in Table I. The activity of 'FeO' was then calculated on the basis of the calculated oxygen contents in the metal and the oxygen partition between slag and metal corresponding to Equations [1] and [2]. It can be seen that the activity of 'FeO' in the slag increases with an increase of the amount of the weight per cent $\underline{O}$ in the metal computed according to Equation [13], i.e., higher oxygen potential in the metal would lead to higher activity of 'FeO' in the slag. This will also lead to a higher sulphur content in the metal as well, which is in accordance with Equation [12].

The oxygen contents computed using sulphur partition for the various heats are plotted in Figure 9. It is seen that the activities of 'FeO' calculated using the sulphur partition are also much fewer than the activites calculated directly from the slag compositions given in Table I using THERMOSLAG®. By comparing Figure 2 with Figure 9, it can be seen that the oxygen content calculated with the sulphur partition strategy Equations [11]–[13] differ from the oxygen partition approach according to Equation [2], by one order of magnitude, the latter being in agreement with accepted plant practice. Further, the mutual consistencies in the oxygen contents in the metal between the various heats confirms the soundness of the present approach. This indicates that great caution must be exercised in the sampling and analysis procedure adopted in the plant practise. Figure 9 also shows that the oxygen level in the end product is higher compared to the steel in the refining

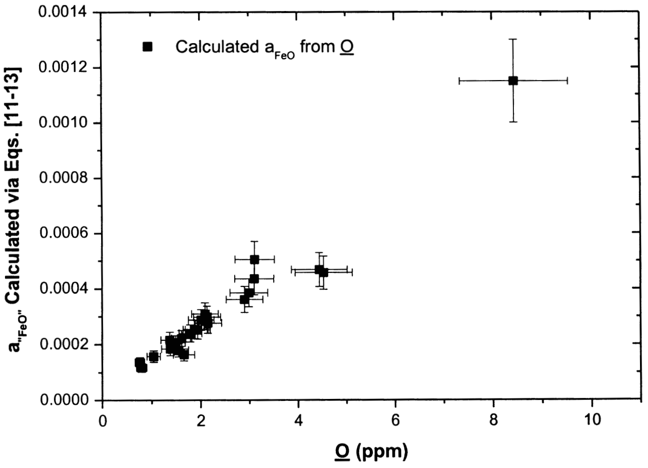


Figure 8. The calculated activity of 'FeO' from the dissolved oxygen in the liquid steel obtained via Equations [11] to [13]

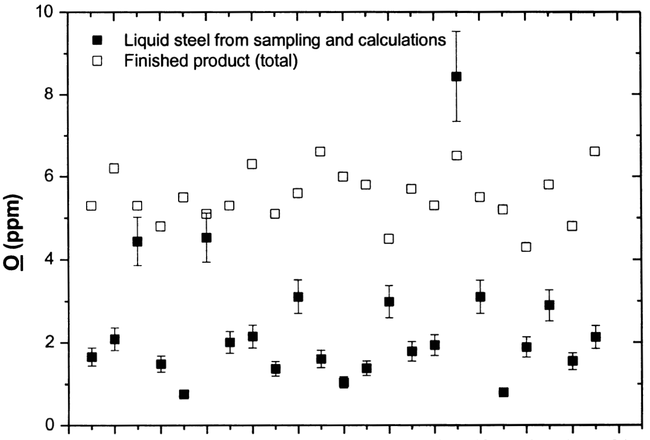


Figure 9. Dissolved oxygen in the liquid steel based on chemical analysis and present calculations for the various heats

step, which is expected in steelmaking and casting practice. The sulphur partition route to estimate the oxygen levels in molten steel is currently incorporated in the THERMOSLAG® software in order to overcome the difficulties experienced by steel industries in oxygen estimations by sampling and analysis.

Summary

Selected experiments were carried out at steelmaking temperatures with gas equilibrium technique in order to generate thermodynamic information of 'FeO' for ladle refining slags. Reassessment of the present results, along with previous investigations, was performed with the KTH slag model. New information was generated, in accordance with the requirements of the model by gas-slag equilibration technique.

Model calculations were performed with the KTH slag software, THERMOSLAG®, by using plant data from OVAKO Steel, Hofors, Sweden. It was found that oxygen estimations in the metal from the 'FeO' analyses of slags, obtained by conventional sampling and analysis methods, were less reliable. Estimation of the oxygen levels utilizing the sulphur partition between the slag and the metal were carried out using THERMOSLAG® software. Reasonable estimations of the oxygen contents in the metal confirmed that this could be a very useful tool for the plant operator.

Acknowledgements

Patrik Undvall, M.Sc. student at OVAKO Steel in Hofors, Sweden, is gratefully acknowledged for providing plant data. The authors are also thankful to Professor Du Sichen for his valuable comments.

References

1. SCHUMAN, R. and ENSIO J.P. Thermodynamics of iron-silicate slags. *Trans. AIME*, 1951. pp. 401–411.
2. BODSWORTH, C. The activity of ferrous oxide in silica melts. *J. Iron Steel Inst.*, vol. 193, 1959. pp. 13–24.
3. FUIJITA, H. and MARUHASHI, S. Activities of the iron-oxide silica slags. *Tetsu-to-Hagane.*, vol. 55, no. 4. 1969. pp. 249–260.
4. DISTIN, P.A., WHITEWAY, S.G., and MASSON, C.R. Thermodynamics and constitution of ferrous silicate melts. *Can. Met. Quart.*, vol. 10, no. 2. 1971. pp. 73–78.
5. WANIBE, Y., YAMAUCHI, Y., KAWAI, K., and SAKO, H. Electrochemical measurement of the activity of iron oxide in the FeO-SiO_2 liquid slag. *ISIJ*. vol. 12. 1972. pp. 472–476.
6. BAN-YA, S., CHIBA, A., and HIKOSAKA, A. Thermodynamics of Fe_tO_y (M_xO_y = CaO, SiO_2, TiO_2, and Al_2O_3) binary melts in equilibrium with solid iron. *Tetsu-to-Hagane.*, vol. 66, no. 10. 1980. pp. 1484–1493.
7. VAN WIJNGAARDEN, M.J.U.T. and DIPPENAAR, R. J. The use of zirconia-based solid electrolytes for the rapid determination of iron oxide activities in iron- and steelmaking slags. *J. S. Afr. Inst. Min. Met.*, vol. 86, no. 11. 1986. pp. 443–453.
8. DHIMA, A., STAFA, B. and ALLIBERT, M. Activity measurements in steel-making-related oxide melts by differential mass spectrometry. *High Temperature Science*. vol. 21, 1986. pp. 143–159.
9. FUJITA, H., IRITANI, Y. and MARUHASHI, S. Activities in the iron-oxide lime slags. *Tetsu-to-Hagane.*, vol. 54, 1968. pp. 359–370.
10. TAKEDA, Y. and YAZAWA, A. Thermodynamic study of the liquid Fe-O-CaO system saturated with iron. *Nippon Kogyokashi.*, vol. 96, 1980. pp. 901–905.
11. IWASE, M., YAMADA, N., NISHIDA, K., and ICHISE, E. Rapid determinations of the activities in CaO-Fe_xO liquid slags by disposable electrochemical oxygen probes. *Trans. ISS.*, vol. 4, 1984. pp.69–75.
12. YAMANAKA, R., KOYAMA, S., and IWASE, M. A thermodynamic study of the system FeO-Al_2O_3-SiO_2 at 1673 K. *Met. Trans.* B, vol. 22B, 1991. pp. 839–845.
13. TAYLOR, C.R. and CHIPMAN, J. Equilibria of iron and simple basic and acid slags in a rotating induction furnace. *Trans. AIME.*, vol. 154, 1943. pp. 225–247.
14. TIMUCIN, M. and MORRIS, E. Phase equilibria and thermodynamics studies in the system CaO-FeO-Fe_2O_3-SiO_2. *Met. Trans.*, vol. 1, 1970. pp. 3193–3201.
15. OGURA, T., FUJIWARA, R., MOCHIZUKI, R., KAWAMOTO, Y., OISHI, T., and IWASE, M. Activity determinator for the automatic measurements of the chemical potentials of FeO in metallurgical slags. *Met. Trans. B.*, vol. 23B, 1992. pp. 459–466.
16. BYGDÉN, J., SICHEN, D., and SEETHARAMAN, S. Thermodynamic activities of FeO in CaO-FeO-SiO_2 slags. *Steel Research.*, vol. 10, 1994. pp. 421–428.
17. BAN-YA, S. and SHIM, J.D. Application of the regular solution model for the equilibrium of distribution of oxygen between liquid iron and steelmaking slags. *Can. Met. Quart.*, vol. 21, no. 4. 1982. pp. 319–328
18. SUITO, H. and INOUE, R. Thermodynamic considerations on manganese equilibria between liquid iron and Fe_tO-MnO-MO_x (MO_x=$PO_{2.5}$, SiO_2, $AlO_{1.5}$, MgO, CaO) slags. *Trans. Iron Steel Inst. Jpn.*, vol. 24, no. 4, 1984. pp. 301–307.
19. SEETHARAMAN, S., SICHEN, D. and ZHANG, J.Y. The computer-based study of multicomponent slag viscosities. *JOM* (*USA*), vol. 51, no. 8. 1999. pp. 38–40.
20. NZOTTA, M.M. Ph.D. Thesis, Division of Metallurgy, Royal Inst. Techl., Stockholm, Sweden, 1998.
21. BJÖRKVALL, J., SICHEN, D., and SEETHARAMAN, S. Thermodynamic description of 'FeO'-MgO-SiO_2 and 'FeO'-MnO-SiO_2 melts—a model approach. *High Temp. Mat. Proc.*, vol. 19, no. 1. 2000. pp. 49–59.
22. BJÖRKVALL, J. and STOLYAROVA, V.L. A knudsen cell mass spectrometric study of Al_2O_3-SiO_2

melts. Internal Report TRITA-MET 066, Dep. of Met., Royal Inst. of Tech., Sweden, 1999.

23. BJÖRKVALL, J., SICHEN, D. and SEETHARAMAN, S. Thermodynamic description of Al_2O_3-CaO-MnO and Al_2O_3-FeO-MnO melts—a model approach. *CALPHAD.*, vol. 24, no. 3. 2000. pp. 353–376.

24. BJÖRKVALL, J., SICHEN, D., and SEETHARAMAN, S. Thermodynamic model calculations in multicomponent liquid silicate systems. *Ironmaking and Steelmaking* (*UK*)., vol. 28, no. 3. 2001. pp. 250–257.

25. TEMKIN, M. Mixtures of fused salts as ionic solutions. *Acta Phys. Chim. URSS.*, vol. 20, no. 4. 1945. pp. 411–420.

26. FREDRIKSSON, P. and SEETHARAMAN, S. Thermodynamic activities of some binary 'FeO' containing slags. To be published.

27. FREDRIKSSON, P. and SEETHARAMAN, S. Thermodynamic activities of some ternary 'FeO' containing slags. To be published.

28. JANAF, *Thermochemical Tables,* 3rd ed., vol. 14, no. 1. 1985. pp. 1190.

29. FREDRIKSSON, P. and SEETHARAMAN, S. Thermodynamic studies of some Fe-Pt alloys by the solid electrolyte galvanic cell method. *Sc. J. of Met.*, vol. 30, no. 4, 2001. pp. 258–264.

30. FREDRIKSSON, P. A differential thermal analysis of the iron-platinum system. Submitted to the *Sc. J. of Met.* in July 2003 for publication.

31. FREDRIKSSON, P. and SUNDMAN, B. A thermodynamic assessment of the Fe-Pt system. *CALPHAD*, vol. 25, no. 4. 2001. pp. 535–548.

32. SIGWORTH, G.E. and ELLIOT, J.F. Thermodynamics of liquid dilute Fe alloys. *Metal Sci.*, vol. 8, no. 9. 1974. pp. 298–310.