

Thermodynamic Calculations Predicting MgO Saturated EAF Slag for Use in EAF Steel

Production

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Keywords: EAF, MgO saturated slags, Thermodynamic calculations

Abstract

Foamy slags are widely used in EAF steel production because the use of these slags result in energy savings, productivity improvements, and enhanced refractory service life. Foamy slag requires the control of slag viscosity to sustain gas bubbles during processing. This is accomplished through the precipitation of magnesium wüstite particles in the slag at the operating temperature. A thermodynamic program, Factsage™, was utilized to study the quaternary oxide system of MgO-CaO-FeO-SiO₂, to predict the dual (saturated with CaO and MgO) and MgO saturated EAF slag chemistry under different oxygen partial pressures, temperatures, and slag basicity. These predictions indicate a linear relationship between oxide components and slag basicity, from which an accurate prediction of the optimum slag chemistry can be made. The results of the Factsage™ models will be compared to models developed by other researchers and experimental data.

Introduction

Foamy slags shield the electrical arcs, increasing productivity, lowering noise level, preventing radiation energy loss, eliminating arc flares, saving overall energy and extending refractory service life. It has been reported (1) that a foamy slag practice can save 3-10% in energy and decrease refractory consumption by 25-63%. Foamy slag is obtained by the injection of O and C through lances. Oxygen reacts with iron to form iron monoxide. Iron monoxide reacts with carbon to generate carbon monoxide gas bubbles and iron. Slag chemistry and viscosity impact the quality of foaming processes. Thin slag can not sustain gas bubbles, while thick slag discourage the formation of gas bubbles. The “good” slag is a molten, MgO saturated slag with the presence of a suspended second phase particle (MgO · FeO magnesium wustite (MW)) at the operating temperature (2). The saturated MgO slag will be not only foam better, but will also decrease refractory wear.

EAF slags typically contain five major oxides: CaO, MgO, SiO₂, FeO and Al₂O₃. In this paper, only CaO, MgO, SiO₂, and FeO are considered because of the complexity of thermodynamic calculations. Eugene Pretorius(2) studied EAF foaming slag and proposed isothermal stability diagrams (ISD) expressed at constant basicity, Figure 1, which is separated into four regions; molten slag, magnesium oxide saturated, calcium oxide saturated, and dual saturated. A point (D) is bounded by these four regions in Figure 1, and is called the dual saturated point in this paper. A straight line separating the molten slag and magnesium oxide saturated region is called the magnesia saturated line. Slag in the magnesium oxide saturated region has the precipitation of magnesium oxide containing phases such as magnesium wüstite ((Mg,Fe)O), while slag in the calcium oxide saturated region has the precipitation of calcium oxide containing phase such as Ca₂SiO₄. Therefore, slag at the dual saturated point contains the initial precipitation of

Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE FEB 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Thermodynamic Calculations Predicting MgO Saturated EAF Slag for Use in EAF Steel Production				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Energy (US DOE),National Energy Technology Laboratory,Pittsburgh,PA,15236				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002300. Presented at the Minerals, Metals and Materials Annual Meeting and Exhibition (138th)(TMS 2009) Held in San Francisco, California on February 15-19, 2009. Sponsored in part by the Navy. U.S. Government or Federal Purpose Rights.					
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15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

magnesium and calcium oxide containing phases. Eugene Pretorius built a computer model based on a mass-balance approach to design target slag compositions, however, a detailed information on his algorithm is unknown.

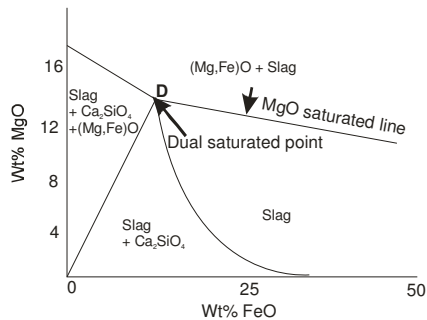


Figure 1 Isothermal stability diagrams at constant basicity (ISD) proposed by Eugene Pretorius

MgO saturated and CaO saturated phase diagrams at 1600°C, in contact with metallic iron were published in the Slag Atlas (3). Both diagrams show contour lines of MgO above 6 wt%. Several linear (straight line) relationships were found among basicity, acidity, and constituents of dual saturated slags from diagrams as shown Table 1. Based on these linear relationships, a computer model was built to calculate dual saturated and MgO saturated EAF slag chemistry for specific basicity indexes (4).

Oxygen partial pressure has a large influence on the formation of FeO or Fe₂O₃ and consequently, on the liquidus temperature of slag. Literature reviews (5,6) and field samples indicate that the oxygen partial pressure in foaming slag varies depending on operational conditions, location in the EAF, and feedstock. Six temperature values from 1600 to 1700°C and three values of oxygen partial pressure per temperature were selected for thermodynamic studies. The lowest PO₂ was set to the interface of Fe-FeO formation. The highest PO₂ was set to the interface of FeO-Fe₃O₄ formation. The medium value was the average of the high and low values. Temperature also affects the formation of Fe, FeO and Fe₂O₃, therefore, these PO₂ set values were varied with different temperatures. Table 2 lists the studied oxygen partial pressure at different temperatures and basicities ranging from 1.3 to 2.9. A basicity B3 (CaO/SiO₂) was used in this paper.

Table 1 The regression fitting quality (R square) between atomic percentages of oxides and acidity (S/C) or basicity (C/S)

Relationships	R Square	Relationships	R Square
S/C - SiO ₂	0.98	C/S - CaO	1.0
S/C - MgO	0.99	MgO - FeO	0.99
S/C - FeO	0.98		

Table 2 Oxygen partial pressures at different temperatures for the input parameters of Factsage™ thermodynamic calculations.

Temperature (°C)	High oxygen	Mediun Oxygen	Low Oxygen
1600	-4.722	-6.491	-8.260
1620	-4.576	-6.350	-8.123
1640	-4.431	-6.208	-7.985
1660	-4.285	-6.067	-7.848
1680	-4.140	-5.925	-7.711
1700	-3.994	-5.784	-7.574

Results and Discuss

The Dual Saturated EAF Slag Chemistry Derived Using Thermodynamic Calculations

Dual saturated EAF slags may not occur under two conditions: 1) when the MgO content in slag is less than about 5 wt%, where the formation of both (Mg, Fe)O and Ca_2SiO_4 together is not possible, and 2) when the temperature is above 1680°C for basicity less than 1.3, the formation of Ca_2SiO_4 is not possible. For simplification and clarification, only “normal” cases will be considered in this paper.

Figure 2 shows the effect of basicity for dual saturated EAF slag chemistry at a constant temperature (1600°C) and high oxygen partial pressure. This figure shows that slag with increasing basicity are dual saturated with decreasing MgO concentration. Table 3 indicates that the constituents of a dual saturated slag have linear relationships with basicity or acidity similar to the results obtained using the Slag Atlas' FeO-MgO-CaO-SiO₂ phase diagram. It also shows that some relationships don't provide good linear regression reliability for predicting the dual saturated slag chemistry when MgO concentration in a dual saturated slag is below 6%.

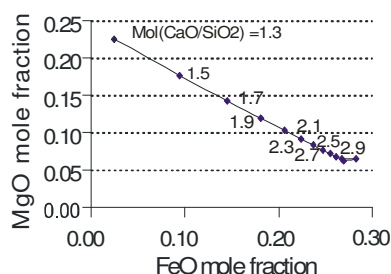


Figure 2 The effect of basicity for a dual saturated EAF slag chemistry at a constant temperature (1600°C) and high oxygen partial pressure

Table 3 The regression reliability of linear relationships with the consideration of all cases and when the MgO content in a dual saturated slag is more than 6 wt%.

Relationships	R Square (All)	R Square (MgO > 6%)
MgO-FeO	0.996	1
SiO ₂ -S/C	0.999	1
FeO-S/C	0.973	0.991
CaO-C/S	0.970	0.996
MgO-S/C	0.964	0.989
Number of Obserations	13	7

Oxygen partial pressure also affects the dual saturated slag chemistry. Table 4 reports the values of FeO and MgO content of dual slags with different oxygen partial pressure and basicity. Table 4 indicates that a dual saturated slag with a given basicity in a high oxygen partial pressure environment should contain higher MgO concentration than in a low oxygen environment. Higher standard deviation of MgO concentration means that oxygen has a greater effect in dual slag chemistry. The oxygen partial pressure has a greater effect on foaming quality and refractory wear when slag basicity is between 1.4 and 1.8.

Table 4 The content of FeO and MgO in a dual saturated slag in different oxygen partial pressures and slag basicity and the standard deviation of FeO and MgO concentration due to the effect of oxygen partial pressure.

	High PO ₂		Medium PO ₂		Low PO ₂		Standard Deviation	
Basicity	FeO mol%	MgO mol%	FeO mol%	MgO mol%	FeO mol%	MgO mol%	FeO Std	MgO Std
1.213	0.025	0.225	0.031	0.220	0.035	0.216	0.005	0.005
1.400	0.095	0.177	0.111	0.166	0.125	0.157	0.015	0.010
1.587	0.146	0.143	0.165	0.132	0.180	0.124	0.017	0.010
1.773	0.181	0.120	0.200	0.110	0.214	0.103	0.016	0.008
1.960	0.206	0.103	0.221	0.094	0.233	0.089	0.013	0.007
2.147	0.224	0.092	0.233	0.083	0.241	0.078	0.009	0.007
2.333	0.237	0.083	0.238	0.073	0.241	0.068	0.002	0.008

Temperature also affects the dual saturated EAF slag chemistry. As temperature increases, higher concentration of MgO and less of FeO are needed to keep slags saturated with CaO and MgO at a constant basicity. Statistic analytic results (table 5) show that good regression fitting exists between constituents of dual saturated slags and temperature at a basicity of 1.7 in high oxygen partial pressure. This also indicates that interpolation is an acceptable way to predict dual saturated slag chemistry at any temperature between 1600 and 1700°C.

Table 5 Regression reliability between oxide concentration in dual saturated slag and temperature from statistic analytic results for cases of dual slag chemistry with a basicity of 1.7 in high oxygen partial pressure.

Relationships	R square	Relationships	R square
CaO-Temperature	0.999	FeO-Temperature	0.999
SiO ₂ -Temperature	0.999	MgO-Temperature	0.989

The MgO Saturated Slag Chemistry Derived by Thermodynamic Calculations

The dual saturated EAF slag chemistry can be predicted using linear relationships among oxides and their basicity (or acidity) as previous discussed. The effect of basicity, temperature, and oxygen partial pressure on the constituent of MgO in a saturated slag should also be explored

The Effect of Basicity

Figure 3 shows MgO saturated lines for different basicity at 1640°C in a high oxygen partial pressure ($10^{-4.43}$). This figure indicates that slags with higher basicity can be saturated using less MgO. However, as iron oxide content in slag increases, higher basicity (more than 1.9) slags require more MgO in order to stay saturated. In addition, slags with lower basicity can be saturated by less MgO.

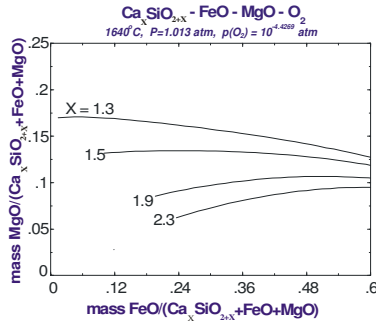


Figure 3 MgO saturated lines for different basicity at 1640 °C in high oxygen partial pressure ($10^{-4.43}$).

Figure 4 shows the linear relationship between CaO-FeO and SiO₂-FeO for MgO saturated slag chemistry at 1700°C in high oxygen partial pressures. These linear relationships among oxides support the model proposed by NETL scientists which will be discussed later in this paper.

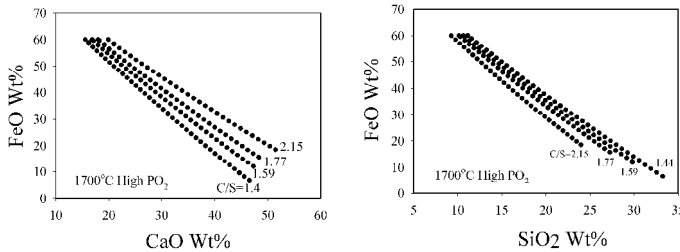


Figure 4 Linear relationship between CaO-FeO and SiO₂-FeO at different C/S ratios for MgO saturated slag chemistry at 1700°C in high oxygen partial pressure.

The Effect of Temperature on MgO Saturated Lines

The effect of temperature on the chemistry of MgO saturated slags was studied in cases where slag basicity was 1.7 at medium oxygen partial pressure. The slag constituents can be drawn against temperatures with the assumption of a constant FeO content. Figure 5 shows the results, and indicates a linear relationship exists between oxide concentrations and temperature.

Therefore, the interpolation method predicting the slag chemistry along the MgO saturated line between temperatures from 1600 to 1700°C is possible.

The Effect of Oxygen Partial Pressure

As previously discussed, the oxygen partial pressure in a EAF is unknown, and depends on the operational conditions and the location within the slag. Slag near the surface or close to the oxygen lance has a higher oxygen partial pressure, while, slag near the molten metal has a lower oxygen partial pressure. In addition, the turbulence of slag and metal may also dynamically change the oxygen partial pressure in the EAF. Figure 6 shows the effect of oxygen partial pressure. Higher MgO levels are needed in higher oxygen partial pressure environment to maintain saturation. Therefore, slag in a higher oxygen partial pressure may dissolve EAF refractory (MgO/C refractory) much more and quickly than in a low oxygen partial pressure.

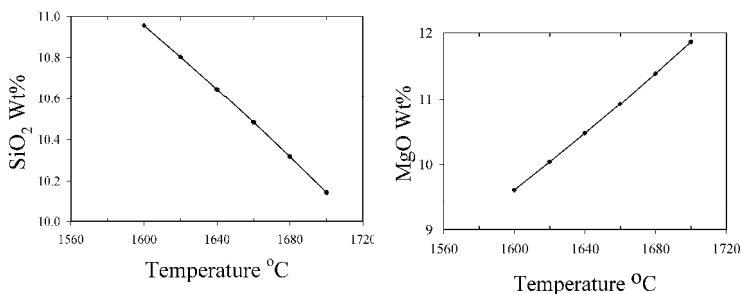


Figure 5 The linear relationship between SiO₂ and MgO with temperature at a constant FeO content.

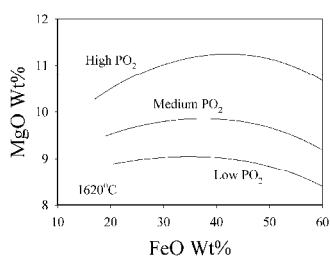


Figure 6 The effect of oxygen partial pressure on MgO saturation level.

The Verification of Modeling Developed by NETL and Thermodynamic Calculations

A model (4) was previously proposed to calculate EAF dual and MgO saturated slag chemistry through the analysis of MgO-FeO-SiO₂-CaO diagrams in the Slag Atlas (3), which is shown in Figure 7. Point D in fig 7 is a dual saturated point which can be predicted by linear relationships among the slag constituents, and their basicity/acidity. The location of point E can be decided by the MgO-FeO_x phase diagram at a designed temperature. Because of the linear relationships already established, the MgO saturated line ($\overline{DE}$) can be created by connecting points D and E.

The linear regressions analysis of data in Figure 4 are summarized in Table 6. This table indicates a highly linear relationship between CaO-FeO and SiO₂-FeO and a common intercept point at 0.8571 (FeO wt%) when both CaO and SiO₂ content are close to zero. This condition means that MgO (0.1429 wt%) and FeO (0.8571 wt%) are major constituents in slags, with compositions similar to point E in Figure 7. Checking the MgO-FeO phase diagrams published by R. E. Johnson and A. Muan (7), a melt at 1700 °C can contain up to about 14.98 wt% MgO without solid precipitation. Therefore, it is a reasonable assumption that the MgO saturation line in an ISD starts at the dual saturation point which can be predicted as previous discussed, and ends at a point decided by the MgO-FeO phase diagram.

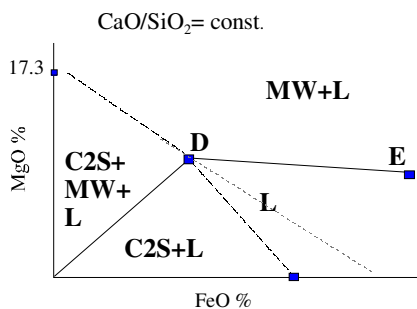


Figure 7 The Isothermal Solubility Diagram Model used to Predict MgO Saturated EAF Slag Chemistry (4)

Table 6 Regression reliability from the statistic analysis for lines in Figure 4

Basicity	CaO-FeO Regression			SiO ₂ -FeO Regression		
	R Square	Intercept	slope	R Square	Intercept	slope
1.40001	0.9995	0.8602	-1.7205	0.9995	0.8602	-2.4087
1.58668	0.9994	0.8574	-1.5711	0.9994	0.8574	-2.4928
1.77335	0.9993	0.8553	-1.4593	0.9993	0.8553	-2.5879
2.14669	0.9992	0.8554	-1.3152	0.9992	0.8554	-2.8233
Average		0.8571			0.8571	
STD		0.0023			0.0023	

The following mathematic expression predicts the MgO-FeO linear relationships for the MgO saturated line ($\overline{DE}$) as follows:

$$\text{CaO} = A \times \text{FeO} + B \quad (1)$$

$$\text{SiO}_2 = C \times \text{FeO} + B \quad (2)$$

$$\text{SiO}_2 + \text{CaO} + \text{FeO} + \text{MgO} = 1 \quad (3)$$

$$\text{MgO} = (1 - 2B) - (1 + A + C) \times \text{FeO} \quad (4)$$

Where

A and C are coefficient of slope

B is a constant of the intercept

Equation 4 indicates that MgO should have a linear relationship with FeO for MgO on the saturation line ($\overline{DE}$), if the linear relationships between CaO-FeO and SiO₂-FeO are recognized. Figure 9 plots the results from above assumption for the cases of 1600°C and 1700°C in high oxygen partial pressure with varying basicity. The discrepancy in MgO saturation content between using Factsage™ calculations and assumption is less than 1%. Therefore, the model proposed is reasonably accurate when FeO content in slag is less than 60 wt%. These simple linear relationships explored in this study and the proposed model will allow EAF operators to predict slag saturation conditions in their EAF and to optimize slag foaming conditions throughout the heat.

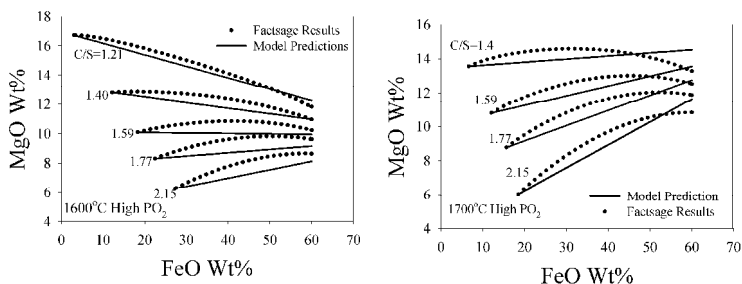


Figure 9 The discrepancy between Factsage calculation results and model assumption for cases at the temperature of a) 1600°C and b) 1700°C in high PO_2 atmosphere.

CONCLUSIONS

A thermodynamic program, FactsageTM, has been utilized to study a simple quaternary oxide system (MgO-CaO-FeO-SiO_2) and to predict the dual (saturated with CaO and MgO) and MgO saturated EAF slag chemistry with variations of oxygen partial pressure, operational temperature, and slag basicity. Results from thermodynamic calculations indicate that there are linear relationships among oxide components, basicity, and acidity which make predicting the optimum slag chemistry possible. Calculation results have very good agreement with the proposed model about these linear relationships. Results also indicated that oxygen partial pressure has some effects on the constituents of dual and MgO saturated slags.

REFERENCES

- 1) D. Capodilupo, P. Masucci, G. Brascugli, and V. De Angelis, "Operating Improvements in Electric Steel Production on Terni EAF after Introduction of Slag Foaming Practice," Proceeding of the Sixth International Iron and Steel Congress, Nagoya, ISIJ, (1990) 98-104.
- 2) E. Pretorius "Slag Fundamentals"; in An Introduction to the Theory and Practice of EAF steelmaking, Iron & Steel Society short course book, New Orleans, LA Nov. 1998
- 3) M. Kowalski, P. J. Spencer, and D. Neuschütz, "Phase Diagrams"; in Slag Atlas, 2nd ed. Edited by Verein Deutscher Eisenhüttenleute, Verlag Stahleisen GmbH, (1995) 21-215.
- 4) K. S. Kwong, and J. P. Bennett, "Balancing MgO for Foamy Slag and Refractory Protection" D.L. Schroeder & Associates, Twenty Second Annual Symposium, Process Systems for Electric Furnace Steelmaking, Orlando, Florida, November 2000.
- 5) R. J. Fruehan, "Optimization of Post Combustion in Steelmaking" DOE report for work performed under Cooperative Agreement No. DE-FC36-97ID13554 March 2004.
- 6) M. Kirschen, V. Veiikorodov and et al. "Off-gas Measurements at the EAF Primary Dedusting System" *Stahl und eisen* 124 (11), 73-89.
- 7) E. Johnson and A. Muan, "Phase Equilibria in System $\text{CaO-MgO-Iron oxide}$ at 1500 Degrees C" *J. Am. Ceram. Soc.*, 48(7) (1965), 359-364.