THERMODYNAMIC STUDIES OF MgO SATURATED EAF SLAG

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ABSTRACT

The use of foamy slags is widely practiced in EAF steel production for electrical energy savings, productivity improvements, lower noise levels and reduced nitrogen pick up, as well as longer refractory service life. To foam a slag and sustain gas bubbles in it requires "optimum" slag chemistry and viscosity. The "optimum" slag is a molten, MgO saturated slag that contains a suspended second phase particle (MgO FeO magnesium wustite (MW)) at the operating temperature. A thermodynamic program, Factsage, has been utilized to study a simple quaternary oxide system of $MgO\text{-}CaO\text{-}FeO\text{-}SiO_2$*, to predict the dual saturation level of CaO and MgO, and the saturation level of MgO 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 are also compared with experimental data and models studied by other researchers.*

INTRODUCTION

Foamy slags are widely practiced in mini mill for electrical energy savings, productivity improvements, lower noise level, and lower nitrogen pick up in the steel. Foamy slags shield the electrical arcs, 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. To foam and sustain these gas bubbles requires *optimum* slag chemistry and viscosity. Thin slag can not sustain gas bubbles, while gas bubbles are hard to form in thick slag. The *optimum* 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, SiO_2, FeO and Al_2O_3. In this paper, only CaO, MgO, SiO_2, and FeO are considered because of the complexity of thermodynamic calculations. The effect of Al_2O_3 on the saturated MgO slag will be discussed in another coming paper. EAF slag chemistry can be represented by the basicity index widely used in the steel industry and represented by a basicity B3 = (CaO/(SiO_2) in this paper. For the production of high carbon steel, slag with a lower basicity is preferred, while, slag with a higher basicity is preferred for low carbon steel. Slag with a lower basicity can foam earlier in the steel making process.

Eugene Pretorius studied EAF foaming slag and proposed isothermal stability diagrams (ISD) 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. For a simple system such as MgO-CaO-SiO_2-FeO, each point on the ISD with a specific basicity represents a unique slag composition. Therefore, slag compositions can be easily calculated from and expressed by the ISD. Slag in the magnesium oxide saturated region has the precipitation of magnesium oxide containing phases such as magnesium wűstite ((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 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.

In the MgO-CaO-SiO_2-FeO phase system, MgO saturated and CaO saturated phase diagrams at 1600ºC in the condition which tested slags in contact with metallic iron were published in the Slag Atlas [3]. Both diagrams show contour lines of MgO above 6 wt%. Several linear relationships were found among basicity, acidicity, and constituents of dual saturated slags from diagrams as shown Table 1. Based on these linear relationships, a computer model was built by scientists at the National Energy Technology Laboratory (NETL) to calculate dual saturated and MgO saturated EAF slag chemistry for specific basicity indexes [4].

Oxygen partial pressure has tremendous influence on the formation of FeO or Fe_2O_3 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 a lot depending on operational conditions, location in the EAF, and feedstock. Six temperature values from 1600 to 1700ºC and three values of oxygen partial pressure per temperature were selected for thermodynamic studies. The lowest PO_2 was set to the interface of Fe-FeO formation. The highest PO_2 was set to the interface of FeO-Fe_3O_4 formation. The medium value was the average of the high and low values. Temperature also affects the formation of Fe, FeO and Fe_2O_3, therefore, these PO_2 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.

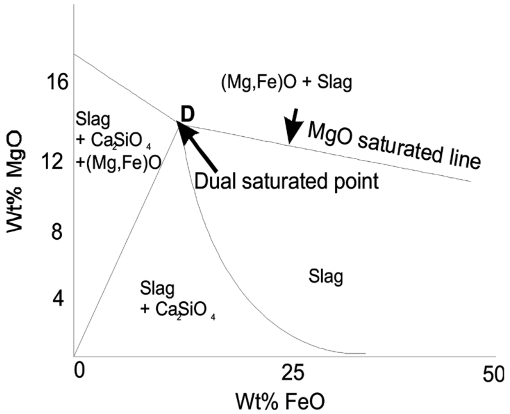

Figure 1: Isothermal stability diagrams at constant basicity (ISD) proposed by Eugene Pretorius

Table 1: The regression fitting quality (R square) between atomic percentages of oxides and acidicity (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	Medium 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

The ISD diagram was drawn using the Factsage phase diagram module and *tweaking* the input by combining CaO and SiO_2 components. For example, if basicity (CaO/SiO_2) is 1.5 then $Ca_{1.5}SiO_{3.5}$ will be typed into the components window. By this way, the ISD diagram with a designed basicity was drawn. If both oxides are keyed in separately, Factsage could not express the binary diagram (FeO-MgO) with a defined basicity as shown in Figure 1.

RESULTS AND DISCUSSION

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 higher basicity are dual saturated with less 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 Altas' FeO-MgO-CaO-SiO_2 phase diagram. However, as temperature increases, the linear relationship does not hold when MgO concentration in a dual saturated slag is less than 6%. Therefore, the linear model used to predict dual saturated EAF slag chemistry should be accurate when MgO concentration is greater than 6%.

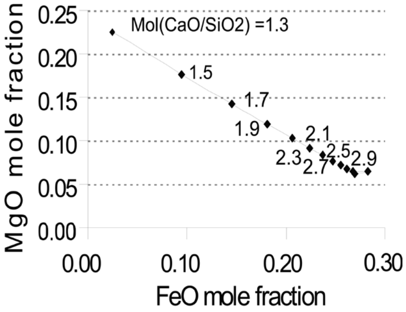

Figure 2: The effect of basicity for a dual saturated EAF slag chemistry at a constant temperature (1600°C) and high oxygen partial pressure

Table 3: The regression reliability of linear relationships with the consideration of all cases and the cases which MgO content in dual saturated slag 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 MgO concentration of dual saturated slags. High ratios of Fe_2O_3/FeO are expected in slag at elevated oxygen partial pressure. Fe_2O_3 is considered a neutral oxide, while, FeO is basic. Therefore for a given basicity, a dual saturated slag containing higher MgO is expected to present in a high oxygen partial pressure environment. Table 4 reports the values of FeO and MgO content of dual slags with different oxygen partial pressure and basicity and the standard deviation of FeO and MgO content due to the effect of oxygen partial pressure. Higher standard deviation means that oxygen has a greater effect in dual slag chemistry and that theoxygen partial pressure has greater effect on foaming quality and refractory wear when the basicity of EAF slag 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 1700ºC, if data exists in phase diagrams or experimental tests.

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	0.999741	FeO-Temperature	0.999139
SiO_2 -Temperature	0.999741	MgO-Temperature	0.989182

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 acidictiy) as previous discussed. The effect of basicity, temperature, and oxygen partial pressure on the constituent of MgO in a saturated slag should be explored for other linear relationship among them.

The Effect of Basicity

Figure 3 shows MgO saturated lines for different basicity at 1640ºC in 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. Slags with lower basicity, however, can be saturated usinf less MgO.

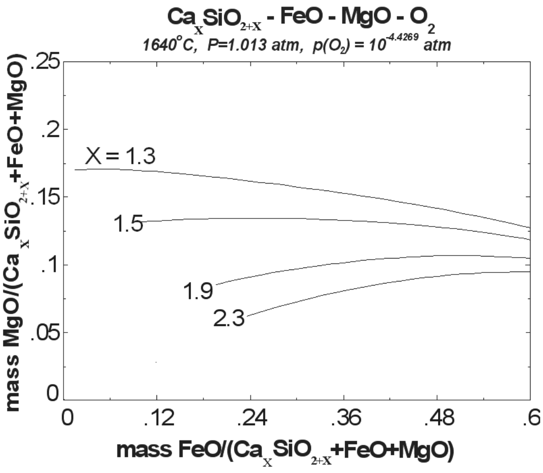

Figure 3: MgO saturated lines for different basicity at 1640°C in high oxygen partial pressure ($10^{-4.43}$)

Figure 4 shows the linear relationship between CaO-FeO and SiO_2-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.

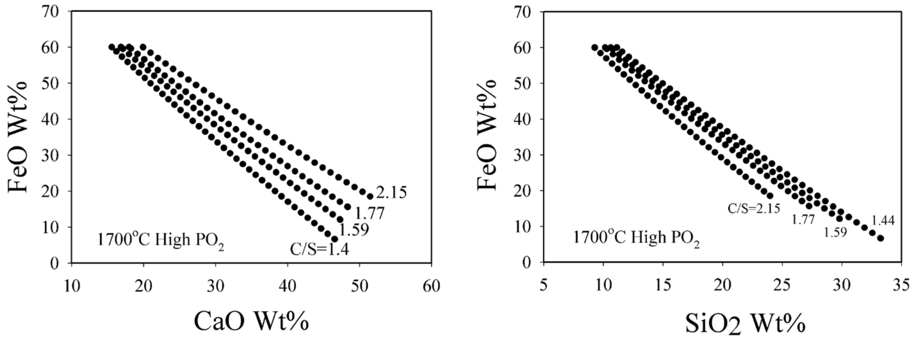

Figure 4: Linear relationship between CaO-FeO and SiO_2-FeO for MgO saturated slag chemistry for examples at 1700°C in high oxygen partial pressure

The Effect of Temperature on MgO Saturated Lines

The effect of temperature on the chemistry of MgO saturated slags was studied in cases when 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.

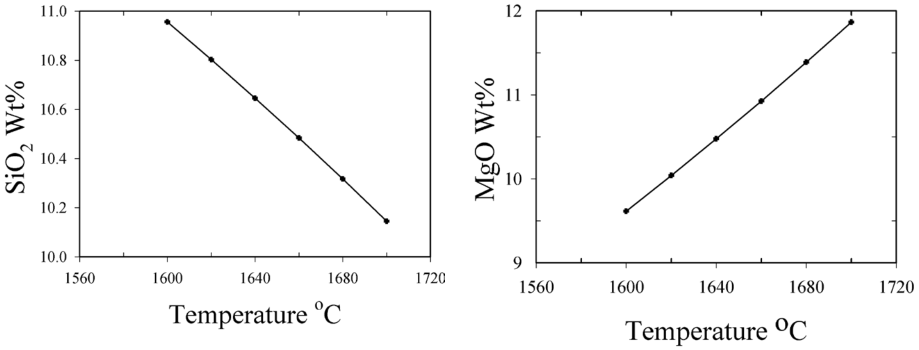

Figure 5: The linear relationship between SiO_2 and MgO with temperature at a constant FeO content

The Effect of Oxygen Partial Pressure

As previous discussed the oxygen partial pressure in EAF is unknown and depends on the operational conditions and the location of 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 much more and quicker than in a low oxygen partial pressure.

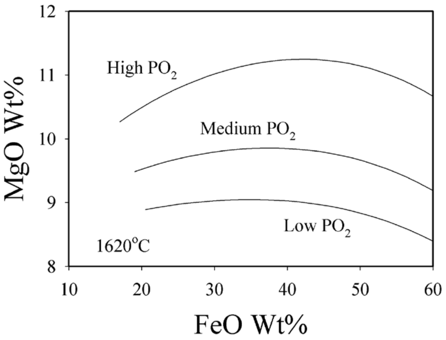

Figure 6: The effect of oxygen partial pressure on MgO saturation level

The Verification of Experimental MgO Saturated Phase Diagram and Thermodynamic Calculations

The discrepancy between thermodynamic calculations and experimental tests was also explored. The chemical compositions were extracted from the Slag Atlas [3] phase diagram using the MgO contour lines (between 6-14%) with these lines redrawn in the Figure 7(a). Note that these lines tend to be parallel. Figure 7(b) is drawn from the results of Factsage calculations for MgO contour lines from 8 to 16% in higher oxygen partial pressure. Both figures show similar trends, with some discrepancies in data, such as for the 8% MgO contour line.

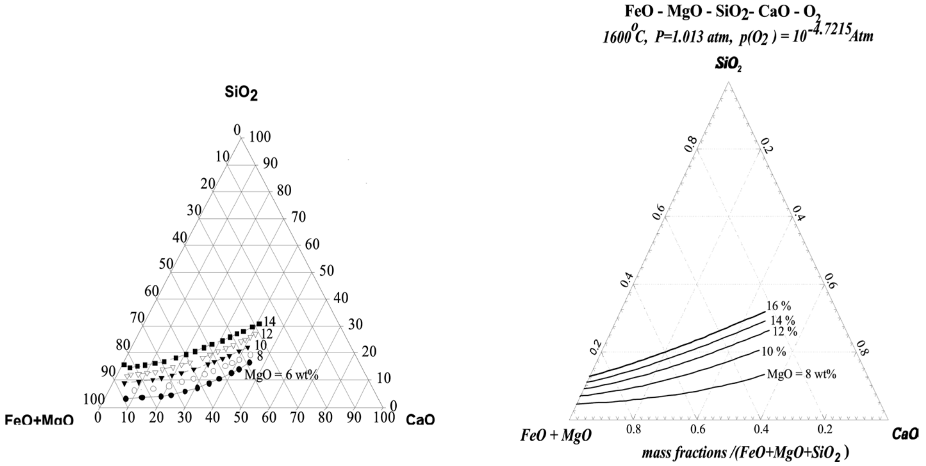

Figure 7: The MgO contour lines (between 6-14%) extracted from (a) slag Atlas and (b) factsage calculations results in a ternary diagram of SiO_2-CaO-FeO+MgO at 1600°C in high oxygen partial pressure

The Verification of Modeling Developed by NETL and Thermodynamic Calculations

Scientists at NETL-Albany proposed a model [4] to calculate EAF dual and MgO saturated slag chemistry through the analysis of MgO-FeO-SiO_2-CaO diagrams in the Slag Atlas [3] which is shown in Figure 8. Point D is a dual saturated point which can be predicted by linear relationships among the slag constituents, and their basicity/acidicity. 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.

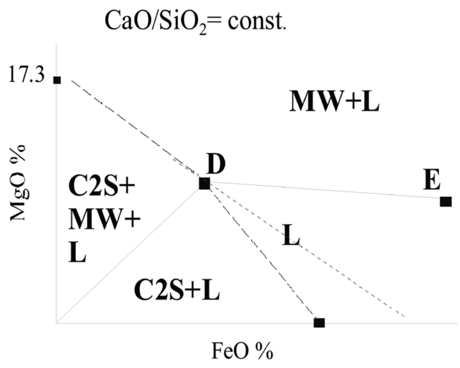

Figure 8: The Isothermal Solubility Diagram Model used to Predict MgO Saturated EAF Slag Chemistry by Scientists at NETL

The linear regressions analyses of data in Figure 4 are summarized in Table 6. This table proves a highly linear relationship between CaO-FeO and SiO_2-FeO and a common intercept point at 0.8571 (FeO wt%) when both CaO and SiO_2 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 8. Checking 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.

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:

$$CaO = A \text{ x } FeO + B \tag{1}$$

$$SiO_2 = C \text{ x } FeO + B \tag{2}$$

$$SiO_2 + CaO + FeO + MgO = 1 \tag{3}$$

$$MgO = (1\text{-}2B) - (1 + A + C)^* FeO \tag{4}$$

Where A and C are coefficient of slope and 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 CaO-FeO and SiO_2-FeO linear relationships 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 NETL-Albany's model is reasonably accurate when FeO content in slag is less than 60 wt%. Therefore, these linear relationships explored in this study will allow EAF operator to predict slag saturation conditions in their EAF and to optimize slag foaming conditions throughout the heat.

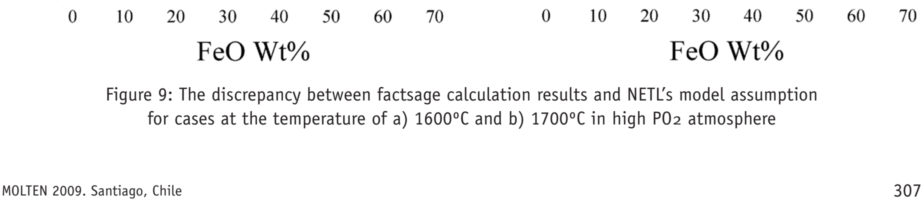

Figure 9: The discrepancy between factsage calculation results and NETL's model assumption for cases at the temperature of a) 1600°C and b) 1700°C in high PO₂ atmosphere

CONCLUSIONS

A thermodynamic program, Factsage, 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 experimental data from the Slag Atlas and a model proposed by NETL scientists about these linear relationships. Results also indicated that oxygen partial pressure has some effects on the constituents of dual and MgO saturated slags.

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