

A COMPUTER MODEL OF MgO SATURATED EAF SLAG CHEMISTRY

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ABSTRACT

The Albany Research Center is conducting research to recycle refractory material removed from EAF operations (such as MgO+C or Dolomite+C) for use as an EAF slag conditioner. The research focuses on optimum slag chemistry to achieve the best slag foaming and the longest refractory service life. A good foaming slag should be saturated with MgO and should contain some solid particles of magnesiowüstite (it will have a creamy appearance). A computer model was developed to calculate the dual saturated (CaO and MgO) EAF slag chemistry, the MgO saturated EAF slag chemistry and the solids content in the melt. The algorithm used for computer modeling as well as the effect of Al_2O_3 and temperature will be discussed. The comparison between industrial slag composition, artificial slags from the laboratory, and a theoretical slag will be made.

INTRODUCTION

Foamy slag practices in the EAF are a widely utilized practice that provides benefits of saving electrical energy, extending refractory service life, improving productivity, lowering noise, and lowering nitrogen pick up in the steel. Energy saving and increased refractory service life are achieved because foamy slags act as a shield for the electrical arc, reducing radiation energy toward the roof and walls. It has been reported (1) that foamy slag practice can result in 3-19% energy saving and can increase refractory service life.

Foamy slags are obtained by the reaction of FeO with C to generate CO gas bubbles. "Optimum" slag chemistry is required to sustain these gas bubbles in the slag. If the slag viscosity is too thin, the gas bubbles cannot be retained. If the slag viscosity is too thick, the gas bubbles are hard to foam. The "optimum" slag is molten and saturated MgO slag with the presence of suspended secondary phase particles, (MgO • FeO) magnesium wüstite (MW), at operational temperature.

EAF slags typically contain five major oxides: CaO, MgO, SiO_2 , FeO and Al_2O_3 . Basicity is a widely used index in the steel industry to characterize these slags. Usually, the steel companies adjust the basicity of their EAF slags between 1.5 and 2. The lower the basicity, the earlier the slag can be foamed (2). There are many different ways to calculate basicity. A basicity $B_3 = (\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3))$ is selected in this paper. No complete CaO-MgO- SiO_2 -FeO- Al_2O_3 phase diagram was published. Because of this, two partial CaO-MgO- SiO_2 -FeO saturation

diagrams were used. No model exists predicting MgO saturated EAF slag chemistry using these two saturation diagrams.

The practice of using DRI (direct-reduced iron) in EAF steel making has become more common in recent years (3). It contains a high level of acid oxide and it should be added to an EAF as quickly as possible to save energy. This practice can cause difficulty in controlling slag foaming. As DRI (direct-reduced iron) becomes more widespread, a model, which can predict slag chemistry, becomes more important.

The Albany Research Center (ARC), US Department of Energy, has developed a model to predict foaming slag chemistry with the goals of recycling spent refractories, extending refractory service life, saving energy and having better slag chemistry for foaming. This project is jointly supported by the Office of Industrial Technology, US DOE, the Steel Manufacturing Institute and 20 participated steel companies. It is conducted with the cooperation with Argonne National Laboratory, Martin Marietta Magnesia Specialties, Baker Refractories, SMI Steel, Georgetown Steel, and Chaparral Steel.

MODEL TO PREDICT MgO SATURATED EAF SLAG CHEMISTRY

Basic model to predict dual saturated EAF slag and MgO saturated EAF slags

Dual saturated EAF slags are defined as slags that start to precipitate a calcium component phase (Ca_2SiO_4) and a magnesium component phase (Fe,MgO) at operational temperatures. MgO saturated EAF slags are defined as slags that start to precipitate a magnesium component phase (Fe,MgO) at operational temperatures. Figure 1 shows the saturation lines of MgO based solid solution phases (Fe,MgO) and $(\text{Fe,Mg})_2\text{SiO}_4$ in the CaO-FeO-MgO-SiO_2 system contacting metallic iron at 1600°C (4). Figure 2 shows the saturation lines of the CaO based phase (Ca_2SiO_4) for the same phase system, environment, and temperature (4). Dual saturation (Ca_2SiO_4 and (Fe,MgO)) points can be determined by overlapping both figures. Dual saturation points at a line 6-11-12-13 represent the slag chemistry with different C/S ratios at 1600°C . Dual saturated slag chemistry is only affected by changing C/S ratios and temperature (in $\text{MgO-CaO-SiO}_2\text{-FeO}$ system).

Data from dual saturation points (6-11-12-13) have been collected, converted and analyzed. Figure 3 shows the linear relationships among the atomic percentage of oxides and C/S ratios or S/C ratios at 1600°C for the different dual saturation points. Table I lists R^2 (regression quality) for each line regression indicating high confidence fitting. For example, SiO_2 , MgO , and FeO atomic percentages have a linear relationship with acidity (S/C). However, CaO atomic percentage has a linear relationship with basicity (C/S). In addition, MgO atomic percentage has a linear relationship with FeO atomic percentage. Similar results also can be obtained if oxide weight percentages were drawn with S/C or C/S ratios. However, the regression fittings confidence (R^2) for atomic percentages of oxides is better than that for weight percentage of oxides.

Based on the relationship findings, an ARC slag model (figure 4) has been proposed to predict dual saturated EAF slag chemistry by a MgO-FeO coordination diagram for the $\text{MgO-CaO-SiO}_2\text{-FeO}$ system. On the left hand side of figure 4, the point A chemistry at the MgO axis represents the condition when $\text{FeO}=0$ and can be found by the phase diagram of MgO-CaO-SiO_2 at a designed operational temperature. The point A material contains 17.5 wt% (23.3 mol%) MgO at the operational temperature of 1600°C . On the bottom right hand side, the point B chemistry at the FeO axis represents the condition

when $\text{SiO}_2=0$ and $\text{MgO}=0$. This point B material contains 58wt% (51.8 mol%) FeO at 1600°C. Point A represents a slag with a $\text{C/S}=1.14$. Point B represents a slag with an infinitely high C/S ratio (when SiO_2 approaches 0 wt%). The chemical composition of any point in the line AB can be calculated by the mixture of A's and B's chemical compositions. The compositions of these points have unique CaO, SiO_2 , MgO, FeO, at a specific C/S ratio and temperature. These compositions represent the dual saturated EAF slag chemistry with a specific C/S.

Iron is a transition metal. Depending on the oxidation/reducing environment, it can have different valences that include Fe_2O_3 , Fe_3O_4 , FeO and Fe. This characteristic places some uncertainties on phase diagrams involving iron. Most phase diagrams mark FeO as FeO_x . Depend on the test conditions, it is no surprise that differences exist among these published phase diagrams. In order to avoid these uncertainties, ARC's dual saturated EAF slag model used two reference points to calibrate dual saturated EAF slag chemistry. These are a point, which C/S is equal to 2, and point A of figure 4.

After finding dual saturated EAF slag chemistry based on atomic percentages, a conversion from atomic percent back to weight percent will be performed. An isothermal solubility diagram with specific C/S ratios and temperatures is used to make figure 5. This diagram predicts MgO saturated EAF slag with specific known FeO contents of actual EAF slags.

Dual saturation chemistry (figure 5 point D) can be obtained by the ARC slag model (figure 4). The chemical composition at C point (figure 5) can be obtained from the liquidus composition of the FeO-MgO phase diagram at 1600°C. Point C represents the condition when CaO and SiO_2 approach zero percent. The line connecting D and C is the MgO saturated line for EAF slags. The chemistry along this line indicates the amount of MgO needed to saturated EAF slags of known C/S ratios, temperature, and FeO content. It means that a MgO saturated EAF slag chemistry is a function of the C/S ratio, temperature, and FeO content. In other words, a MgO saturated EAF slag chemistry can be derived from the information of dual saturated EAF slag chemistry and specific known FeO content. This MgO saturated content is very important because MgO refractory linings in an EAF can be a source of MgO in the slag and because of increasing FeO content in EAF slag during melting. A MgO saturated EAF slag will not dissolve the MgO refractory lining extending the service life of refractories.

The CaO saturation line is not as important as the MgO saturation line. For the CaO saturated line DB in figure 5, the chemical composition at point B can be obtained by a CaO-FeO- SiO_2 phase diagram (4) at a specific C/S ratio crossing the 1600°C isothermal line. The dotted line between D and B points represents some ambiguities and requires additional research. Data have been collected from figure 2 to study the CaO saturation line. Figure 6 indicates a high possibility that this CaO saturation "curve" is a straight line. Only the case with a low C/S ratio ($\text{C/S}=1.5$), did not show a linear relationship, all other cases showed linear relationship.

Extension of the Model to Consider Temperature Effects and Al_2O_3 Effects

The relationship discussed above among oxides and S/C (or C/S) ratio at 1600°C can also be extended to the condition at 1700°C and used to predict the dual saturated EAF slag chemistry. For example at 1700°C, the MgO content at point A (figure 4) was 15.8 wt% (21.18 mol%), the iron content at point B should be 42.8 wt% (36.87 mol%). Dual

saturated EAF slag chemistry at other temperatures can be interpolated and calculated from the dual saturated slag chemistry at 1600°C and 1700°C (or 1500°C). To predict the dual saturated slag chemistry in the SiO₂-CaO-MgO-FeO system is not recommended at temperatures below 1500°C, because the phase boundary line in CaO-MgO-SiO₂ phase diagram is not straight below 1500°C.

Al₂O₃ is a fifth important components in EAF slags and its effects on dual saturated EAF slag chemistry should be studied. Data from the SiO₂-CaO-MgO-Al₂O₃ (4) phase diagram were collected and analyzed to reveal Al₂O₃ effects along 1600°C isothermal line. Figure 7 shows that Al₂O₃ may decrease MgO and SiO₂ content in solution in a dual saturated EAF slag and may increase the CaO value. In addition, the total amount of Al₂O₃ and SiO₂ is nearly constant. This means that added Al₂O₃ will replace the equivalent amount of SiO₂ in a dual saturated EAF slags. It is because of this that the B3 ratio ($B3 = \text{CaO} / (\text{SiO}_2 + \text{Al}_2\text{O}_3)$) was adopted to predict the dual saturated EAF slag chemistry in this study.

Data from the Al₂O₃-CaO-SiO₂-FeO (4) phase diagram were also collected and analyzed to determine Al₂O₃ effects. This information was collected along isothermal lines at 1600°C and 1700°C with 5, 10, 15, 20 wt% FeO. Figure 8 shows that Al₂O₃ replaces the equivalent amount of SiO₂ for higher FeO content (>20wt % FeO) slag at a temperature of 1600°C. At 1700°C, the Al₂O₃ replaces the equivalent amount of SiO₂ with about 15wt% FeO. Most EAF foaming slags contain more than 15 wt% FeO.

It is reasonable, therefore, to assume that the MgO content in a dual saturated EAF slag will decrease if Al₂O₃ replaces the equivalent amount of SiO₂. CaO content in a dual saturated EAF slag will increase slightly and FeO content in a dual saturated EAF slag may be the same if Al₂O₃ replaces the equivalent amount of SiO₂. Based on the above discussions about the effect of Al₂O₃, several models have been considered. For engineering consideration, a model was selected that will give the highest MgO value in a dual saturated slag

MODEL TO PREDICT SOLID CONTENT FOR MgO OVER SATURATED EAF SLAGS

The solid content of an EAF slag affects the foaming quality. Good EAF foaming slags should contain some solids, however, too much precipitated solids in the slag will cause it to be too viscous and have poor foaming qualities. Therefore, it is important to predict the solid content in a EAF slag that is over saturated with MgO. The composition of the precipitated solid for a MgO over saturated EAF slag is magnesium wüstite ((Mg,Fe)O). FeO reacts with MgO, forming a solid solution (Mg,Fe)O. Depending on the furnace operating temperature, the precipitated solids chemistry should comply with the solidus line of MgO-FeO. Industrial EAF foamed slags have been analyzed by EDAX. EDAX analysis confirmed that the major components of magnesium wüstite precipitated solids are MgO and FeO and that their compositions complied with the MgO-FeO phase diagram.

As previously mentioned, this study considered five major oxide components in an EAF slag: FeO, MgO, SiO₂, CaO, and Al₂O₃. The overall compositions of an EAF slag can be expressed as the sum of molten slag components and precipitated solids by the following equations:

$$\begin{bmatrix} \text{Al}_2\text{O}_3 \\ \text{CaO} \\ \text{FeO} \\ \text{MgO} \\ \text{SiO}_2 \end{bmatrix}_{\text{Total}} \equiv X \cdot \begin{bmatrix} \text{Al}_2\text{O}_3 \\ \text{CaO} \\ \text{FeO} \\ \text{MgO} \\ \text{SiO}_2 \end{bmatrix}_{\text{Molten}} + Y \cdot \begin{bmatrix} 0 \\ 0 \\ \text{FeO} \\ \text{MgO} \\ 0 \end{bmatrix}_{\text{Solid}}$$

and

$$X + Y = 1$$

The above equation can be illustrated on an isothermal solubility diagram (figure 9) which helps explain the chemical composition of the molten slag. The chemical composition of point G can be obtained from the FeO-MgO phase diagram by the solidus of FeO-MgO at a given operational temperature. The chemical composition of point H is the total composition of slag, which is known or can be measured. A straight line through the points G and H will cut the MgO saturation line (a line connecting points C and D) at point K. Based on the lever rule from phase diagram's quantitative calculation, the chemical composition at K point is molten slag chemistry. The distance proportion (K-H)/(G-K) is the solid content Y and the distance proportion (H-G)/(G-K) is the liquid content X.

COMPUTER PROGRAMMING

Based on the above-discussed algorithm, a computer program was designed using visual basic. The input factors are the CaO/(SiO₂+Al₂O₃) weight ratio (C/S ratio), the Al₂O₃/(SiO₂+Al₂O₃) weight ratio (the Al₂O₃ ratio), and the temperature (°C). The output values are the dual saturated slag chemistry, the saturated MgO slag chemistry, and the solid content (MW solid contents). This model was also based on the atomic percentage used to calculate the dual saturated EAF slag chemistry. All data and figures were output as weight percentage for the convenience of users. This program will be available for use by the steel companies participating in the joint OIT/SMA steel program.

MODEL VALIDATION

The MgO saturated slag chemistry predicted from the model was compared with experimental and industrial EAF slags. Table II indicates good agreement between the data collected from figure 1 and 2 (MgO and CaO saturated phase diagram) and predictions calculated from the model for a dual saturated EAF slag chemistry

Table III lists actual slag chemical compositions from two steel plants participating in the joint OIT/SMA program and the model's prediction for the MgO saturated slag chemistry. For plant1, the MgO content in the slag is higher than the model's MgO saturated content. These slags should be saturated with MgO and should not attack the MgO refractories. A MgO cup test filled with the slag (figure 10) indicated no obvious corrosion.

Table III also lists the slag chemical compositions from plant 2 and the model's prediction. Samples were obtained by freezing slag on steel rods. These samples contained too much Fe₂O₃ and FeO, probably contamination from the rod. Because of this, no conclusions could be drawn from the data. A better sampling procedure should be adopted to avoid the Fe₂O₃ contamination.

C/S, ALUMINA AND TEMPERATURE EFFECTS ON MgO SATURATION CONTENT

Figure 11 shows the effect of C/S ratio on MgO saturation content. While MgO saturation is about 17.3% at a C/S=1.14; it drops to 9.3% when the C/S ratio is 2. It has been reported that slag viscosity increases with increasing C/S ratio. Low viscosity slags will penetrate the pores in refractories more easily, causing high wear. Low slag viscosity is also somewhat detrimental to phosphorous and sulfur removal from the steel (5)

The effect of alumina on MgO saturation content has been considered in this model. Figure 12 indicates that when Al_2O_3 equivalently replaces SiO_2 , MgO content would linearly decrease at dual saturation. Because the same approach was used between oxide components in the slag at 1600°C and 1700°C, it is no surprise that MgO content at dual saturation linearly increases with increasing operational temperature.

CONCLUSIONS

Foamy slags are widely practiced in EAF steel making. Benefits include electrical energy saving, extended refractory service life, productivity improvements, lower noise levels, and lower nitrogen pick-up. The Albany Research Center (ARC), US Department of Energy, has developed a model to predict foaming slag chemistry with the goals of recycling spent refractories as part of the slag conditioning charge. Use of this model should extend refractory service life, save energy and give better control of foamy slag chemistry.

An ARC slag model can predict dual saturated EAF slag chemistry based on a linear relationship between atomic percentages of oxides and slag acidity (or basicity) ratios. MgO saturated EAF slag chemistry can be derived from the dual saturated EAF slag chemistry and the known FeO content in the slag. This model predicts solid contents of MgO over saturated EAF slags. The predicted results from ARC model have good agreement with the data collected from phase diagrams and the tests from industrial EAF slags.

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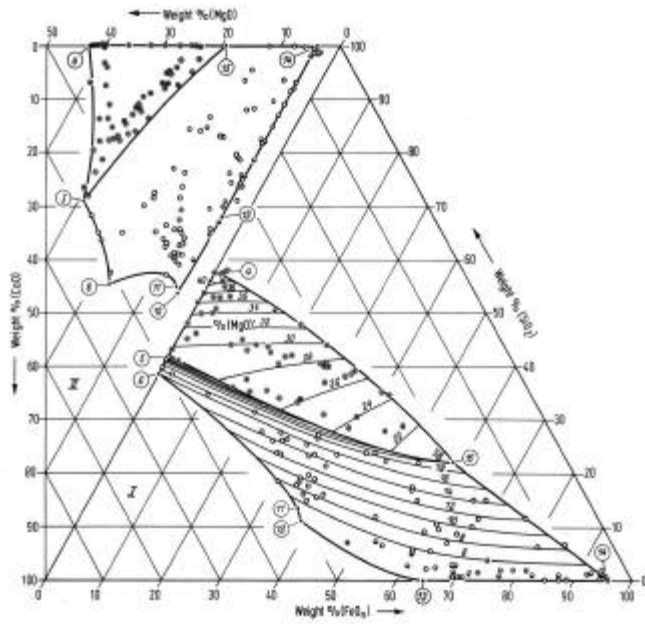


Figure 1. The saturation lines of MgO-based solid solution phases ((Fe,Mg)O) and (Fe, Mg)₂SiO₄) in the CaO-FeO-MgO-SiO₂ system in contacting metallic iron as projected on the CaO-SiO₂-FeO system at 1600°C.

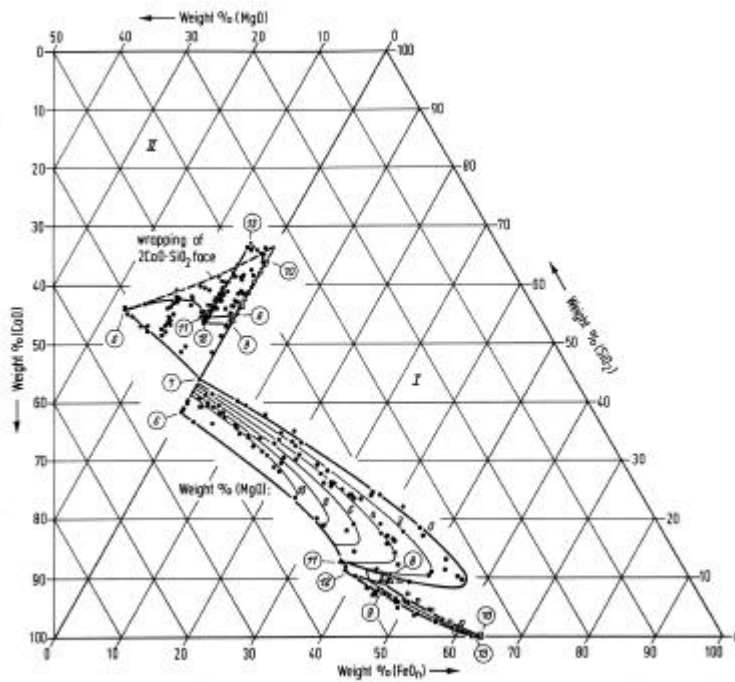


Figure 2. The saturation lines of CaO-based phases in the CaO-FeO-MgO-SiO₂ system in contacting metallic iron as projected on the CaO-SiO₂-FeO system at 1600°C.

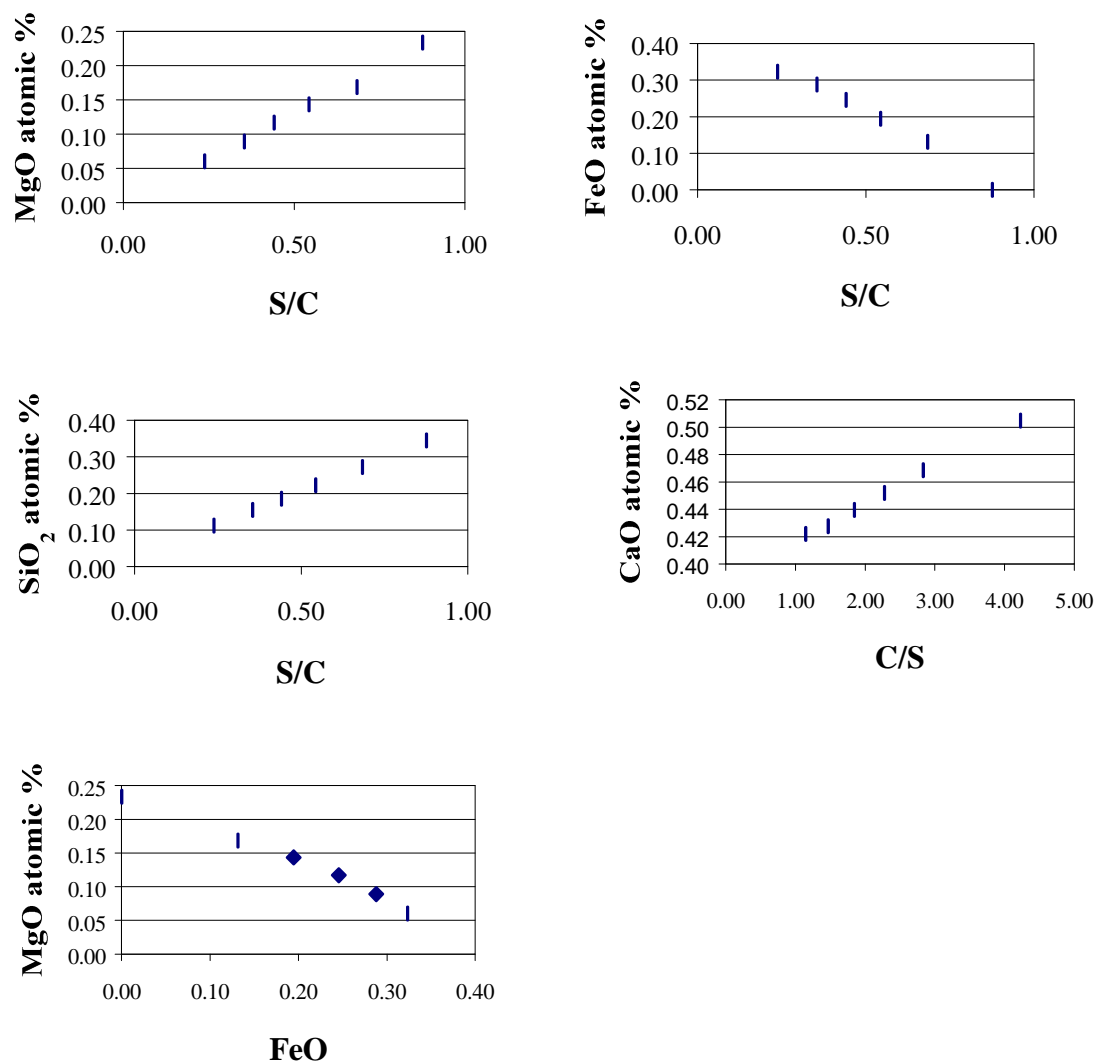


Figure 3. A linear correlation between atomic percentages of oxides and acidity (S/C) or basicity(C/S).

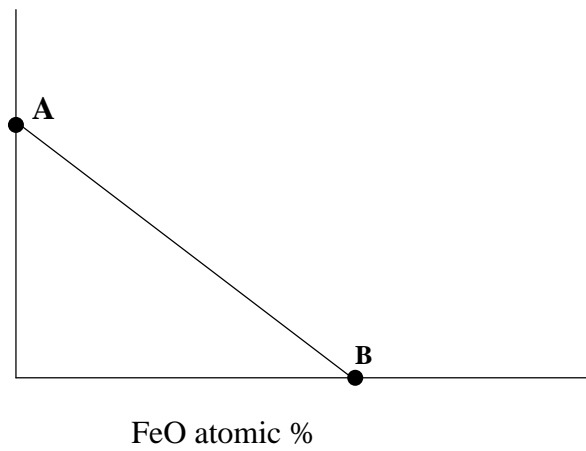


Figure 4. The ARC model used to predict dual saturated EAF slag chemistry

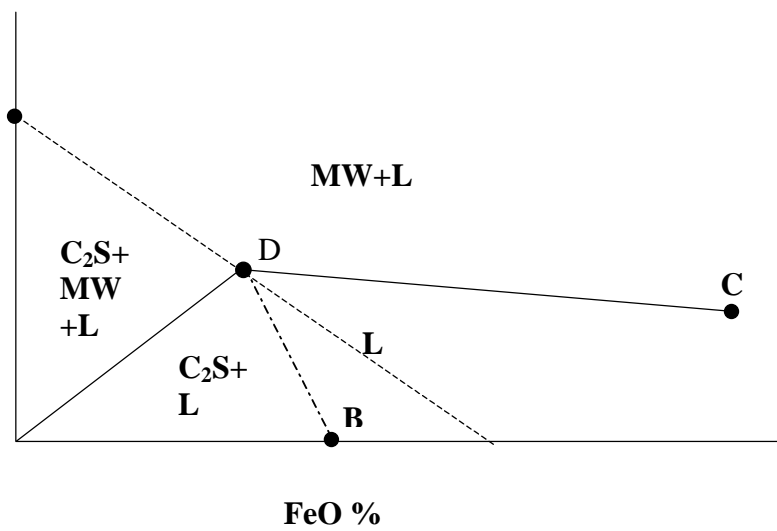


Figure 5. The ARC model used to predict MgO saturated EAF slag chemistry

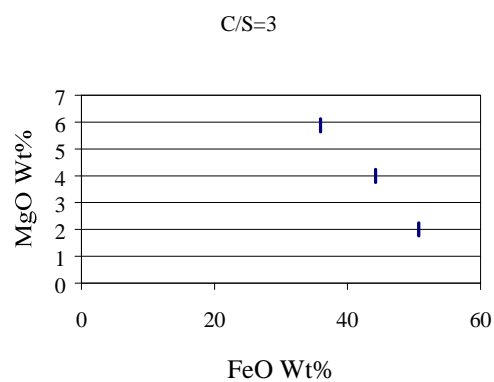
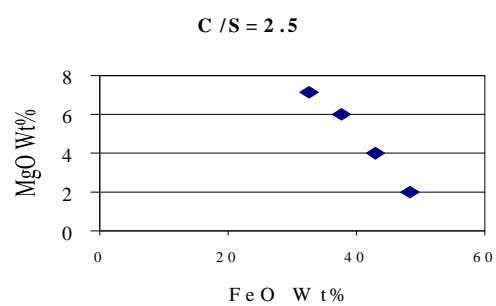
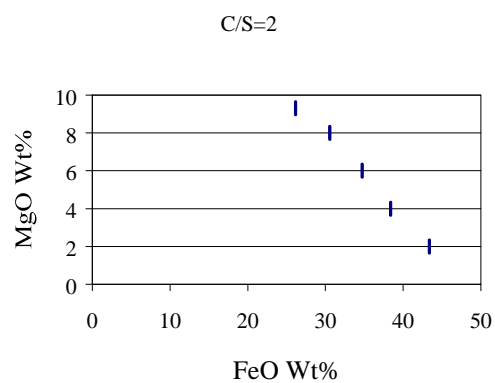
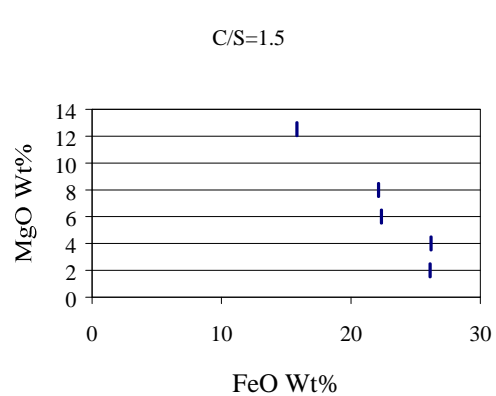


Figure 6. The CaO saturation lines for basicities of 1.5, 2, 2.5, and 3.

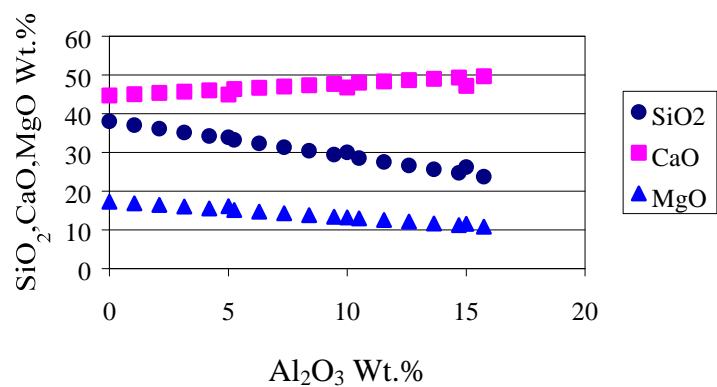
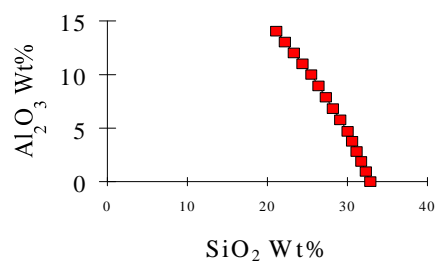
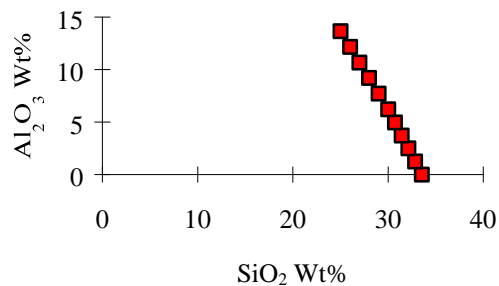


Figure 7. The effect of Al₂O₃ on SiO₂, CaO and MgO concentration along 1600°C isothermal line. Data was collected from phase diagrams of Al₂O₃-CaO-MgO-SiO₂



(a)



(b)

Figure 8. The constant total amount of Al₂O₃ and SiO₂ when (a) FeO is more than 20% at 1600°C and (b) FeO is more than 15% at 1700°C.

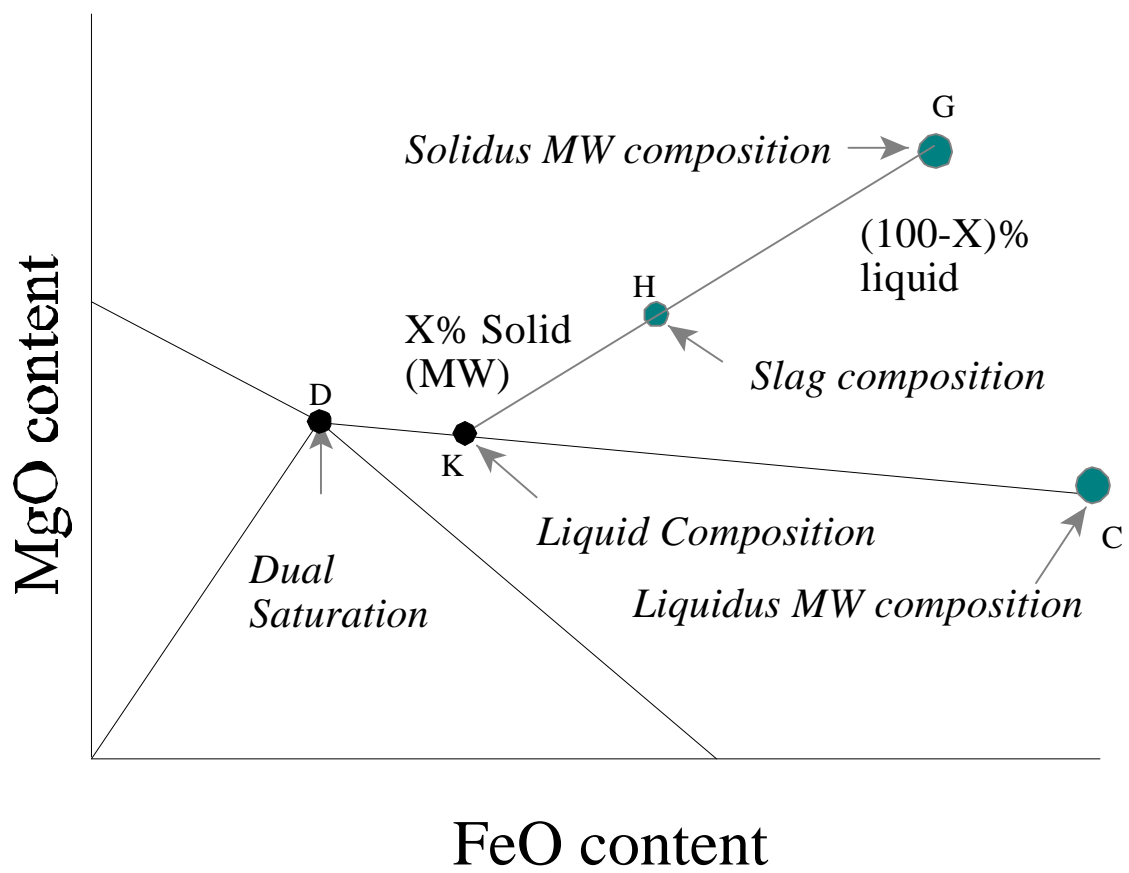


Figure 9. The model developed by the Albany Research Center used to predict solid contents in a slag

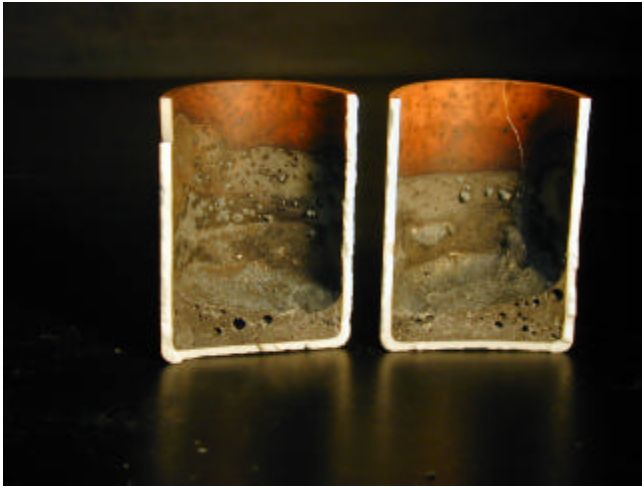


Figure 10. A MgO cup test with saturated MgO EAF slag indicating no obvious corrosion

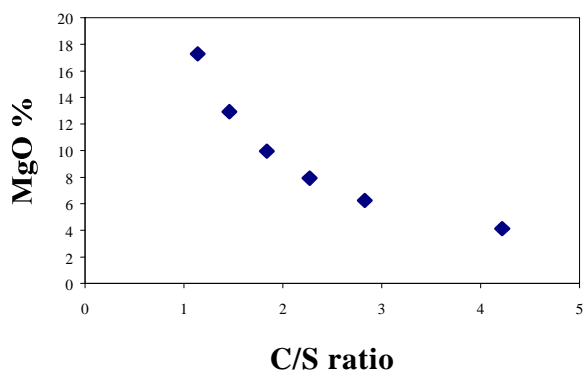


Figure 11. The effect of C/S ratio on MgO content for a dual saturated EAF slag

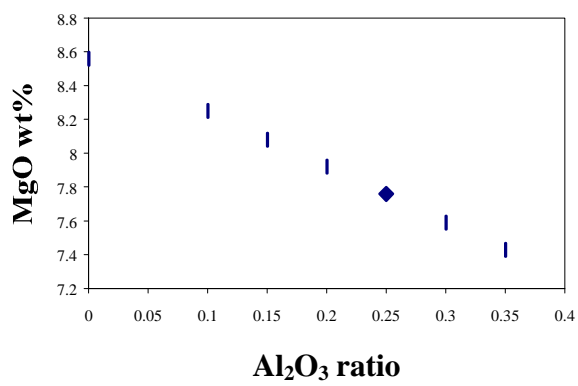


Figure 12. The effect of Al_2O_3 ratio on MgO content for a dual saturated EAF slag.

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

Relationships	R Square
C/S - CaO	1.0
S/C - SiO_2	0.98
S/C - MgO	0.99
S/C - FeO	0.98
MgO - FeO	0.99

Table II The predicted results using the ARC model and the phase diagram data for dual saturated EAF slag chemistry.

C/S	MgO		FeO		SiO_2		CaO	
	Model	Phase	Model	Phase	Model	Phase	Model	Phase
2.83	6.26	6.00	34.97	34.57	15.34	15.53	43.42	43.90
2.27	7.92	8.00	30.37	30.00	18.87	18.95	43.05	43.05
1.84	9.96	10.00	24.12	24.19	23.21	23.16	42.71	42.65

Table III Actual EAF slag chemical composition from two participated steel plants compared with saturated MgO slag chemistry predicted by the model

Plant 1:

	EAF Slag1		Model	EAF Slag 2		Model
Al_2O_3	5.70	5.86	5.86	5.47	5.61	5.61
SiO_2	14.07	14.52	14.52	14.31	14.72	14.72
CaO	37.10	37.45	37.45	36.00	36.24	36.24
$\text{FeO}+\text{Fe}_2\text{O}_3+\text{MnO}$	33.91	33.91	33.91	34.96	34.96	34.96
MgO	9.22	8.23	8.23	9.26	8.47	8.47

Plant 2:

	Slag 3Model		Slag 4Model		Slag 5Model		Slag 6Model	
Al_2O_3	3.81	3.91	2.57	2.57	2.77	2.83	3.76	3.68
SiO_2	13.58	13.95	10.46	10.48	11.36	11.63	15.44	15.08
CaO	38.02	38.30	28.75	28.24	31.81	31.94	32.32	31.11
$\text{FeO}+\text{Fe}_2\text{O}_3+\text{MnO}$	36.48	36.48	51.55	51.56	46.52	46.52	41.07	41.06
MgO	8.11	7.33	6.66	7.11	7.54	7.07	7.42	9.05

