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Phosphide capacities of ferromanganese smelting slags

Maramba, Blessing

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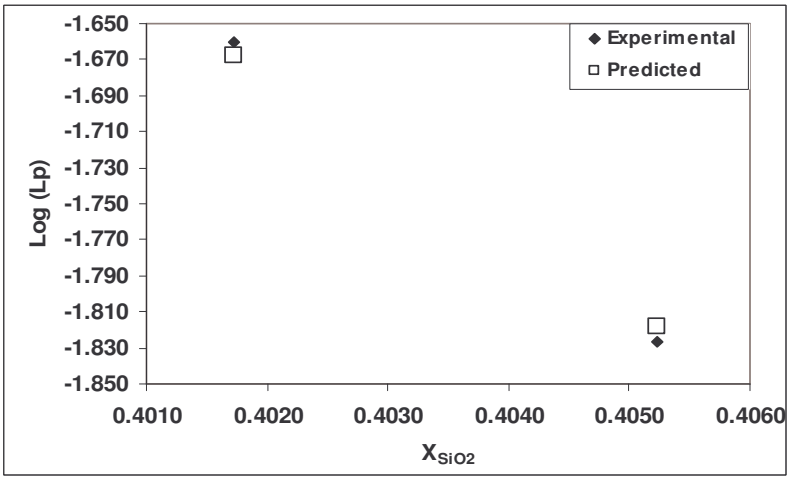
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APPENDIX A

LISTING OF EXPERIMENTAL RESULTS

A1 Relationship Plots for Slag-Metal Equilibrium Experiments under Carbon Monoxide Atmosphere at 1500°C

(a)



(b)

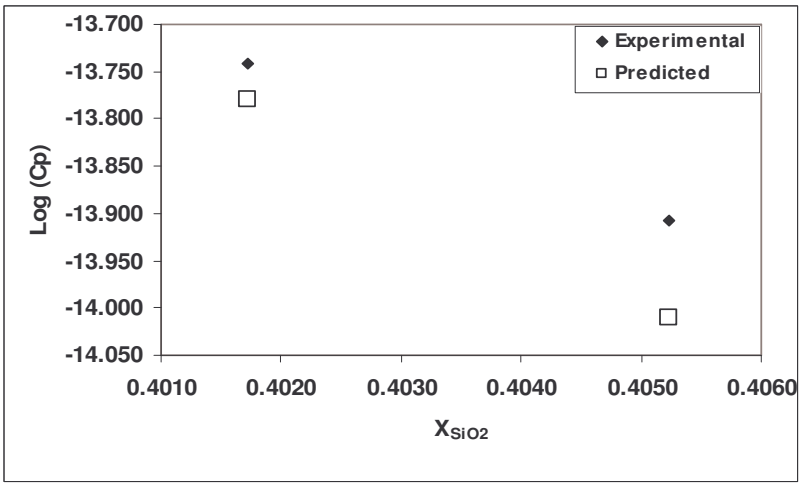
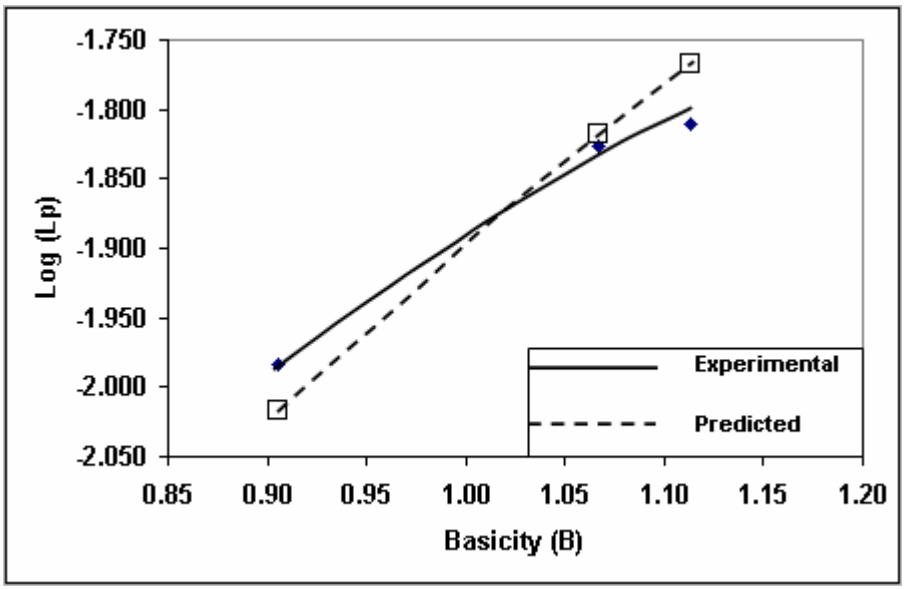


Figure A1 The variation of (a) Lp and (b) C_P^{3-} with silica (X_{SiO2}) in MnO-SiO_2-Al_2O_3-MgO-P_2O_5-CaO slag under CO atmosphere at 1500°C; Basicity (B): 1.067 – 1.083

(a)



(b)

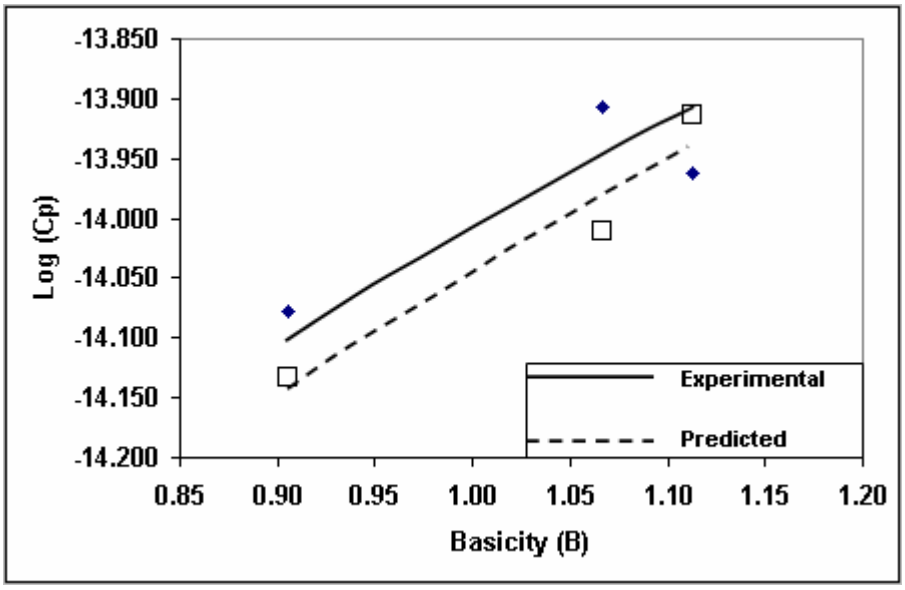
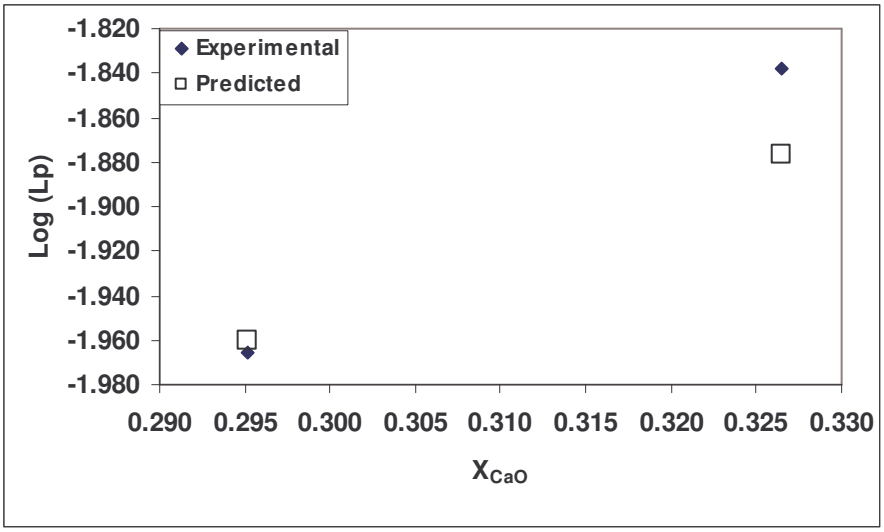


Figure A2 The variation of (a) Lp and (b) C_P^{3-} with MnO-SiO_2-Al_2O_3-MgO-P_2O_5-CaO slag basicity (B) under CO atmosphere at 1500°C

(a)



(b)

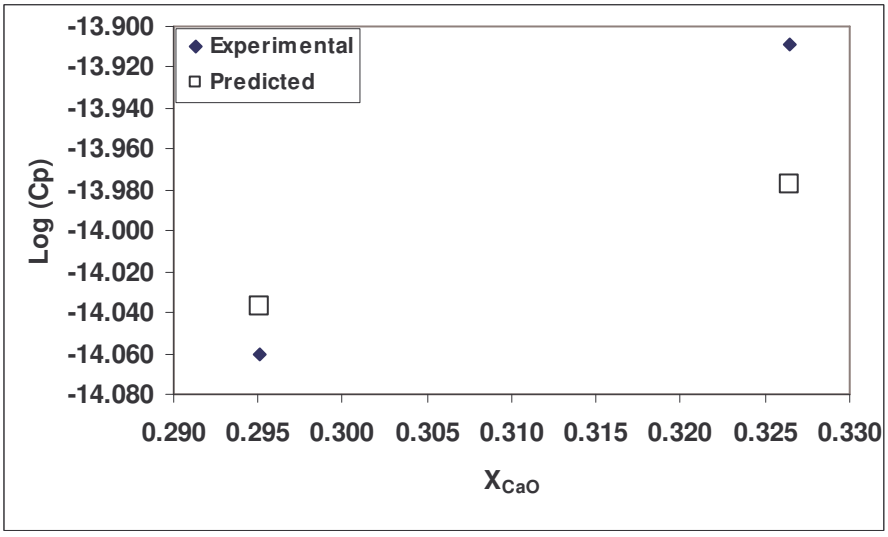
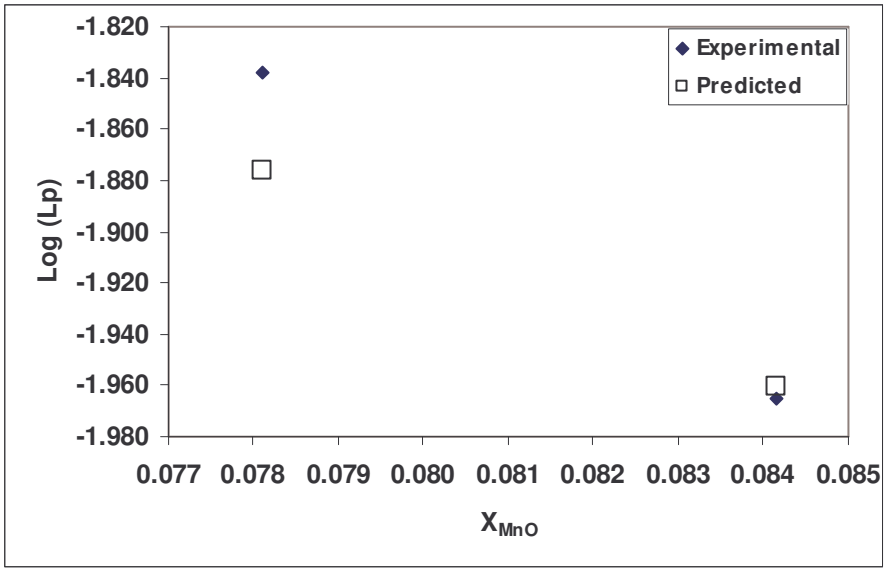


Figure A3 The variation of (a) Lp and (b) C_P^{3-} with calcium oxide (X_{CaO2}) in $MnO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}P_2O_5\text{-}CaO$ slag under CO atmosphere at 1500°C; Basicity (B): 0.894 – 0.986

(a)



(b)

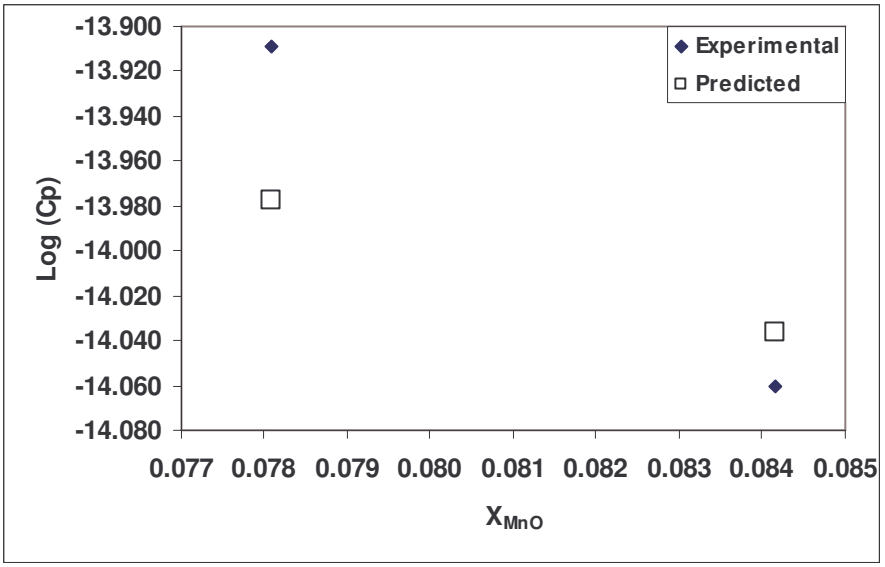
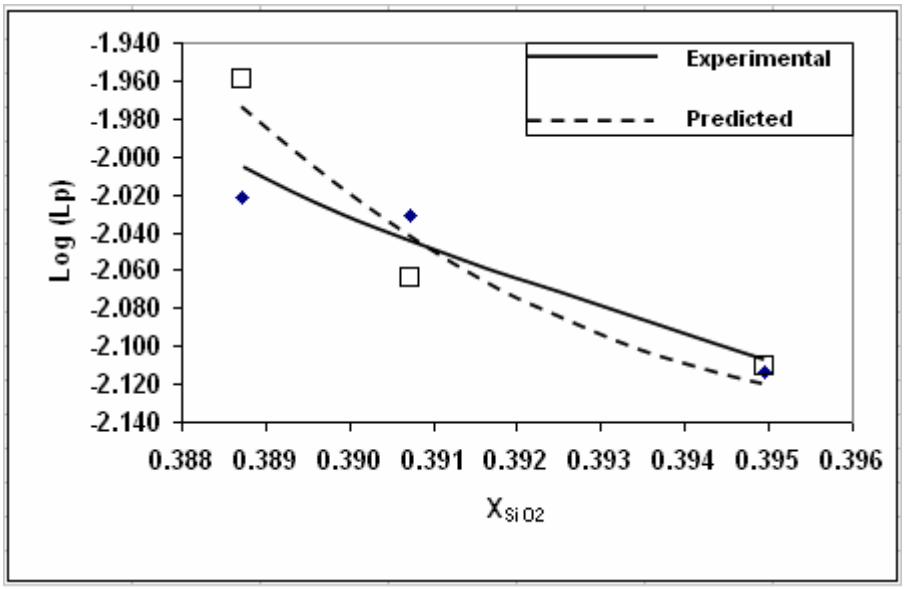


Figure A4 The variation of (a) Lp and (b) C_P^{3-} with manganese oxide (X_{MnO}) in $MnO-SiO_2-Al_2O_3-MgO-P_2O_5-CaO$ slag under CO atmosphere at 1500°C, Basicity (B): 0.894 – 0.986

(a)



(b)

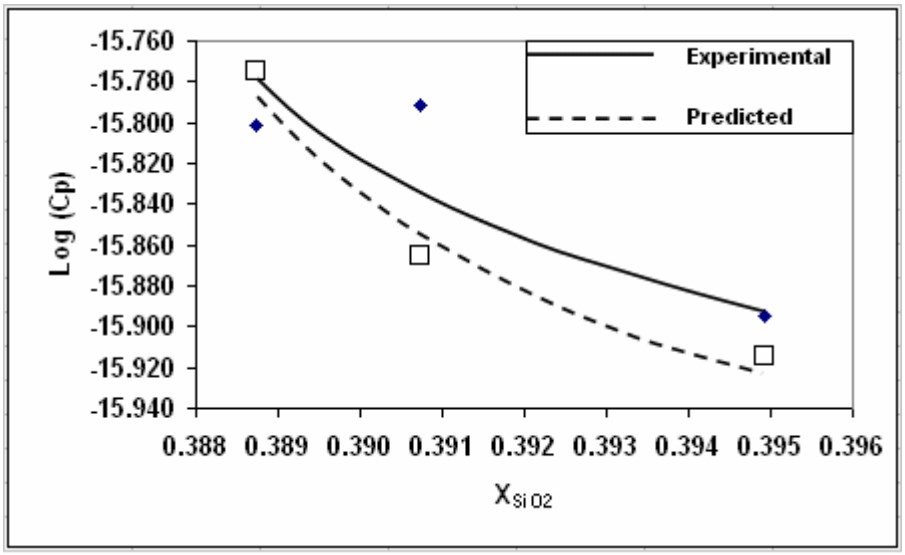
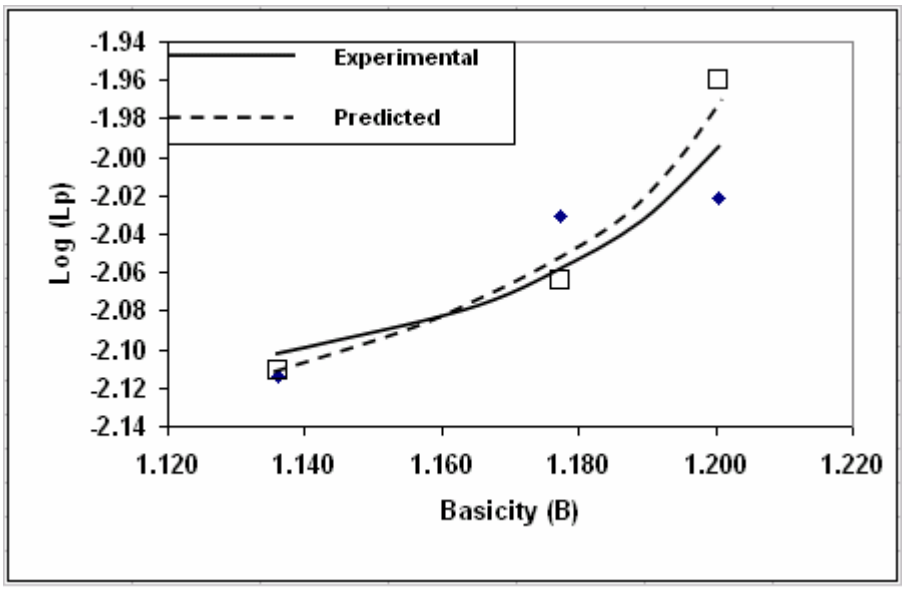


Figure A5 The variation of (a) Lp and (b) C_P^{3-} with silica (X_{SiO2}) in MnO-SiO_2-Al_2O_3-MgO-P_2O_5-CaO slag under Ar/ CO atmosphere at 1500°C, Basicity (B): 1.200 - 1.136

(a)



(b)

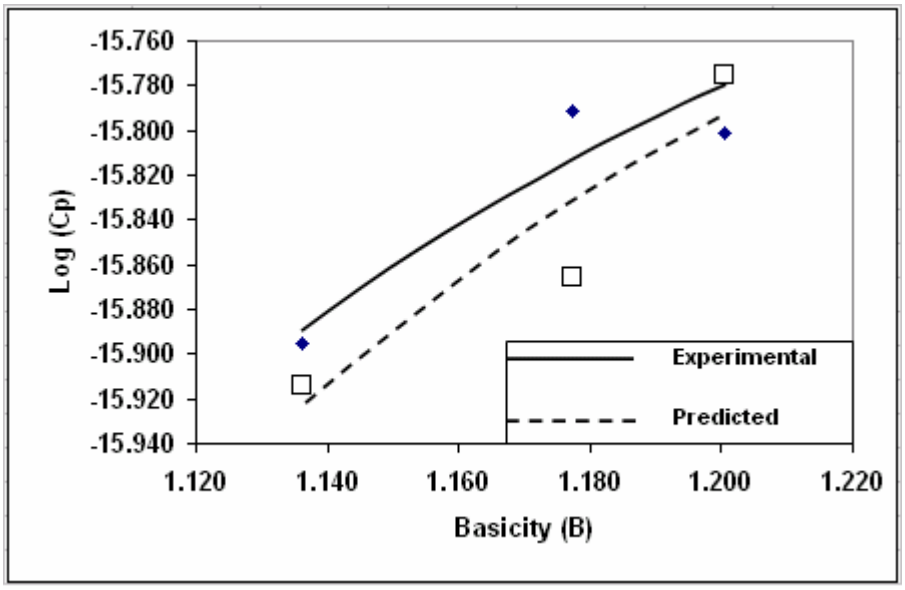
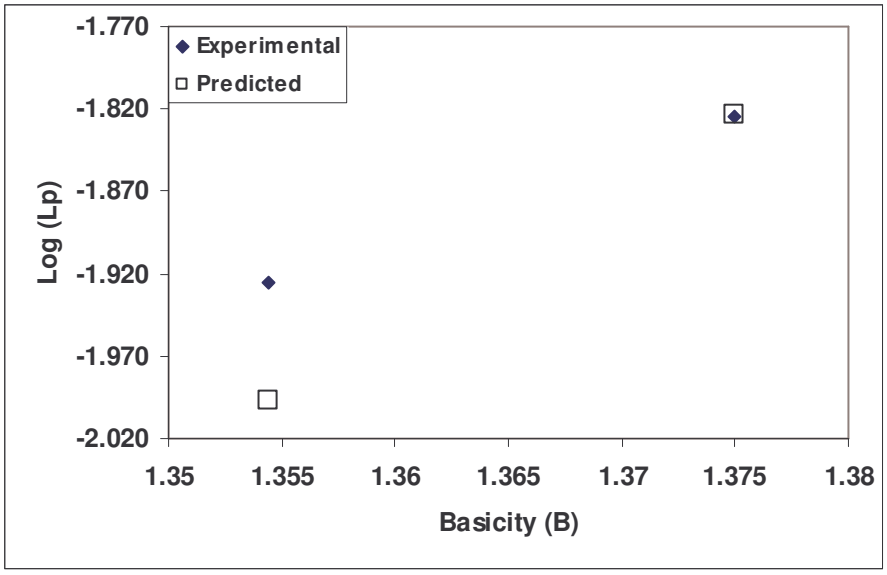


Figure A6 The variation of (a) Lp and (b) C_p^{3-} with $MnO-SiO_2-Al_2O_3-MgO-P_2O_5-CaO$ slag basicity (B) under Ar/CO atmosphere at 1500°C

(a)



(b)

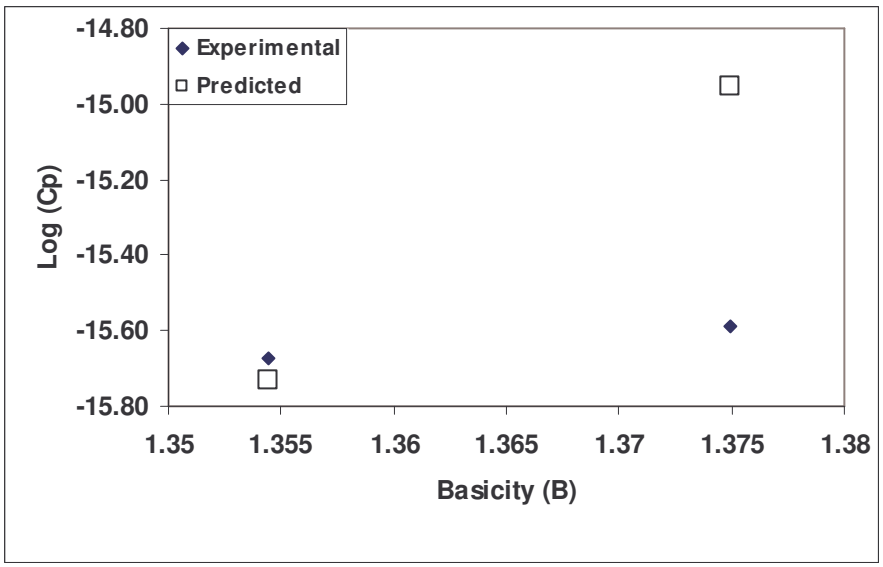
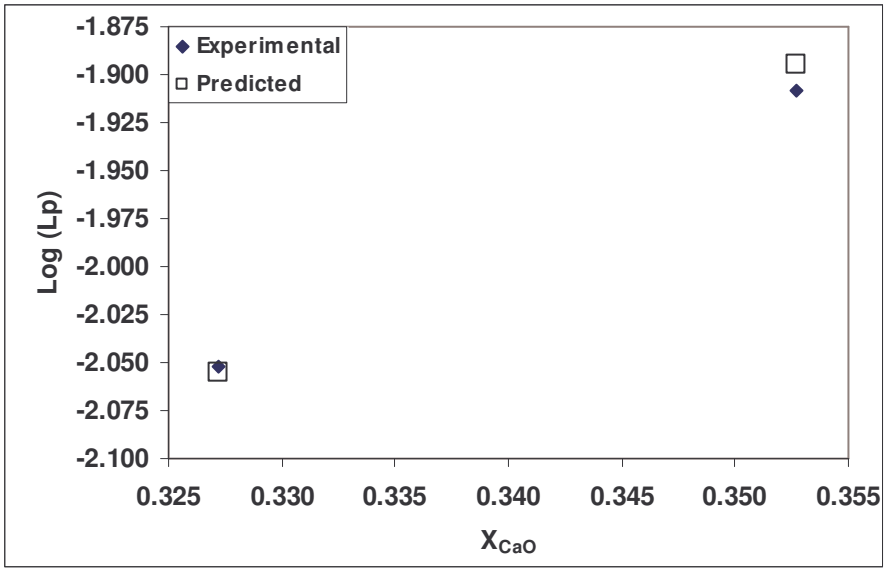


Figure A7 The variation of (a) Lp and (b) C_P^{3-} with $MnO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}P_2O_5\text{-}CaO$ slag basicity (B) under Ar/CO atmosphere at 1500°C

(a)



(b)

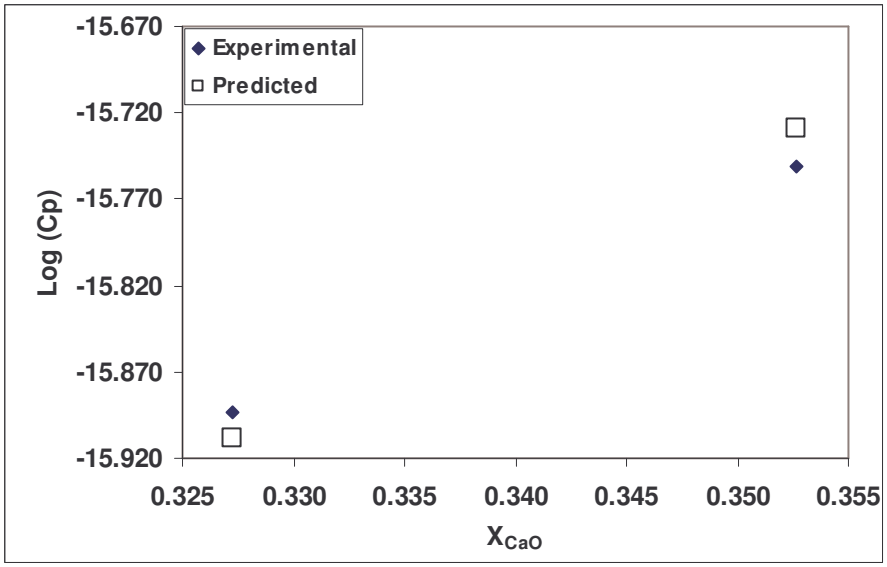
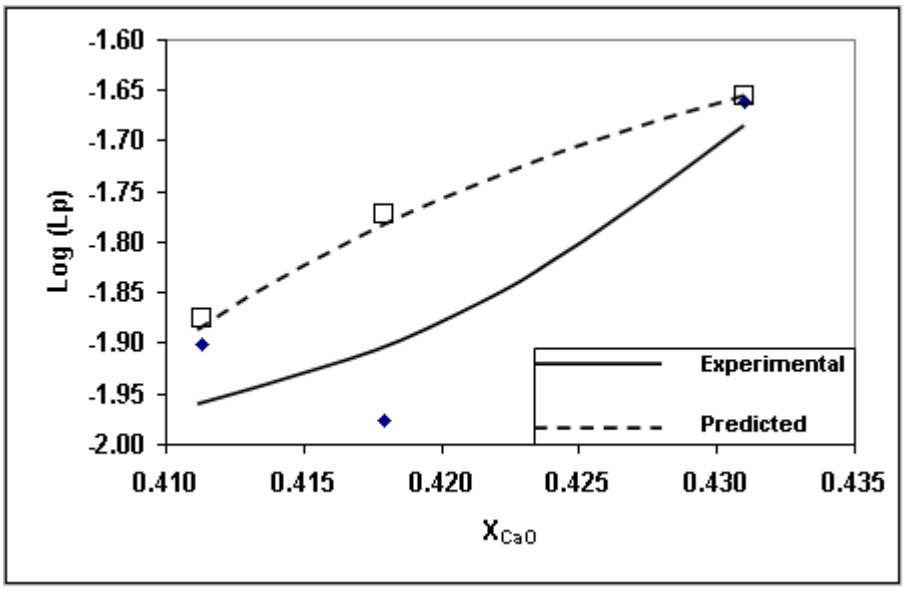


Figure A8 The variation of (a) Lp and (b) C_P^{3-} with calcium oxide (X_{CaO}) in $MnO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}P_2O_5\text{-}CaO$ slag under Ar/CO atmosphere at 1500°C, Basicity (B): 1.104 – 1.235

(a)



(b)

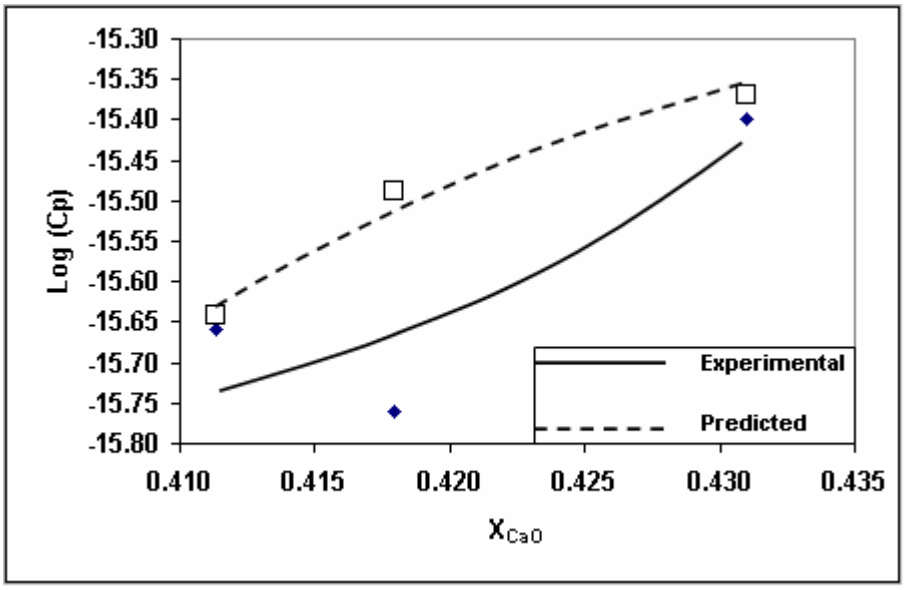
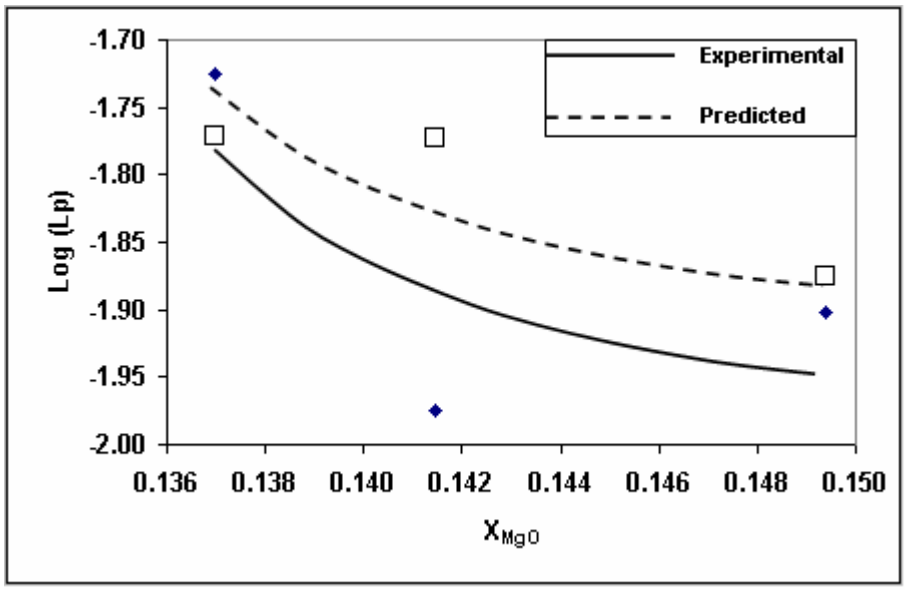


Figure A9 The variation of (a) Lp and (b) C_P^{3-} with calcium oxide (X_{CaO}) in $MnO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}P_2O_5\text{-}CaO$ slag under Ar/CO atmosphere at 1500°C, Basicity (B): 1.235 – 1.352

(a)



(b)

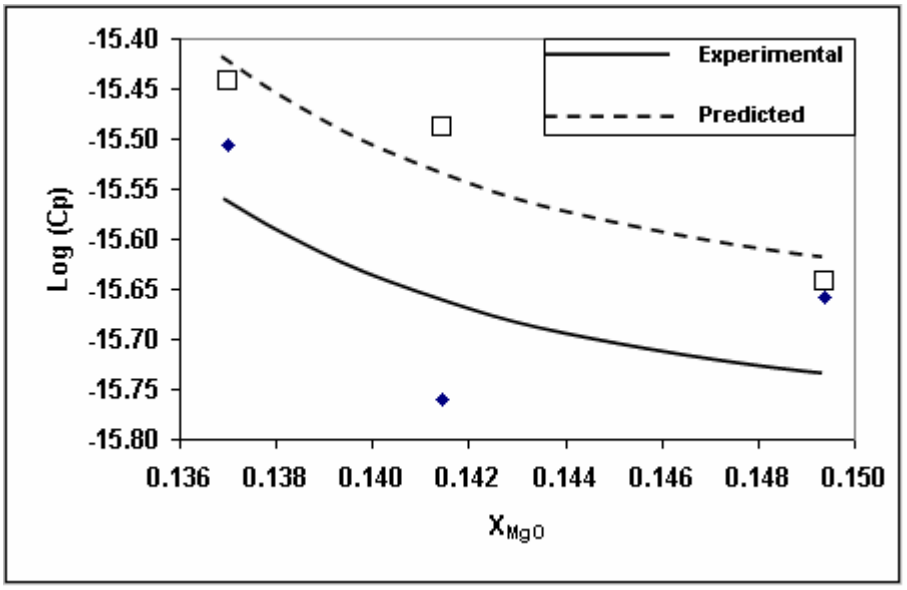
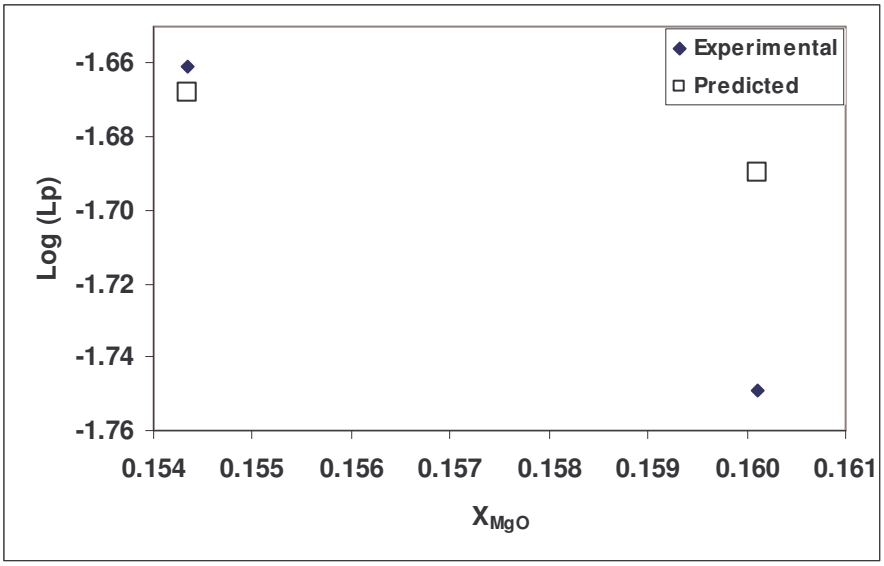


Figure A10 The variation of (a) Lp and (b) C_P^{3-} with magnesium oxide (X_{MgO}) in $MnO-SiO_2-Al_2O_3-MgO-P_2O_5-CaO$ slag under Ar/CO atmosphere at 1500°C, Basicity (B): 1.235 – 1.245

(a)



(b)

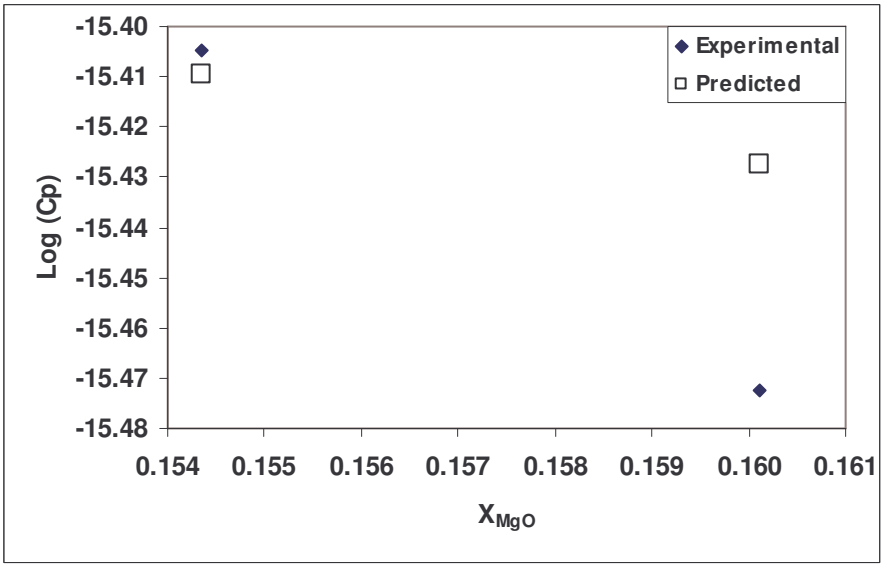
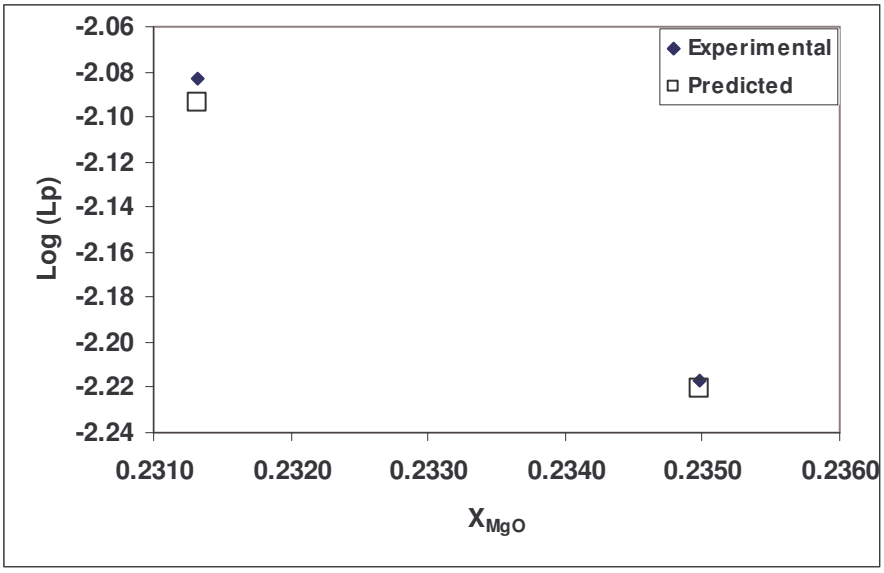


Figure A11 The variation of (a) Lp and (b) C_P^{3-} with magnesium oxide (X_{MgO}) in $MnO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}P_2O_5\text{-}CaO$ slag under Ar/CO atmosphere at 1500°C, Basicity (B): 1.331 – 1.347

(a)



(b)

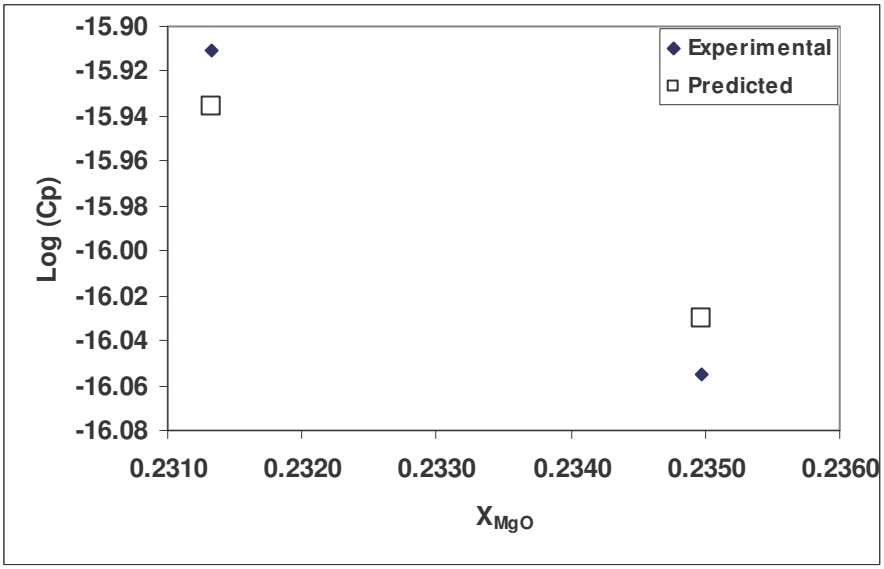
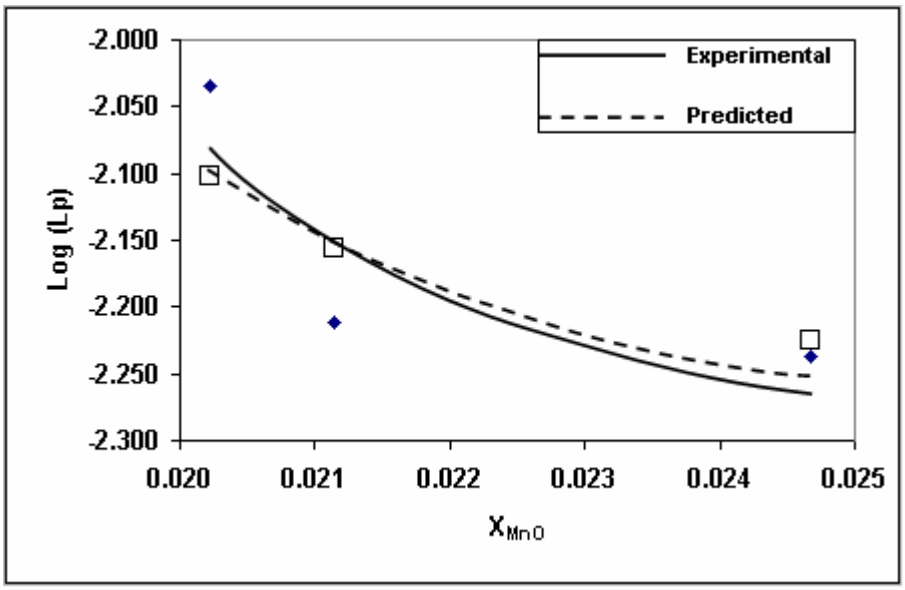


Figure A12 The variation of (a) Lp and (b) C_P^{3-} with magnesium oxide (X_{MgO}) in $MnO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}P_2O_5\text{-}CaO$ slag under Ar/CO atmosphere at 1500°C, Basicity (B): 1.097 – 1.281

(a)



(b)

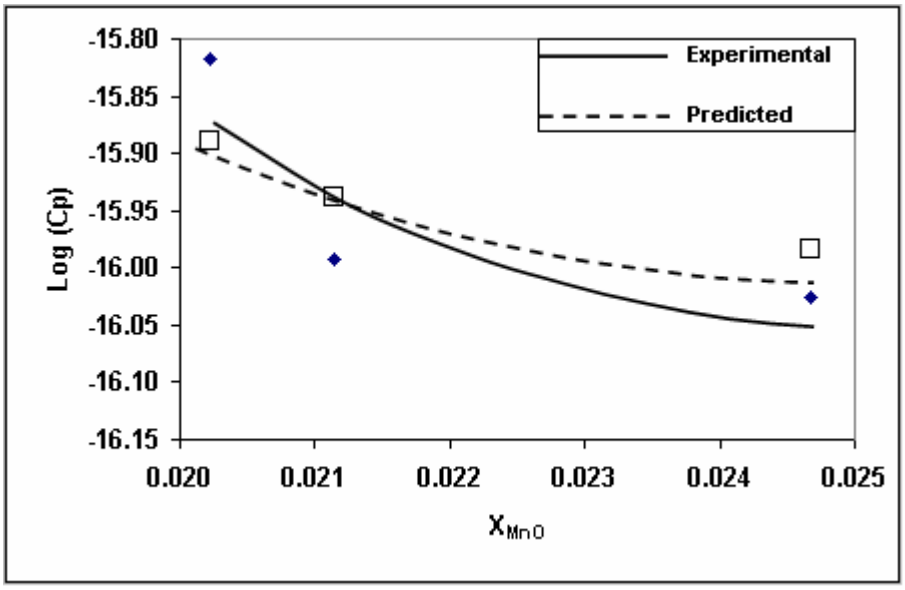


Figure A13 The variation of (a) Lp and (b) C_P^{3-} with magnesium oxide (X_{MnO}) in $MnO-SiO_2-Al_2O_3-MgO-P_2O_5-CaO$ slag under Ar/CO atmosphere at 1500°C, Basicity (B): 1.184 – 1.202

APPENDIX B

DETERMINATION OF THE ACTIVITY COEFFICIENT OF PHOSPHOROUS IN FERROMANGANESE

The activity coefficients in Tables 4.3 and 4.6 were calculated as shown equation B1 below assuming ideality in Fe-Mn solution.

$$\log f_P = e_P^P(wt.\%P) + e_P^C(wt.\%C) + e_P^{Si}(wt.Si) \quad (7) \qquad \text{B1}$$

The interaction coefficients used were taken from tables published by Bodsworth, C. and Bell, H. B.[7] and are repeated here in Table B1 below.

Table B1 Interaction coefficients of Phosphorous[7]

Solute X	e_P^x
Si	0.118
C	0.24
P	0.122

APPENDIX C

THE COMPOSITION OF GASES USED AND KEY TO SYMBOLS USED

Table C1: Chemical composition of CO and Ar gases.

CONSTITUENTS / GAS TYPE	MIN. PURITY %	N_2 vpm	O_2 vpm	Ar vpm	H_2 vpm	CO vpm	MOISTURE vpm	CO_2 vpm	THC as CH_4 vpm
CO	99.97	<150	<20 (incl Ar)		<150	-	<10	<30	<2
Ar (UHP)	99.999	<4	<2	-	-	<0.5	<1	<0.5	<0.5

Table C2: Key to symbols used in the tables with initial sample compositions

SYMBOL	MEANING
Mn-S	FeMn SLAG sample
M	FeMn METAL ALLOY sample
Mn-MSTR	FeMn MASTER SLAG sample

APPENDIX D

DETERMINATION OF EXPERIMENTAL DESIGN POINTS DESIGNATIONS IN THE MIXTURE MODEL[36 - 39]

The procedure to determine the experimental design point designations in Table 3.2 and Table D5 is given below. The applicable slag composition range is given in Table D1. The content of Al_2O_3 and MgO in the slag were fixed to reduce the number of experimental runs to be carried out. As a result, only four variable factors were considered in the experimental design instead of all six factors.

Table D1: Ferromanganese slag composition range

MnO (wt. %)	**MgO (wt. %)**	**SiO_2 (wt. %)**	**Al_2O_3 (wt. %)**	**CaO (wt. %)**	**P_2O_5 (wt. %)**
5 – 10	10 (Fixed)	36 – 54	5 (Fixed)	18 – 36	1 – 4

The lower boundary (a_i) and upper boundary (b_i) conditions for the four variable factors for the system considered are MnO (X_1) 5 to 10%, SiO_2 (X_2) 36 to 54%, CaO (X_3) 18 to 36% and P_2O_5 (X_4) 1 to 4%. These conditions are clearly illustrated in Table D2.

Table D2: Lower boundary (a_i) and Upper boundary (b_i) conditions for the four variable factors

Factor	**a_i**	**b_i**
X_1= MnO	0.05	0.1
X_2= SiO_2	0.36	0.54
X_3= CaO	0.18	0.36
X_4= P_2O_5	0.01	0.04

Step 1:

All the possible combinations of q – 1 factors are listed at a time by using the a_i and b_i values for all the factors except for one which is left blank, that is to say a_1, a_2, a_3, and a_4 are lower bounds and b_1, b_2, b_3, and b_4 are upper bounds for the four factors, X_1, X_2, X_3, and X_4. The three level (q – 1) combinations that are equal to $q*(2^{q-1})$ in number are shown in Table D3.

Table D3: All the possible combinations of (q – 1) factors

Group 1				**Group 2**				**Group 3**				**Group 4**			
X_1	**X_2**	**X_3**	**X_4**	**X_1**	**X_2**	**X_3**	**X_4**	**X_1**	**X_2**	**X_3**	**X_4**	**X_1**	**X_2**	**X_3**	**X_4**
a_1	a_2	a_3	-	a_1	a_2	-	a_4	a_1	-	a_3	a_4	-	a_2	a_3	a_4
a_1	a_2	b_3	-	a_1	a_2	-	b_4	a_1	-	a_3	b_4	-	a_2	a_3	b_4
a_1	b_2	a_3	-	a_1	b_2	-	a_4	a_1	-	b_3	a_4	-	a_2	b_3	a_4
a_1	b_2	b_3	-	a_1	b_2	-	b_4	a_1	-	b_3	b_4	-	a_2	b_3	b_4
b_1	a_2	a_3	-	b_1	a_2	-	a_4	b_1	-	a_3	a_4	-	b_2	a_3	a_4
b_1	a_2	b_3	-	b_1	a_2	-	b_4	b_1	-	a_3	b_4	-	b_2	a_3	b_4
b_1	b_2	a_3	-	b_1	b_2	-	a_4	b_1	-	b_3	a_4	-	b_2	b_3	a_4
b_1	b_2	b_3	-	b_1	b_2	-	b_4	b_1	-	b_3	b_4	-	b_2	b_3	b_4

In Table D3 the blanks spaces (-) represent the proportion to be filled by the factor which is left out of the combinations that is the fourth factor (Phosphorus pentoxide) in the first group, the third factor (Calcium oxide) in the second group, the second factor (Silica) in the third group, and the first factor (Manganese oxide) in the fourth group. The proportion to be filled into the blank is simply calculated by subtracting the total of the other three factors from 1(100%) under normal cases. When there are fixed variables such as Al_2O_3 and MgO in this work the remaining components must sum to $\mathbf{(1 - \sum X_{i\ (Fixed)})}$.[39]

Step 2:

The design points are obtained by calculating the blank proportion for all the combinations and by establishing feasible vertices of the polyhedron that fulfills the boundary conditions. At each point defining the particular vertex in the polyhedron, the sum of the proportions of the four factors must equal to unity, in this work because of the fixed variables that is Al_2O_3 at 0.05 and MgO at 0.1 the four factors must equal to 0.85. The values for the three level combinations and the calculated values of the missing factors given above are presented in Table D4 below. The shaded rows represent the vertices that fall inside the defined region of the slag system and are numbered from 1 to 12.

Having defined the feasible vertices of the polyhedron, the next step is to determine the points that are located centrally (centroids) on the edges, faces and on the overall center of the polyhedron. There is one centroid located in each bounding two or more dimensional faces where $K \leq q - 2$ (for a K-dimensional face) as well as the overall centroid of the polyhedron. The overall centroid is the component combination obtained by averaging all of the factor levels that define the existing feasible vertices. The centroid of the two dimensional faces are found by isolating all vertices which have $q - 3$ factor levels identical and by averaging the factor levels of each of the three remaining factors.

All remaining centroids are found in a similar fashion using all vertices which have $q - r - 1$ factor levels identical for an r – dimensional face where $r \leq K \leq q - 2$. For example the 2 – dimensional faces are found by grouping the vertices of the polyhedron into groups of three or more vertices where each vertex has the same value X_i for one of the components. It should be noted that K might be less than $q - 2$ since the constraints listed and applied to the proportions may reduce the dimensionality of the hyper-polyhedron to less than $q - 1$. There are eight 2-dimensional faces to the polyhedron and the coordinates of the centroids of the 8 faces are listed as the design points 13 to 20 in Table D5. The overall centroid is

defined as the average of 12 vertices (vertices 1 to 12) and is listed as point 21. Vertices 14, 16, 17, and 18 in Table D5 were not used in the actual experimental work to reduce the number of slags made and thus the size of the experiments. These vertices were thus omitted in Table 3.2.

Table D4: Treatment combinations for the FeMn slag composition in the defined constraint region with four variable factors

Group 1					Group 3			
X_1	X_2	X_3	(X_4)	Vertices	X_1	(X_2)	X_3	X_4
0.050	0.360	0.180	**0.260**		0.050	**0.610**	0.180	0.010
0.050	0.360	0.360	**0.080**		0.050	**0.580**	0.180	0.040
0.050	0.540	0.180	**0.080**	7	**0.050**	**0.430**	**0.360**	**0.010**
0.050	0.540	0.360	**-0.100**	8	**0.050**	**0.400**	**0.360**	**0.040**
0.100	0.360	0.180	**0.210**		0.100	**0.560**	0.180	0.010
0.100	**0.360**	**0.360**	**0.030**	1 9	**0.100**	**0.530**	**0.180**	**0.040**
0.100	**0.540**	**0.180**	**0.030**	2 10	**0.100**	**0.380**	**0.360**	**0.010**
0.100	0.540	0.360	**-0.150**		0.100	**0.350**	0.360	0.040
Group 2					**Group 4**			
X_1	X_2	(X_3)	X_4	Vertices	(X_1)	X_2	X_3	X_4
0.050	0.360	**0.430**	0.010		**0.300**	0.360	0.180	0.010
0.050	0.360	**0.400**	0.040		**0.270**	0.360	0.180	0.040
0.050	**0.540**	**0.250**	**0.010**	3	**0.120**	0.360	0.360	0.010
0.050	**0.540**	**0.220**	**0.040**	4 11	**0.090**	**0.360**	**0.360**	**0.040**
0.100	0.360	**0.380**	0.010		**0.120**	0.540	0.180	0.010
0.100	**0.360**	**0.350**	**0.040**	5 12	**0.090**	**0.540**	**0.180**	**0.040**
0.100	**0.540**	**0.200**	**0.010**	6	**-0.060**	0.540	0.360	0.010
0.100	0.540	**0.170**	0.040		**-0.090**	0.540	0.360	0.040

Reducing the number of design points

When omitting face centroids 14, 16, 17 and 18 the following considerations where taken into account.

i. Gorman [40,41] pointed out that there can be clusters of points in parts of the experimental region thus some can be dropped from the experiment.

ii. Centroids belonging to the even dimensional faces can be deleted.[38]

iii. Another method for reducing the size of the design would be to compute a normalized distance between points of the design and randomly omit points that are less than a certain minimum distance from other design points. The minimum distance and the method of normalization, which would be required if certain components are more sensitive than others would have to be chosen by the experimenter.[38]

It is important to note that for a four factor design a minimum design size of 9 design points is required to get an optimum design.[38]

Table D5: Coordinates of the 21 design points for the FeMn slag composition in the defined constraint region

Design Point Designation	Type of Boundary	X_1 = MnO	X_2 = SiO_2	X_3 = CaO	X_4 = P_2O_5	Combination of Vertices
1	Vertex	0.100	0.360	0.360	0.030	
2	Vertex	0.100	0.540	0.180	0.030	
3	Vertex	0.050	0.540	0.250	0.010	
4	Vertex	0.050	0.540	0.220	0.040	
5	Vertex	0.100	0.360	0.350	0.040	
6	Vertex	0.100	0.540	0.200	0.010	
7	Vertex	0.050	0.430	0.360	0.010	
8	Vertex	0.050	0.400	0.360	0.040	
9	Vertex	0.100	0.530	0.180	0.040	
10	Vertex	0.100	0.380	0.360	0.010	
11	Vertex	0.090	0.360	0.360	0.040	
12	Vertex	0.090	0.540	0.180	0.040	
13	Face centroid	0.100	0.452	0.272	0.027	1,2,5,6,9,10
***14**	Face centroid	0.097	0.360	0.357	0.037	1,5,11
15	Face centroid	0.078	0.386	0.360	0.026	1,7,8,10,11
***16**	Face centroid	0.078	0.540	0.206	0.026	2,3,4,6,12
***17**	Face centroid	0.097	0.537	0.180	0.037	2,9,12
***18**	Face centroid	0.050	0.478	0.298	0.025	3,4,7,8
19	Face centroid	0.075	0.473	0.293	0.010	3,6,7,10
20	Face centroid	0.080	0.455	0.275	0.040	4,5,8,9,11,12
(21)	Overall centroid	0.082	0.460	0.280	0.028	all 1,2,. . .12

APPENDIX E

CALCULATION OF THE PREVAILING PARTIAL PRESSURE OF OXYGEN (Po_2) IN THE REACTION TUBE

Option 1: Using 100% CO gas that is $P_{CO} = 0.83$ atm

The gas flow meter indicator was maintained at a set point of 6, which was equivalent to a gas flow rate of 579.39cm^3/ min. The equilibrium equation controlling the partial pressure of oxygen is given by equation E1:

$$C_{(s)(graphite)} + 1/2O_{2(g)} = CO_{(g)} \qquad \text{E1}$$

$$K = \frac{P_{CO}}{(a_C)P_{O_2}^{1/2}} \qquad \text{E2}$$

$a_c = 1$ (since the graphite crucible was pure solid carbon) and
$P_{CO} = 0.83$ atm (since chemically pure carbon monoxide gas was used.)

Thus $$K = \frac{0.83}{P_{O_2}^{1/2}} \qquad \text{E3}$$

Given $\Delta G^o = -112\,000 - 87.6T$ J/mole[13] E4

@ 1500^{o}C (1773^{o}K) $\Delta G^o = -112\,000 - 87.6(1773)$

$\Delta G^o = -267\,314.8$ J/mole

but $\Delta G^o = -RT\ln K$ E5

Therefore $$\ln\left(\frac{0.83}{P_{O_2}^{1/2}}\right) = \frac{+267{,}314.8}{(8.3143)(1773)}$$ E6

$$= 18.1338$$

$$\frac{0.83}{P_{O_2}^{1/2}} = e^{18.1338}$$

$$P_{O_2}^{1/2} = 1.1058\,x\,10^{-8}$$

$Po_2 = 1.223x10^{-16}$ atm

Option 2: Using Ar/CO gas mixture in a proportion of 92% Ar to 8% CO gas at 0.83 atm (such that Ar/CO mixture in a ratio of 0.92/0.08), therefore $P_{CO} = 0.0664$ atm

The gas flow meter indicators were maintained at set points of 12 and 2 for the Ar and CO gases respectively which were equivalent to gas flow rates of 1 249.44 cm^3/ min and 111.98 cm^3/ min. The equilibrium equation controlling the partial pressure of oxygen is given by equation E1 above.

@ 1500°C (1773°K) $\Delta G^o = -267\ 314.8$ J/mole [13]

But $\Delta G^{o} = -RT\ln K$

$a_c = 1$ (since the graphite crucible was pure solid carbon) and

$P_{CO} = 0.0664$ atm (since Ar was mixed with CO in a ratio of 0.92/0.08)

Therefore $$\ln\left(\frac{0.0664}{P_{O_2}^{1/2}}\right) = \frac{+267{,}314.8}{(8.3143)(1773)} \qquad \text{E7}$$

$$\frac{0.0664}{P_{O_2}^{1/2}} = e^{18.1338}$$

$$P_{O_2}^{1/2} = e^{-18.1338} x 0.0664$$

$$= 8.8463 \times 10^{-10}$$

Therefore **$Po_2 = 7.826 \times 10^{-19}$ atm**

APPENDIX F

CALCULATION OF *X* THE EQUIVALENT CATION FRACTION

From equation (2.52) repeated below the bulk or average value of Λ for a slag of any composition can be calculated.

$$\Lambda = X_A\Lambda_A + X_B\Lambda_B + X_C\Lambda_C + \ldots \qquad (2.52)$$

In equation (2.52) X is the equivalent cation fraction, based on the fraction of negative charge "neutralized" by the charge on the cation concerned. For any component, X can be evaluated in various ways. Where the composition is expressed in terms of mole fractions, the most convenient relation is:[15]

$$X = \frac{mole\ \ fraction\ of\ component\ \ x\ \ number\ of\ oxygen\ atoms\ in\ oxide\ molecule}{\sum mole\ fraction\ of\ component\ \ x\ \ number\ of\ \ oxygen\ atoms\ in\ oxide\ molecule\ all\ components} \qquad F1$$

Thus in a $CaO\text{-}SiO_2$ melt, for example,

$$X_{SiO_2} = \frac{2N_{SiO_2}}{N_{CaO} + 2N_{SiO_2}} \qquad F2$$

$$X_{CaO} = \frac{N_{CaO}}{N_{CaO} + 2N_{SiO_2}} \qquad F3$$