T-3604

REJECTION OF HALOGEN IMPURITIES TO THE FLAME REACTOR SLAG

By

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T-3604

A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science - Metallurgical Engineering.

Golden, Colorado

Date: Aug. 16 1988

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ABSTRACT

The solubility of chlorine and fluorine in liquid slags has been measured for slag compositions corresponding to the flame reactor processing of EAF dust. A high temperature slag/gas equilibration system was constructed and the solubility of chlorine and fluorine measured as a function of temperature and slag composition. The gas composition was adjusted to correspond to that experienced in the flame reactor when processing EAF dust. The solubility results were correlated using chlorine and fluorine capacity functions similar to the sulfur capacity function used to characterize sulfur solubility in slags.

The chlorine and fluorine capacity functions derived:

$$C_{Cl} = (\%Cl)^2 (P_{O2})^{1/2} / (P_{Cl2})$$

$$C_f = (\%F)^2 (P_{O2})^{1/2} / (P_{F2})$$

were based on the following solubility reactions:

$$Cl_{2(g)} + O^{=}_{(slag)} = 2Cl^{-}_{(slag)} + (1/2)O_{2(g)}$$

$$F_{2(g)} + O^{=}_{(slag)} = 2F^{-}_{(slag)} + (1/2)O_{2(g)}$$

The chlorine and fluorine capacity functions were correlated with temperature for constant slag compositions (slag basicity):

$$\log(C_{Cl}) = (10003/T) - 7.78 \qquad R = 0.341\text{-}0.437$$
$$\log(C_{Cl}) = (5166/T) - 4.52 \qquad R = 0.626\text{-}0.917$$

$$\log(C_{f}) = (38654/T) - 13.28 \qquad R = 0.341\text{-}0.437$$
$$\log(C_{f}) = (22785/T) - 3.39 \qquad R = 0.626\text{-}0.917$$

where R = slag basicity = $\dfrac{(\%MgO + \%CaO)}{(\%SiO_2 + \%Al_2O_3)}$

Modest levels of chlorine and fluorine solubility were observed. A significant increase could be anticipated for basicities greater than 1. The chlorine and fluorine content of the slag was increased to 0.20-0.30% and 0.5-0.8% respectively. Results for log halogen capacity - reciprocal temperature plots indicated improved halogen solubility will be obtained with a decrease in temperature.

The major problem encountered in this study, was the dissolution of the alumina sample crucible in the slag. This resulted in the formation of more acidic slags than desired and in the investigation of a rather narrow range of slag basicities.

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ACKNOWLDEGMENTS

The author would like to express his sincere thanks to Dr. J. P. Hager for his professional advice and guidance throughout the course of this work.

Financial support of this research was provided by the Horsehead Resource and Development Co. Incorporated. Thanks are extended to Mr. John Pusateri and Mr. Lou Lherbier for their assistance throughout this research work.

Many thanks are extended to the author's colleagues; Robert Shanks, Nick Gomez, Dan Ash, Bruce Lanning, and Wendy Moore for their friendship and support. A special thanks is given to Steve and Kay Weber as well as Harry and Judy Walker for their love and friendship throughout the author's tenure at the Colorado School of Mines.

The author would also like to acknowledge his brother Trevor (a budding psychologist) for his curiosity at what a metallurgist does.

Finally, the author wishes to acknowledge his parents Bill and Mary Hall for their love, patience, support, and understanding throughout his academic career.

I. INTRODUCTION

In recent years, enviromental legislation has caused considerable interest in the treatment and handling of secondary and waste materials. Such materials can be low grade mineral deposits, electric arc furnace dusts, or residues produced from various metallurgical processes. The need for this technology has created new challenges to the extractive metallurgical industry. In response to these challenges, high-intensity smelting processes have been developed to handle such material as economically as possible. One such process is Horsehead Resource and Development's (HRD) Flame Reactor.

The use of the HRD Flame Reactor has been documented (1) to show the successful treatment of various secondary and waste materials. One such material is electric arc furnace (EAF) dust produced in steelmaking operations. EAF dust has been designated as a hazardous waste material by the Enviromental Protection Agency. The current practice of handling EAF dust is by disposal to landfills. In the future, this practice of handling EAF dust will be prohibited, creating the need for metallurgical process treatment.

The HRD Flame Reactor is a two-stage, carbon fueled flash smelting reactor. It is principally designed to treat oxidic feeds. Fuel combustion and metal oxide reduction reactions are achieved in separate adjoining stages. The first stage, termed the pilot stage, is separated into upper and lower sections. In the upper section, coal or coke fines are pneumatically injected and ignited with O_2 enriched air. The fuel rich mixture then enters the lower section where additional O_2 enriched air is added and flame temperatures in excess of 2000 ^{o}C are developed.

The second stage, termed the reactor stage directly follows the pilot stage. Secondary or waste material is pneumatically injected at the head of the reactor stage where contact with the reducing gas mixture is achieved. The temperature in the reactor stage is approximately 1600 ^{o}C.

The reactor stage is followed by a water-cooled horizontal cyclone for gas/solid separation. The molten slag is recovered at this point in the process. The slag is then either cast or granulated. The reactor off-gas that leaves

the cyclone is combusted with excess air to convert the CO to CO_2 and the H_2 to H_2O. Oxidation of the metal vapors present produces metal oxide particulates. The metal oxide product is then collected in a bag house.

In the treatment of EAF dust employing the Flame Reactor, the primary constituents are zinc and iron which occur as zinc ferrites. Iron contained in the zinc ferrite reports to the slag as iron oxide. The zinc present is first vaporized to the gaseous species. Following the horizontal cyclone, the zinc is re-oxidized to produce a zinc oxide product. Again, the oxide product is collected at the bag house. The slag produced meets EPA toxicity levels and can be disposed of.

The use of the HRD Flame Reactor appears to be an effective method in the treatment of EAF dusts. However, the presence of chlorine and fluorine contained in some EAF dusts creates process problems. The zinc oxide product may become contaminated due to the presence of chlorine and fluorine. Also, unreacted chlorine and fluorine will report to the waste stack as HCl and HF gas.

One possible solution to the above problem would be the segregation of chlorine and fluorine from the gas phase to the Flame Reactor slag. This would be achieved through modification of the slag's properties, by the addition of fluxes, such that the chlorine and fluorine would be solubilized in the slag. If successful, the chlorine and fluorine would be contained in a non-toxic material and could be readily discarded.

The objective of this study was to determine experimentally the saturation solubility of chlorine and fluorine for a flame reactor slag produced from a processed EAF dust sample to which fluxes have been added. The effects of temperature and slag basicity on chlorine and fluorine were investigated.

II. LITERATURE REVIEW

The purpose of a literature review is to research all available information that pertains to a given study. The objective of this study was to investigate chlorine and fluorine solubility for a slag generated from electric arc furnace dust. Computer searches of the existing literature have indicated no data regarding halogen solubility for slags in general.

Since the measurement and evaluation of halogen solubility data was the purpose of this study, a method of analysis was required. The measurement of sulfur solubility in slags has long been described by the sulfide capacity function (C_S). Through the use of this concept, a direct analogous argument was used to define chlorine (C_{Cl}) and fluorine (C_f) capacity functions. This development is presented in detail in Chapter III.

The sulfide capacity function describes the slag's ability to act as a desulfurizer. The chemical reaction used is as follows:

$$(1/2)S_{2(g)} + O^{=}_{(melt)} = S^{=}_{(melt)} + (1/2)O_{2(g)} \qquad (2.1)$$

From equation 2.1, the sulfide capacity may be derived and is given below:

$$C_S = (\text{Wt.\% S})(P_{S2})^{(1/2)}/(P_{O2})^{(1/2)} \qquad (2.2)$$

Since the derivation of the halogen capacity functions have been developed by analogy with the sulfide capacity function, it was thus deemed appropriate to include in this chapter a discussion of studies which have investigated sulfur solubility through use of the sulfide capacity function.

Fincham and Richardson (2) are acknowledged to be the first investigators to describe sulfur solubility in slags in terms of both sulfide and sulfate capacity functions. Their research studied the equilibrium distribution of sulfur in silicate and aluminate melts.

The procedure used by Fincham and Richardson for their experiments was as follows. One gram samples were weighed into platinum cups. These cups were then placed into a pre-heated nitrogen purged furnace. The N_2 gas (from the

purge) was then replaced with the desired gas mixture of known composition. At the conclusion of the experiment, the melt samples were quenched in air or nitrogen then assayed for sulfur. Six hour equilibration periods were used for all experiments.

Fincham and Richardson postulated that the two most probable forms of sulfur present in an equilibrated melt would be sulfides (under reducing conditions) or sulfates (under oxidizing conditions). Given this assumption, the following chemical equations and their equilibrium expressions would apply:

$$(1/2)S_{2(g)} + O^{=}_{(melt)} = (1/2)O_{2(g)} + S^{=}_{(melt)} \quad (2.3)$$

$$K = [(A_{S^{=}})(P_{O2})^{(1/2)}]/[(A_{O^{=}})(P_{S2})^{(1/2)}] \quad (2.4)$$

$$(1/2)S_{2(g)} + (3/2)O_{2(g)} + O^{=}_{(melt)} = SO_4^{=}{}_{(melt)} \quad (2.5)$$

$$K = (A_{SO4^{=}})/[(A_{O^{=}})(P_{S2})^{(1/2)}(P_{O2})^{(3/2)}] \quad (2.6)$$

Equations 2.4 and 2.6 were then re-written as follows:

$$\log K = \log[(\%S)(P_{O2})^{(1/2)}/(P_{S2})^{(1/2)}] = \log(C_S) \quad (2.7)$$

$$\log K = \log[(\%S)(P_{O2})^{(-3/2)}(P_{S2})^{(-1/2)}] = \log(C_{SO4}) \quad (2.8)$$

where K is now the equilibrium constant divided by the activity of oxygen.

Equations 2.7 and 2.8 were (and are) the definitions for sulfide and sulfate capacities. Fincham and Richardson stated that the following assumptions must hold for capacity functions to apply for a given equilibrated melt:

(i) that the activity of replacable oxygen in the melt is not significantly altered by the substitution of small amounts of sulfur, and

(ii) that for low concentrations of sulfur encountered in these experiments, the activities of (S) and (SO_4) are porportional to the sulfur concentrations.

Fincham and Richardson established that sulfide and sulfate capacity functions were valid to describe the data obtained. This was done by plotting measured values of sulfide and sulfate capacities against oxygen partial pressure. For partial pressures of oxygen < 10^{-6} atm.,

it was observed that all sulfur found in the equilibrated melts occured exclusively as sulfides. For partial pressures of oxygen > 10^{-4} atm., all sulfur contained in the equilibrated melts occurred exclusively as sulfates. Thus Fincham and Richardson had established the validity of equations 2.7 and 2.8 . Although the measurements were made at 1500 ^{o}C, the same trends were also observed at other temperatures.

Since Fincham and Richardson proposed the use of sulfide or sulphate capacity functions for sulfur solubility measurements, many papers have used this concept to describe a slag's solubility characteristics. These papers provide useful reference material for sulfide capacity function prediction for multiple oxide slag systems.

Chan and Fruehan (3) measured both the sulfide capacity function and the sulfur partition ratio for carbon saturated iron and Na_2O-SiO_2 slags. All measurements were made at a constant temperature of 1200 ^{o}C. The experimental procedure used was similar to that used by Fincham and Richardson.

The results of Chan and Fruehan showed that for plots of log (C_S) or log (sulfur partition ratio) against the mole fraction of Na_2O, the solubility would increase with an increase in the mole fraction of Na_2O. The authors observed that higher partition ratios and capacities were obtained with Na_2O-based slags than with $CaO-SiO_2$ slags.

Kor and Richardson (4) have investigated the sulfide capacity behavior of slags in the $CaO-Al_2O_3-CaF_2$ system. The effect of slag composition on the sulfide capacity function was investigated.

Kor and Richardson noted the following results. For slag compositions that contained little CaO, negligible sulfur solubility was observed. For CaF_2-CaO slags, the sulfur solubility gave a distinct maximum for variations in the mole fraction of CaO. This is shown in Figure 2.1 . The maximum solubility at $X_{CaO} = 0.26$ was attributed to the saturation limit of CaO in the CaF_2-CaO system for a temperature of 1500 ^oC . These results were found for a constant $(P_{S2}/P_{O2})^{(1/2)}$ ratio of four. For experiments where this ratio was allowed to vary, improved sulfur solubility was observed as this ratio was increased.

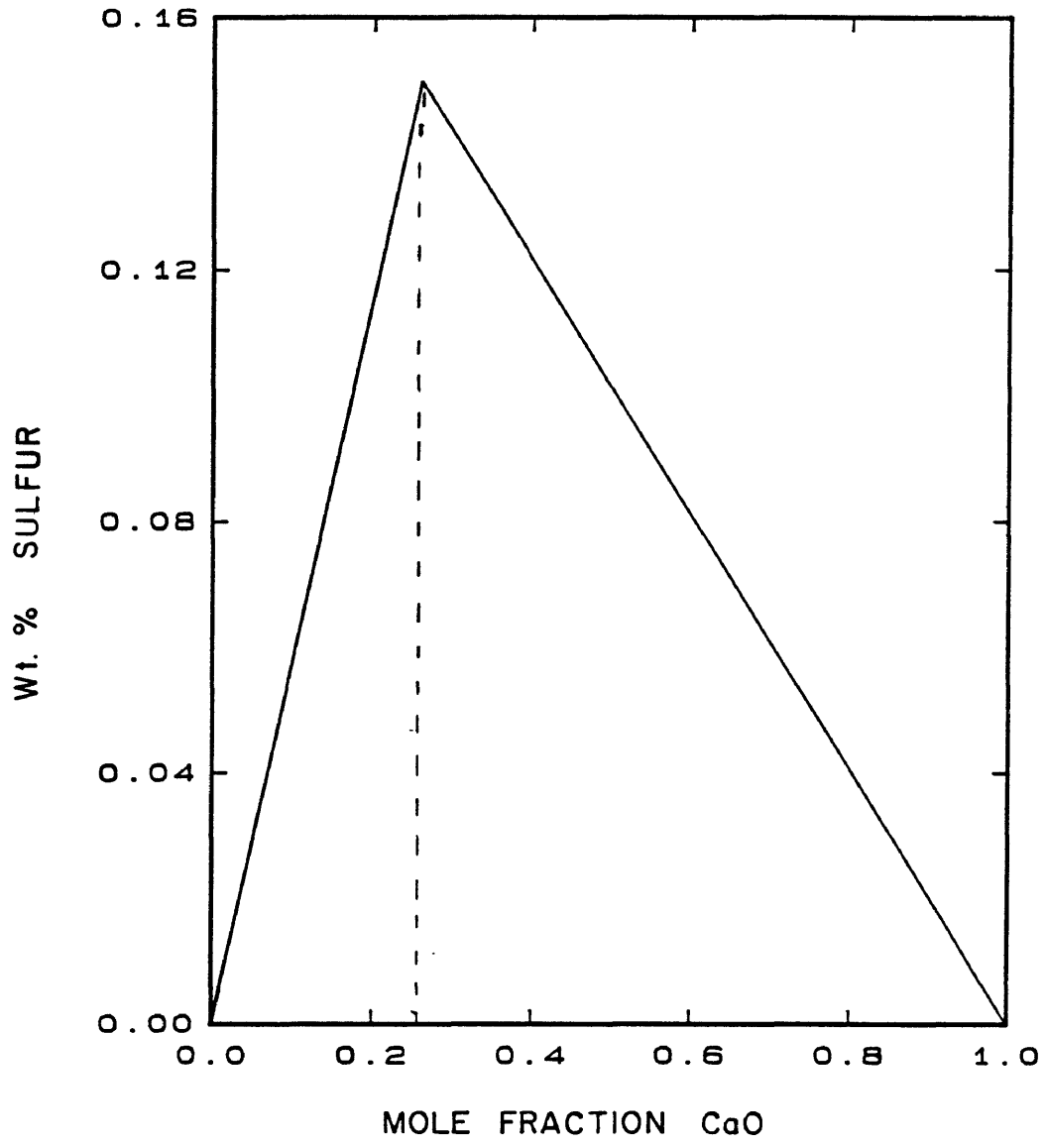

Figure 2.1 - Sulfur Concentration obtained in CaF_2 - CaO melts (3)

For $CaO-Al_2O_3-CaF_2$ slag mixtures, the sulfide capactiy function was found to be directly effected by the CaO content present. This is shown in Figure 2.2 . Kor and Richardson cite that the decrease of (C_S) (following the observed maximum) in Figure 2.2 is attributed to the prescence of "free solid phases". Such phases occur as the melt solidifies. An example of a free solid phase would be tri-calcium aluminate found in the $CaO-Al_2O_3$ system. The authors noted that when these solid phases were omitted, (C_S) values should become constant rather than decrease as indicated in Figure 2.2 . Calculations were done to verify this point and are plotted as triangles in Figure 2.2 .

Sosinsky and Sommerville (5) have investigated the correlation of the sulfide capacity function with temperature and slag composition. The slag composition was characterized using the concept of optical basicity. Sosinsky and Sommerville pointed out that in previous studies where a basicity ratio has been used to characterize slag composition, the basicity expressions used were generally arbitrary. A further problem cited is the determination of a slag's basicity when there is a lack of recognized acidic components.

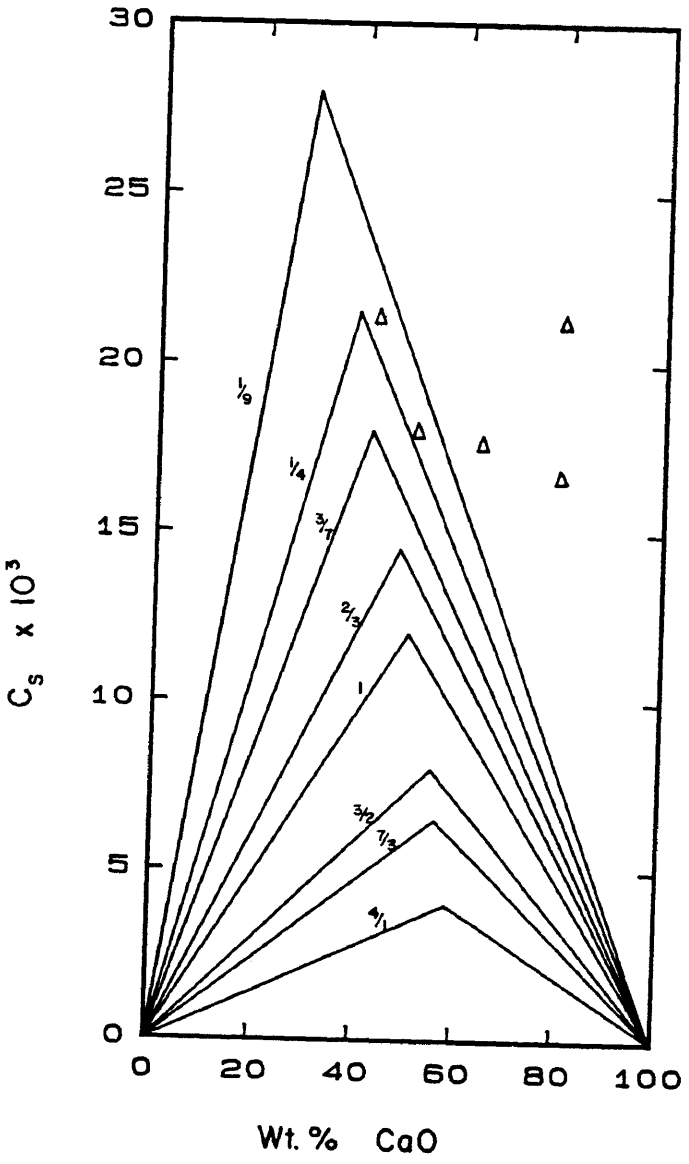

Figure 2.2 - Curves showing how sulfide capacities change as CaO is added to constant weight ratios of Al_2O_3/CaF_2 (4)

The concept of optical basicity was first used to measure glass basicity spectroscopically by thin section. Briefly, the optical basicity represents the ratio of electron donar power of oxides present in the glass to electron donar power of the free oxide ions present. Spectroscopic measurement cannot be applied to slags produced in pyrometallurigical processes due to the prescence of transition elements. Transition elements render the material opaque.

Since direct measurement of a slag's optical basicity is not possible, Sosinsky and Sommerville have given an alternative equation that may be used to find the optical basicity for a multiple oxide slag. This equation is as follows:

$$\Lambda = X_A \Lambda_A + X_B \Lambda_B + \ldots \qquad (2.9)$$

where: Λ = average optical basicity for a slag
Λ_A = optical basicity for an individual oxide AO
X_A = equivalent cation fraction for oxide AO
A = oxide AO, B = oxide BO, etc.

The optical basicity for an individual (non-transition) oxide may be calculated from its Pauling electronegativity value. Thus for an oxide AO, Λ_A is found from the following equation:

$$\Lambda_A = \frac{0.74}{(x-0.26)} \qquad (2.10)$$

where x is the electronegativity value for the specific cation.

Sosinsky and Sommerville have tabulated the optical basicity values for various metal oxides using equation 2.10 . These are re-produced in Table 2.1 .

The equilvalent cation fraction (X) is based on the fraction of negative charge neutralized by the charge on the cation concerned. When the composition is given in mole fraction, X can be calculated as follows:

$$X = \frac{\text{mole fraction of component} \quad \text{number of oxygen atoms in oxide molecule}}{\sum \text{mole fraction of component} \quad \text{number of oxygen atoms in oxide molecule}}$$

TABLE 2.1

Optical Basicty Values Calculated By Sosinsky-Sommerville (5)

Oxide	Electronegativity	Λ
K_2O	0.8	1.4
Na_2O	0.9	1.15
BaO	0.9	1.15
Li_2O	1.0	1.0
CaO	1.0	1.0
MgO	1.2	0.78
Al_2O_3	1.5	0.61
SiO_2	1.8	0.42
P_2O_5	2.1	0.40
CO_2	2.5	0.33
SO_3	2.5	0.33

Thus, for a $CaO-Al_2O_3$ melt, for example

$$X_{CaO} = \frac{N_{CaO}}{N_{CaO}+3N_{Al2O3}+2N_{SiO2}} \quad (2.11)$$

$$X_{Al2O3} = \frac{3N_{Al2O3}}{N_{CaO}+3N_{Al2O3}+2N_{SiO2}} \quad (2.12)$$

$$X_{SiO2} = \frac{2N_{SiO2}}{N_{CaO}+3N_{Al2O3}+2N_{SiO2}} \quad (2.13)$$

where N = mole fraction of component involved.

Sosinsky and Sommerville plotted sulfide capacity data ($\log C_S$) against optical basicty for 7 oxide systems. All data had been measured for a constant temperature of 1500 ^oC. The following linearly regressed equation (for 183 data points) was obtained:

$$\log(C_S) = 12.6 - 12.3 \quad r^2=0.965 \quad (2.14)$$

To determine optical basicities for slags that contained transition oxides, Sosinsky and Sommerville used sulfide capacity data (from existing literature) for 14 additional oxide systems. Each system contained at least one transition metal oxide. From this data and equation

2.14, Sosinsky and Sommerville were able to determine optical basicity values for slag systems containing transition oxides. These values were termed the "effective" optical basicity and were designated (Λ_s). The results are shown in Table 2.2 . For temperatures of 1500 ^{o}C, Sosinsky and Sommerville had shown the sulfide capacity function could be calculated for any oxide slag using equations 2.9 and 2.14 .

Sosinsky and Sommerville noted that their above findings applied to data collected at 1500 ^{o}C only. To show that the sulfide capacity function was temperature dependant, similar plots of data for temperatures of 1550 and 1650 ^{o}C were done. Linearly regressed equations similar to equation 2.14 were found and are shown in Table 2.3 .

All sulfide capacity data described above was then re-plotted as $\log(C_s)$ against reciprocal temperature. Several $\log(C_s)$-1/T plots were made, each at a constant optical basicity value. The purpose of these plots was to establish a relationship between the sulfide capacity function and temperature. Linearly regressed equations showing good correlation ($r^2 > 0.92$) were achieved.

TABLE 2.2

Optical Basicity Values Calculated From Sulfide Capacity Data (5)

Oxide	Λ_s
TiO_2	0.61
Fe_2O_3	0.70
FeO	1.03
MnO	1.21

TABLE 2.3

Experimental Sulfide Capacity-Optical Basicity Correlations (5)

Temp. (^oC)	Equation	r^2
1500	$\log(C_s)=12.6G-12.3$	0.965
1550	$\log(C_s)=14.1G-13.1$	0.863
1650	$\log(C_s)=15.0G-13.3$	0.848

From the equations in Table 2.3, and the results described above, Sosinsky and Sommerville derived the following equation correlating both temperature and optical basicity:

$$\log(C_S) = \frac{(22690 - 54640\Lambda)}{T} + 43.6\Lambda - 25.2 \qquad (2.15)$$

where: T is temperature (^{o}K)
Λ is average optical basicity

With equation 2.15, Sosinsky and Sommerville could predict for a specified temperature and slag composition, the sulfide capacity (C_S) value that should result. Results using equation 2.15 gave reasonable correlations in comparison with curves plotted from actual data.

Finally, Turkdogan (6) has listed other capacity functions that have been derived in the literature. These are listed below:

Water Vapor Capacity

$$C_H = (\text{ppm OH})/(P_{H2O})^{(1/2)} \qquad (2.10)$$

Nitrogen Capacity

$$C_N = (\%N)[(P_{CO})^{(3/2)}/(P_{N2})^{(1/2)}] \quad (2.11)$$

Cyanide Capacity

$$C_{CN} = (\%CN)(P_{CO}/P_{N2})^{(1/2)} \quad (2.12)$$

Carbide Capacity

$$C_C = (\%C)P_{CO} \quad (2.13)$$

Carbonate Capacity

$$C_{car} = (\%CO_2)/P_{CO2} \quad (2.14)$$

This literature review has given several examples of investigative studies involving the use of the sulfide capacity function. Further, the use of capacity functions (other than sulfide) to describe solubility in slags provides a good foundation for the derived chlorine and fluorine capacity functions presented in Chapter III.

III. DEVELOPMENT OF CHLORINE AND FLUORINE CAPACITY FUNCTIONS

It is common to express sulfur solubility in slags in terms of a sulfur capacity function. Since the measurements of this study involve chlorine and fluorine solubility in a slag, a chlorine capacity function (C_{Cl}) and a fluorine capacity function (C_f) have been developed to correlate the data.

The following derivation of the sulfur capacity function is given as a basis for the development of the chlorine and fluorine capacity functions.

Sulfur Capacity

The equation defining the sulfur capacity is a function of the sulfur and oxygen potentials, and the wt. % sulfur present in the slag. This equation is given below:

$$C_S = (\%\ S)(P_{O2})^{(1/2)}/(P_{S2})^{(1/2)} \qquad (3.1)$$

Equation 3.1 is derived from the following chemical reaction:

$$(1/2)S_{2(g)} + O^{=}_{(slag)} = S^{=}_{(slag)} + (1/2)O_{2(g)} \qquad (3.2)$$

The equilibrium expression (K) for reaction 3.2 is given by:

$$K = (P_{O2})^{(1/2)}(A_S{=})/(P_{S2})^{(1/2)}(A_O{=}) \qquad (3.3)$$

The oxygen activity should not change appreciably for small amounts of sulfur that dissolve into the slag and can be considered constant. Thus, equation 3.3 can be written:

$$(K)(A_O{=}) = (A_S{=})(P_{O2})^{(1/2)}/(P_{S2})^{(1/2)} \qquad (3.4)$$

For low concentrations of sulfur, the activity of sulfur is porportional to the weight % sulfur by Henry's Law:

$$(A_S{=}) = (\%S)(f_S) \qquad (3.5)$$

where f_S is the activity coefficient of $S^{=}$ in the slag. Re-writing equation 3.4 by substituting equation 3.5 gives:

$$(K)(A_{O^=})/(f_S) = (\%S)(P_{O2})^{(1/2)}/(P_{S2})^{(1/2)} \quad (3.6)$$

The left hand side of equation 3.6 is a function of temperature and slag composition only, and is termed the sulfide capacity (C_S). Equation 3.6 can thus be written:

$$C_S = (\%S)(P_{O2})^{(1/2)}/(P_{S2})^{(1/2)} \quad (3.7)$$

The value of equation 3.7 is that for a given temperature and slag composition the value of (C_S) is a constant and can be used to calculate the sulfur for different combinations of P_{O2} and P_{S2}:

$$(\%S) = (C_S)(P_{S2})^{(1/2)}/(P_{O2})^{(1/2)} \quad (3.8)$$

Chlorine & Fluorine Capacity

Using the derivation given above, chlorine and fluorine capacities can be derived. The analogous equations for chlorine and fluorine solubility are given as follows:

$$Cl_{2(g)} + O^{=}_{(slag)} = 2Cl^{-}_{(slag)} + (1/2)O_{2(g)} \quad (3.9)$$

$$F_{2(g)} + O^{=}_{(slag)} = 2F^{-}_{(slag)} + (1/2)O_{2(g)} \quad (3.10)$$

The equilibrium constants for reactions 3.9 and 3.10 can be written as follows:

$$K1 = (P_{O2})^{(1/2)}(A_{Cl}-)^{(2)}/(P_{Cl2})(A_{o}=) \quad (3.11)$$

$$K2 = (P_{O2})^{(1/2)}(A_{f}-)^{(2)}/(P_{F2})(A_{o}=) \quad (3.12)$$

Again, considering the oxygen activity to be constant, equations 3.11 and 3.12 can be re-written as:

$$(K1)(A_{o}=) = (P_{O2})^{(1/2)}(A_{Cl}-)^{(2)}/(P_{Cl2}) \quad (3.13)$$

$$(K2)(A_{o}=) = (P_{O2})^{(1/2)}(A_{f}-)^{(2)}/(P_{F2}) \quad (3.14)$$

The activity of chlorine ($A_{Cl}-$) and fluorine ($A_{f}-$) in the slag can also be expressed in terms of the weight percent chlorine and fluorine:

$$(A_{Cl}-) = (\%Cl)(f_{Cl}) \quad (3.15)$$

$$(A_{f}-) = (\%F)(f_{f}) \quad (3.16)$$

The substitution of equations 3.15 and 3.16 into equations 3.13 and 3.14, respectively, leads to the following equations where (C_{Cl}) and (C_f) are defined as the chlorine and fluorine capacities.

$$C_{Cl} = (\%Cl)^{(2)}(P_{O2})^{(1/2)}/(P_{Cl2}) \quad (3.17)$$

$$C_f = (\%F)^{(2)}(P_{O2})^{(1/2)}/(P_{F2}) \quad (3.18)$$

where:

$$C_{Cl} = (K1)(A_o=)/(f_{Cl})^{(2)} \quad (3.19)$$

$$C_f = (K2)(A_o=)/(f_f)^{(2)} \quad (3.20)$$

The halogen capacities given by equations 3.17 and 3.18 should be constant for a given temperature and slag composition. Thus, once determined, they can be used to calculate the solubility of chlorine and fluorine for different gas compositions:

$$(\%Cl) = (C_{Cl})^{(1/2)}(P_{Cl2})^{(1/2)}/(P_{O2})^{(1/4)} \quad (3.21)$$

$$(\%F) = (C_f)^{(1/2)}(P_{F2})^{(1/2)}/(P_{O2})^{(1/4)} \quad (3.22)$$

The variation of the halogen capacities with temperature can now be examined. From the following equations:

$$Cl_{2(g)} + O^{=}_{(slag)} = 2Cl^{-}_{(slag)} + (1/2)O_{2(g)} \quad (3.9)$$

$$F_{2(g)} + O^{=}_{(slag)} = 2F^{-}_{(slag)} + (1/2)O_{2(g)} \quad (3.10)$$

both (C_{cl}) and (C_f) have been shown to be related to the equilibrium constants for these reactions by:

$$C_{cl} = (K1)(A_o{}^{=})/(f_{cl})^2 \quad (3.19)$$

$$C_f = (K2)(A_o{}^{=})/(f_f)^2 \quad (3.20)$$

where $A_o{}^{=}$, f_{cl}, and f_f will be determined primarily by the basicity.

The derivative of $\ln(C_f)$ and $\ln(C_{cl})$ with respect to (1/T) gives the following equations assuming that $A_o{}^{=}$, f_f, and f_{cl} do not change with temperature and provided R (the basicity) is constant.

$$\frac{d(\ln(Ccl))}{d(1/T)} = \frac{d(\ln(K1))}{d(1/T)} \quad (3.23)$$

$$\frac{d(\ln(Cf))}{d(1/T)} = \frac{d(\ln(K2))}{d(1/T)} \quad (3.24)$$

Using the van't Hoff equation

$$\frac{d(\ln K)}{d(1/T)} = -\Delta H^{o}/R \quad (3.25)$$

equations 3.23 and 3.24 can be written in the following form:

$$\frac{d(\log(Ccl))}{d(1/T)} = -\Delta H^{o}_{1}/(2.303R) \quad (3.25)$$

$$\frac{d(\log(Cf))}{d(1/T)} = -\Delta H^{o}_{2}/(2.303R) \quad (3.26)$$

where:

ΔH^{o}_{1} = heat of reaction for the solution of chlorine in the liquid slag.

ΔH^{o}_{2} = heat of reaction for the solution of fluorine in the liquid slag.

R = universal gas constant

From the above derivation, the enthlapy of solution for reactions 3.9 and 3.10 can be found by plotting the log capacity function against reciprocal temperature for constant slag composition (basicity).

IV. EXPERIMENTAL PROGRAM

The following sections describe the experimental program implemented to measure the halogen saturation solubility for a slag produced from a processed EAF dust. The experimental system contained two principal sections, these were the gas train assembly, and the reactor assembly. These are discussed in section 4.2 .

4.1 Overview Of The Experimental Program

This section presents a brief description of the experimental program developed for this study. A detailed description of the experimental procedure and the apparatus are presented later in this chapter.

The objective of this study was to measure experimentally the saturation solubility of chlorine and fluorine for a Flame Reactor slag produced from a processed EAF dust. This master slag sample was supplied by HRD. The effects of temperature, and slag basicity were investigated.

The gas composition was fixed to correspond to the compositions observed in HRD's Flame Reactor when treating EAF dust.

The slag samples were heated in a high temperature, molybdenum disilicide heating element tube furnace. For a fixed slag composition and temperature, the charge (slag + flux additions) was equilibrated with a gas mixture similar to the gas composition found in the Flame Reactor (see section 4.5). Fluxing agents added were lime and alumina. The addition of lime was used to improve halogen solubility. Equilibration periods of either 4 or 6 hours were used for all experiments. Following the equilibration period, the samples were cooled and prepared for assay. The samples were then sent to Hazen Research Incorporated (HRI) and Horsehead Resource and Development (HRD) for fluorine and chlorine analysis.

The charge (slag + fluxes) was contained in a set of high purity inner and outer alumina crucibles. The crucibles were separated by loose alumina powder. This was done to minimize damage to the reactor system in the event of slag breakout. Alumina additions were also added

directly to the charge and were maintained at an overall 15 wt. % concentration. Frequent slag breakouts were encountered during the initial experiments run, the practice of adding alumina to the slag was undertaken to alleviate this problem.

From analysis of the as-received slag (see section 4.4), a large iron oxide content was observed. Consultation of the $FeO-Al_2O_3$ phase diagram indicated that for temperatures of interest, operation in a liquid phase region had occured. The addition of alumina to the slag raised the liquidus temperature of the $FeO-Al_2O_3$ system thus allowing slag containment.

For experiments where higher temperatures (1480-1500 ^oC) were tried, slag breakout was again observed. It was suspected that at these higher temperatures, the system had again moved back into the liquid phase region. Increased alumina additions to a 30 wt. % concentration improved slag containment.

4.2 Description Of The Apparatus

The reactor system can be divided into two principal sections. These are the gas train assembly and the reactor assembly. Figure 4.1 shows a schematic of the complete reactor system. Figure 4.2 shows a photograph of the complete reactor system.

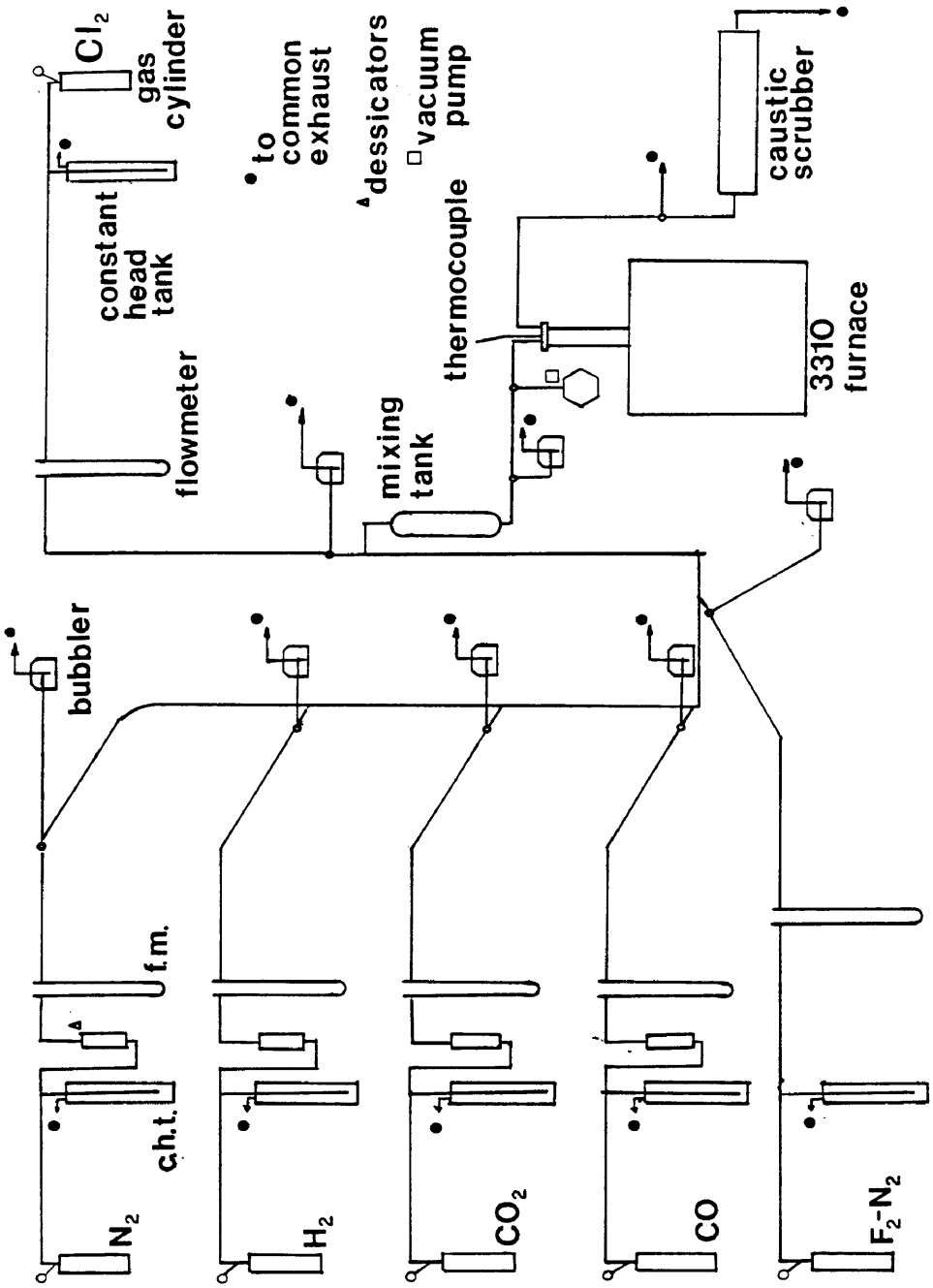

Figure 4.1 - Reactor System Schematic

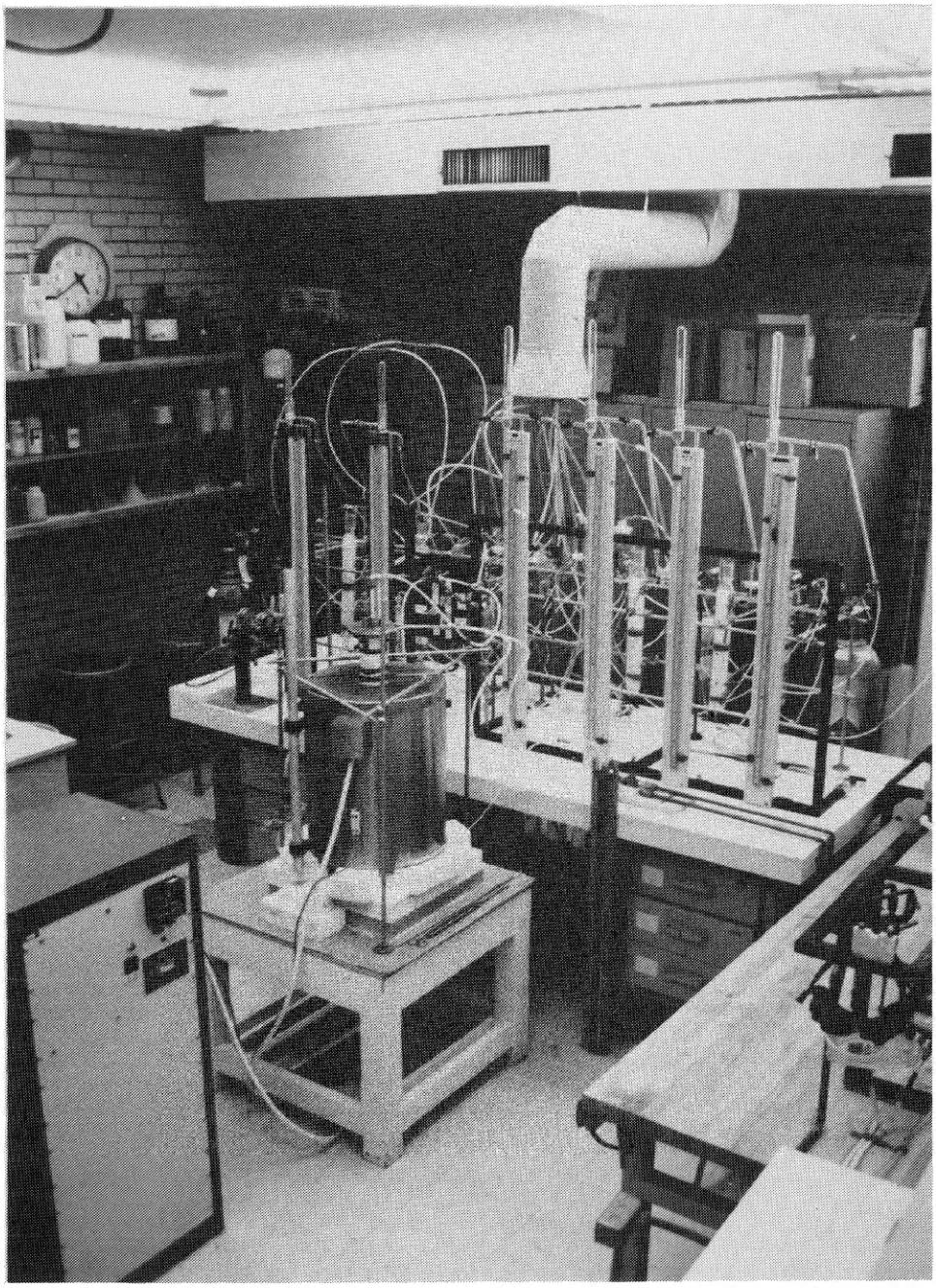

Figure 4.2 - Photograph Of The Reactor System

4.2.1 Gas Train Assembly

High purity gases were supplied from commericial compressed gas cylinders. These gases were CO_2, CO, N_2, H_2, Cl_2, 20% F_2-balance N_2. Individual gas flow rates were controlled by valves downstream from the gas regulators and by constant head tanks containing either mineral oil or carbon tetrachloride. Further control of the total gas flowrate (to and from the reactor assembly) was facilitated through a series of valves housed in a fabricated control panel. The total gas flowrate could be sent to the reactor assembly or directly to exhaust.

Prior to metering, each gas (with the exception of Cl_2 and F_2) was pre-dried by being passed through silica gel and magnesium perchlorate dessicants contained in 5 cm diameter x 40 cm bed length columns. The purified gases were metered using precision capillary flowmeters containing halocarbon oil. All flowmeters were calibrated using the method described by Annamali (7).

The equilibrated gas mixture enters the reactor assembly through a alumina tube, passes over the molten charge and then exits through the exhaust port to the exhaust fan system.

All gas exits were fitted with bubblers to check gas flow at all times during the experiments. Connections used between the gas train assembly and the reactor assembly were made with polyethylene tubing (3/8" O.D.) and stainless steel swagelock fittings.

4.2.2 Reactor Assembly

The reactor assembly was comprised of the following equipment and materials. An Applied Test Systems Model #3310 tube furnace capable of temperatures of up to 1650 ^{o}C was used for all experiments. The furnace was equipped with molybdenum disilicide heating elements (trade name: Super Kanthal 33). Temperature control was provided by an LFE 2010 process microprocessor with a Type B (Pt-6% Rh/Pt-30% Rh) controlling thermocouple mounted within the heated cavity of the furnace.

Figure 4.3 shows the furnace reactor tube schematic. The reactor shell, tubing, and crucibles used (with the exception of the exhast port tube) were made from high

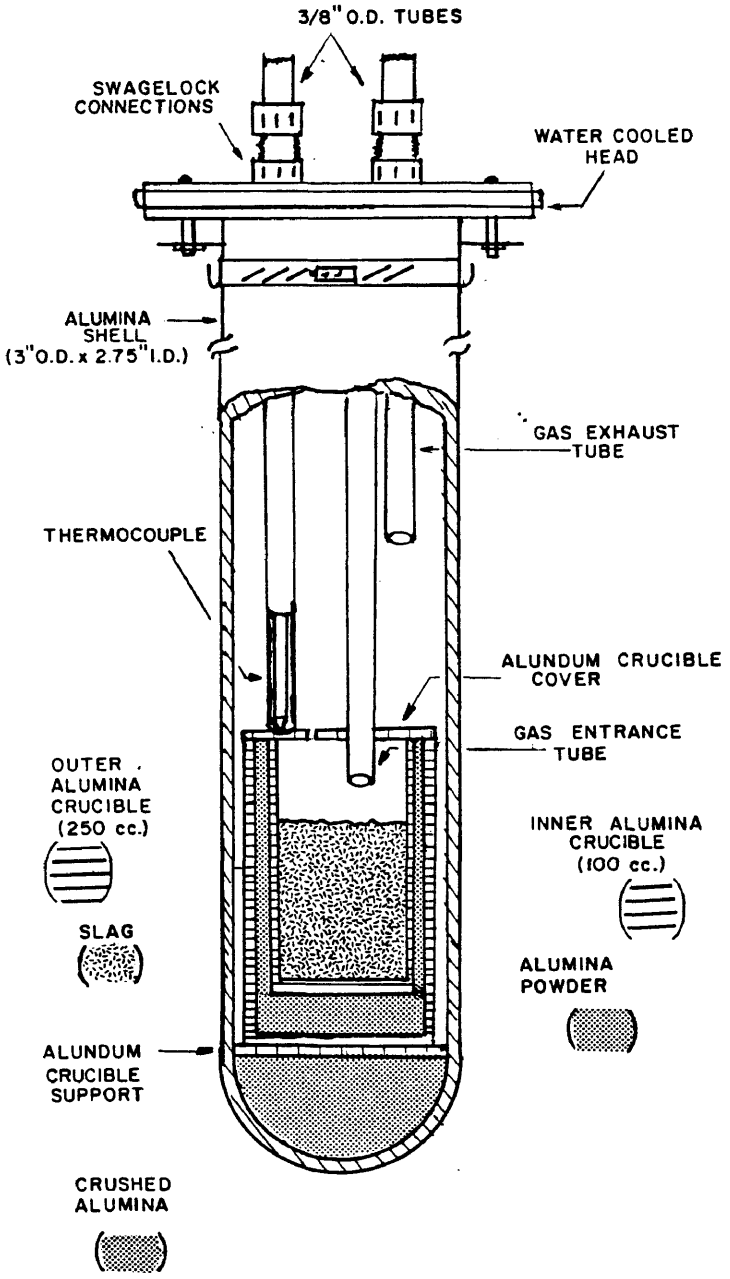

Figure 4.3 - Furnace Reactor Tube Schematic

purity alumina manufactured by either Coors Porcelain or the McDanel Refractory Company. The exhaust port tube was constructed of 6 inch long 316 stainless steel tubing (3/8" O.D.).

The water cooled head (see Figure 4.4) was constructed from 316 stainless steel. All swagelock fittings contained teflon ferrules. The water coolant tube was also constructed of 316 stainless steel. Neoprene rubber was used as the head gasket material.

The measuring thermocouple was a Type S (Pt/Pt-10% Rh). This thermocouple was contained in an alumina sheath (1/4" O.D.) and positioned in the alundum lid. The thermocouple was correlated against a new Type S thermocouple placed inside the inner crucible (slag bath position). After every other run fresh wire was used and a new bead formed. This was done to assure that the thermocouple did not become contaminated. At approximately every 6 experiments a new thermocouple was installed. All thermocouples were prepared from the same batch of thermocouple wire and a test thermocouple was calibrated against the melting point of pure copper and was found to be within $\pm$ 5 ^{o}C of the published melting point.

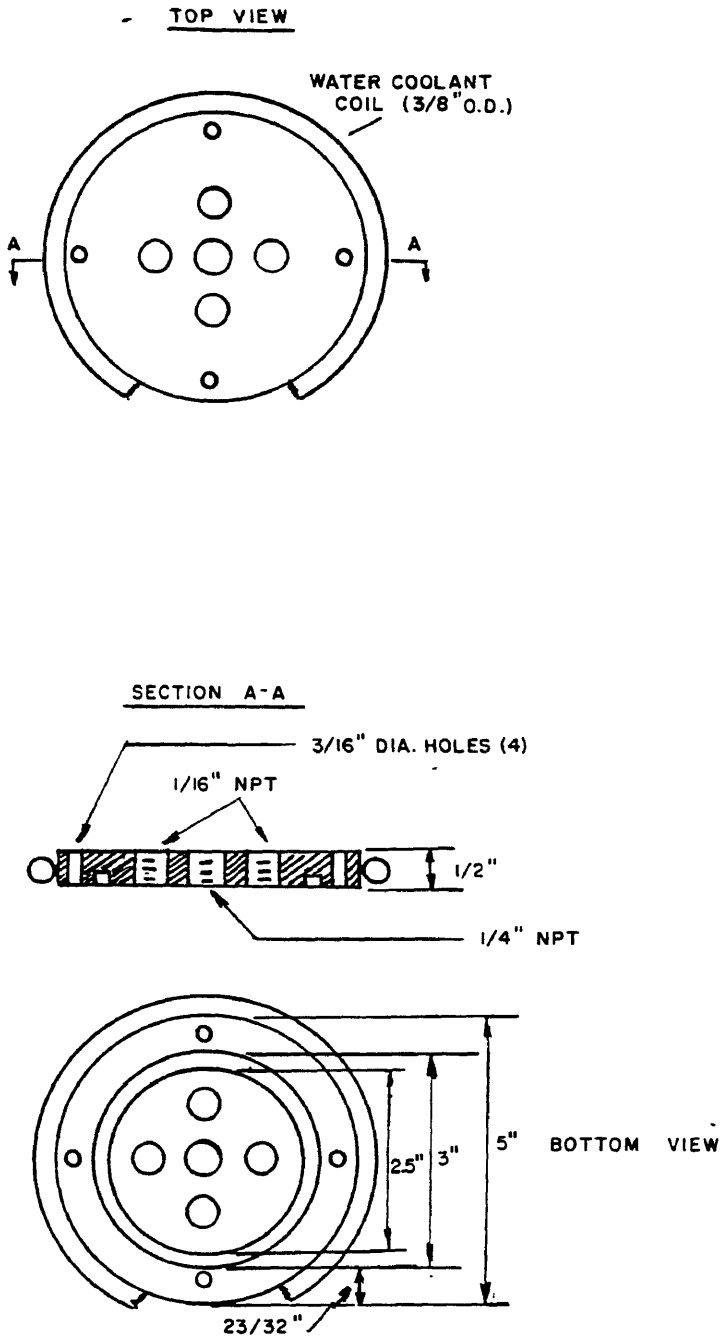

Figure 4.4 - Water Cooled Head

Further indication of consistancy in the temperature measurement was the observed temperature difference between the type B thermocouple used as the control thermocouple and the type S measuring thermocouple.

Figure 4.5 shows the reactor assembly. Figure 4.6 shows the reaction tube header with the associated tubing and crucibles.

4.3 Experimental Procedure

The experimental procedure used in this study is given below:

A throughly mixed charge of master slag, lime, and alumina were placed in a 100 cc alumina crucible (termed the inner crucible). This crucible was then placed into a 250 cc alumina crucible (termed the outer crucible). Alumina powder was then loosely packed between the two crucibles. This arrangement confined slag breakouts to the adjacent outer crucible. The crucible assembly was then positioned inside the alumina reaction tube. The reaction tube was of high purity alumina with dimensions 3" O.D. X 2.75" I.D. X 2' long.

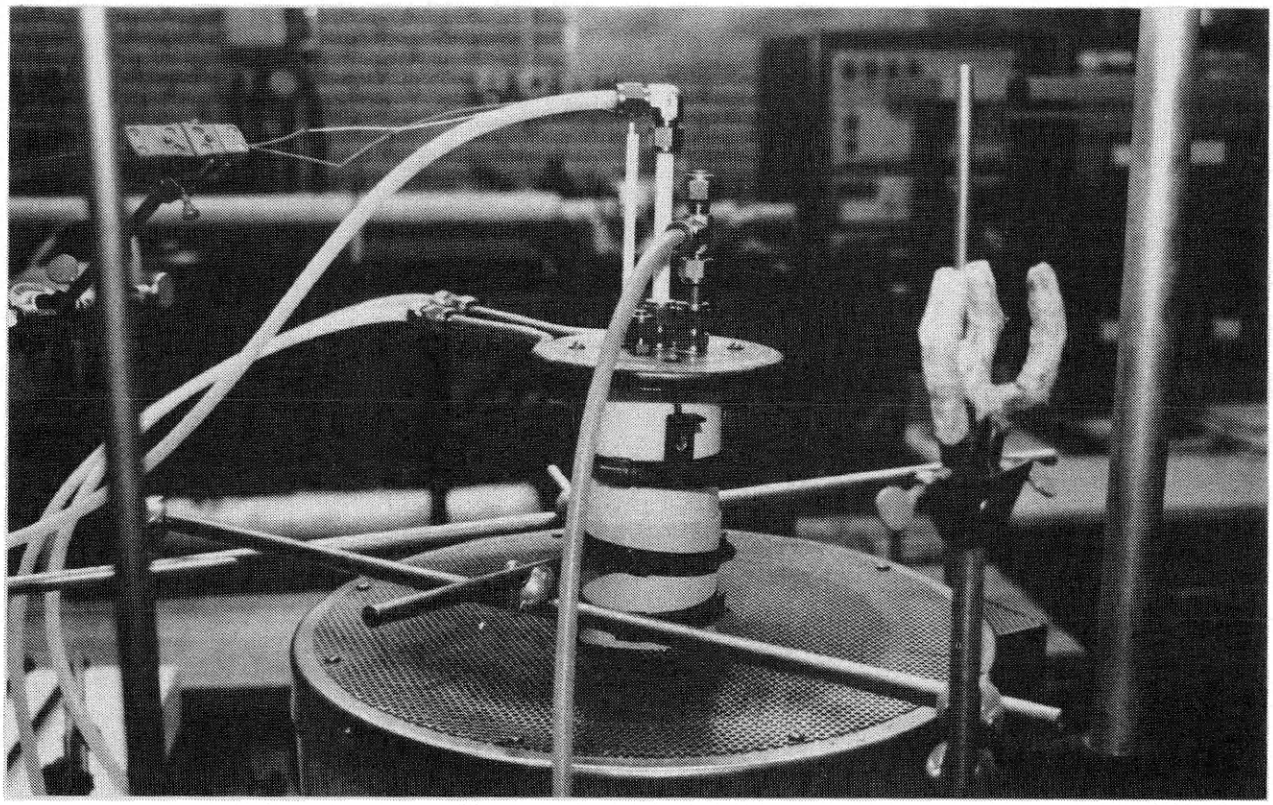

Figure 4.5 - Photograph Of Reactor Assembly

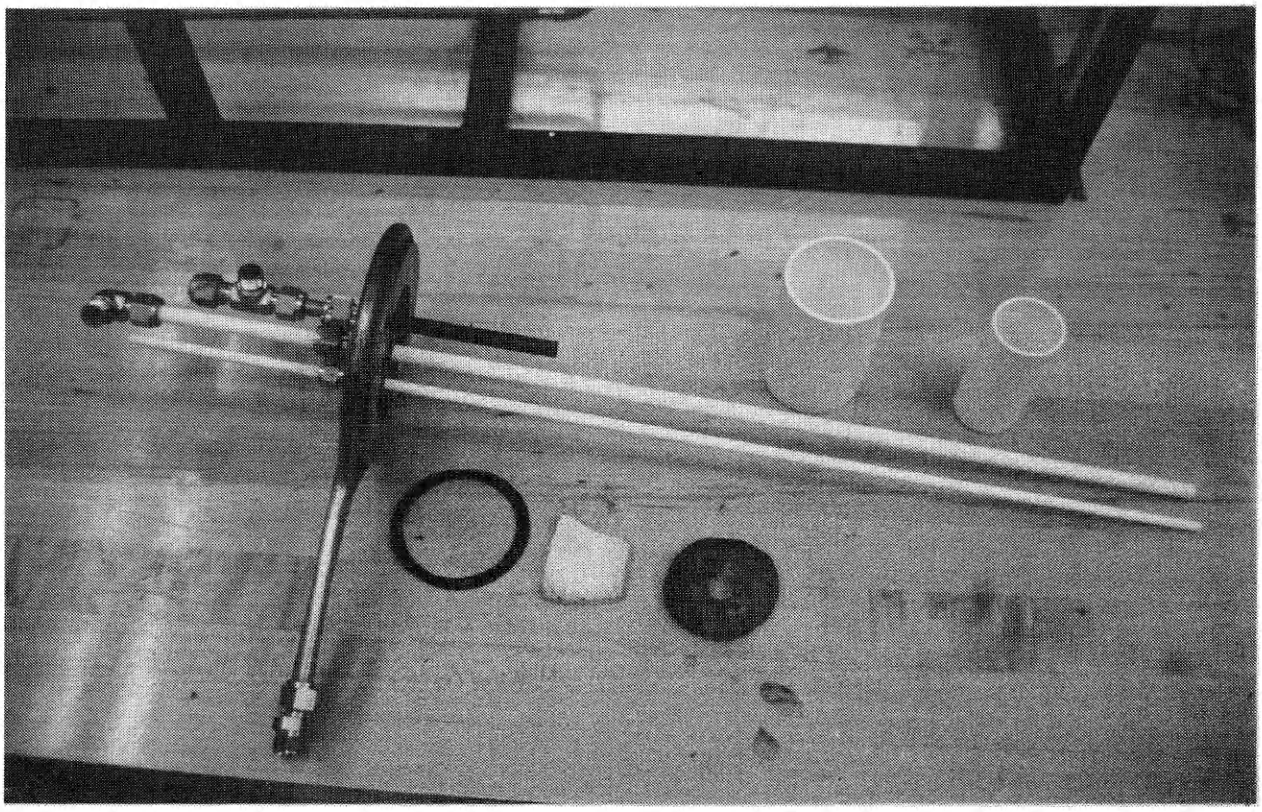

Figure 4.6 - Reaction Tube Header with Tubing and Crucibles

The reaction tube was then placed in the Applied Test Systems tube furnace and sealed with the water-cooled head. All inlet and exhaust tubing was then inserted into the head. Gas-line connections from the gas train assembly to the reactor tube were made. All connectors used were stainless steel swagelocks with teflon ferrules. Tubing used to connect the gas train and the reactor assemblies was polyethylene tubing. The apparatus was now completely assembled and is ready to run.

The air was pumped out of the reaction tube assembly using a Welch Duo-seal pump. A mercury manometer connected to the vacuum system was used to ensure no air-leaks were present in the reactor assembly during evacuation. Following evacuation, nitrogen gas was gradually added to the reactor tube. All remaining gases from the gas train were turned on and were temporarily sent to the exhaust system.

The furnace was manually heated to the specified temperature in 300 ^{o}C intervals. The average heating rate was 5 ^{o}C per minute. When the furnace temperature had reached 600 ^{o}C, the remaining gases, which are pre-mixed, are sent to the reaction tube assembly.

Once the equilibration temperature was reached, the temperature was maintained constant for either a 4 or 6 hour period.

After conclusion of the equilibration period, the furnace was cooled to 900 ^{o}C where all gases except nitrogen are turned off. The furnace was then further cooled to 500 ^{o}C, the power shut off and allowed to cool overnight to room temperature.

After cooling, the reactor assembly was disassembled. The equilibrated slag sample and the inner crucible were broken apart. Separation of the alumina crucible and the slag sample was done by hand. The charge was then crushed, pulverized, and mixed in preparation for assay. Representative samples were sent to Hazen Research Incorporated (HRI) and Horsehead Resource and Development Co. (HRD) for chlorine and fluorine analysis.

A temperature range of 1380 to 1500 ^{o} C was investigated. Alumina additions were adjusted to provide 15 wt. % Al_2O_3 except at the highest temperatures (1480 and 1500 ^{o}C), where 30 wt. % additions were required to achieve slag containment. Lime additions were varied from 0 to 30 grams. All charges consisted of 76.5 grams master

slag mixed with the appropriate amounts of alumina and lime.

The same gas composition and flowrate was used for all experiments with one exception. The equilibration period was typically 4 hours. However, a special run refered to later as enhanced run conditions was undertaken where the run time was increased by 50%. The purpose of this experiment under these enhanced run conditions was to verify that equilibrium saturation was indeed achieved. The run under these conditions was made under the temperature and slag composition as a previous run, moreover a duplicate run was made for the same temperature and slag composition but for the standard time (4 hours) and gas flowrate. Thus three sets of data were generated for temperature, gas and slag composition.

4.4 Slag Characterization

The Flame reactor master slag sample used for this project was generated from an EAF dust sample processed by Horse Head Resource and Development's Flame Reactor. To characterize the slag composition, slag samples were split and assayed by both Hazen Research Incorporated (HRI) and Horsehead Resource and Development (HRD). The slag sample was designated 121186. Figure 4.7 summarizes all slag

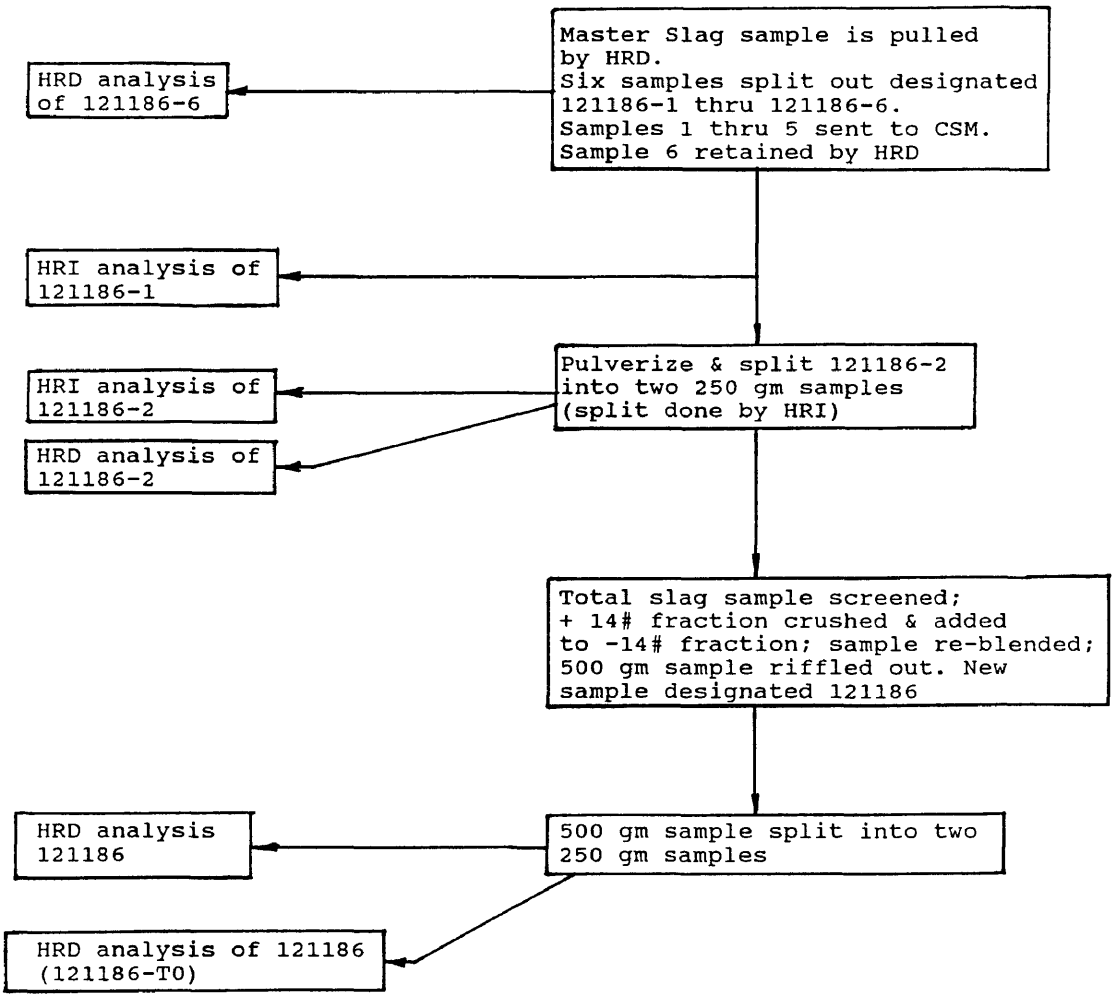

Figure 4.7 - Flowchart Of Master Slag Characterization

samples split out for analysis. After examination of all assay results, final slag characterization was completed using the four sets of data which gave most the consistant assay results.

The final slag composition on a elemental basis is shown in Table 4.1 . From the selected head assay given in Table 4.1, the slag composition on a compound basis was calculated with the results shown in Table 4.2 .

4.5 Gas Equilibration Model

Selection of an equilibrated gas composition for experimental work was based on actual gas composition data determined from a computer simulation of HRD's Flame Reactor. This data was then normalized and used as the target gas composition. This composition is shown in Table 4.3 .

A computer program was developed to calculate from a prepared room temperature gas mixture the equilibrated gas composition at the reactor temperature. This program was used to determine the gas composition of the prepared gas mixture that, when equilibrated at high temperatures would give the same gas composition as shown in Table 4.3 .

TABLE 4.1

Final Characterization of Master Slag Composition

Sample:	121186-2 (1)	(2)	121186 (3)	121186-T0 (4)	Selected Head Assay(*)
Element	HRI	HRD	HRD	HRD	
Zn	2.78	2.78	2.75	2.96	2.77 (1,2,3)
Pb	0.058	0.096	0.073	0.075	0.076 (1,2,3,4)
Cl	0.02	-	<0.05	0.01	0.015 (1,4)
F	0.32	0.29	0.20	0.16	0.24 (1,2,3,4)
Fe	46.40	46.20	47.80	47.50	47.00 (")
Ca	4.78	4.35	4.34	4.51	4.56 (")
S	-	0.18	0.18	0.18	0.18 (2,3,4)
C	-	<0.10	<0.10	<0.10	0.10 (")
Cd	-	<0.001	0.0009	0.0064	0.004 (3,4)
Cr	1.00	0.95	0.88	0.89	0.93 (1,2,3,4)
As	-	-	<0.001	<0.001	0.001 (")
Sb	-	-	-	0.025	0.025
Al	2.57	2.51	2.44	2.44	2.49 (1,2,3,4)
Si	4.11	4.03	3.98	3.99	4.03 (")
Mg	2.25	2.32	2.30	2.31	2.30 (2,3,4)
Mn	5.88	5.57	5.59	5.61	5.59 (")
K	0.044	0.028	0.002	0.089	0.054 (1,3,4)
Na	0.285	0.16	0.30	0.26	0.282 (")
Cu	-	0.089	0.099	0.11	0.099 (2,3,4)

*Selected head assay averaged from column # given.
HRD - Horsehead Resource & Development Company,Inc.
HRI - Hazen Research Inc.

TABLE 4.2

Characterization of Master Slag Composition
Based On Oxide Components

Species	Slag Compound Comp.	Normalized Comp
ZnO	3.449 %	3.564 %
PbO	0.082	0.085
$CaCl_2$	0.023	0.024
CaF_2	0.493	0.509
FeO	60.44	62.449
CaO	5.899	6.095
CaS	0.405	0.418
C	0.100	0.103
CdO	0.005	0.005
Cr_2O_3	0.930	0.961
As_2O_3	0.001	0.001
Sb_2O_3	0.030	0.031
Al_2O_3	4.704	4.860
SiO_2	8.620	8.906
MgO	3.813	3.940
MnO	7.217	7.457
K_2O	0.065	0.067
Na_2O	0.380	0.393
CuO	0.128	0.132
	96.786 %	100.000 %

TABLE 4.3

Selected Flame Reactor Gas Composition

Gas Species	Computer Simulation Results	Normalized Gas Composition
N_2	20.618	21.004
H_2	0.355	0.362
H_2O	6.973	7.104
CO	10.146	10.336
CO_2	54.070	55.082
HCl	3.000	3.056
HF	3.000	3.056
Cl_2	0.000	0.000
F_2	0.000	0.000
	98.162%	100.000%

CO/CO_2 ratio = 0.188

Gases supplied from the commerical cylinders were N_2, Cl_2, F_2-N_2, CO_2, H_2, and CO. These combined gases constituted the unequilibrated gas mixture. The gas species that are assumed to exist in an equilibrated gas mixture are N_2, Cl_2, F_2, CO, H_2, CO_2, HF, HCl, and H_2O. For a gas mixture containing these 8 species for 5 reactive components, there are 3 independant reactions. The reactions chosen are given as follows:

$$H_{2(g)} + CO_{2(g)} = H_2O_{(g)} + CO_{(g)} \quad (4.1)$$

$$(1/2)H_{2(g)} + (1/2)Cl_{2(g)} = HCl_{(g)} \quad (4.2)$$

$$(1/2)H_{2(g)} + (1/2)F_{2(g)} = HF_{(g)} \quad (4.3)$$

An equilibration model was developed to calculate the equilibrated gas composition based on the above independant reactions. The model constituted 5 linear and 3 non-linear simultaneous equations which were resolved using the Newton-Raphson technique. The data required to use the program was temperature, total pressure, and gas flowrates. The output from the program was the equilibrated gas composition.

The above model was found not to converge for some gas mixtures. It was discovered that the very small mole numbers of Cl_2 and F_2 were the culprit. Thus, a second model was developed that assumed that all available F_2 and Cl_2 gas would be directly converted to HF and HCl gases respectively. With this assumption, only 4.1 (the water-shift reaction) need be considered. The equilibrium amounts of H_2 and CO_2 that would react in reaction 4.1 were determined using interval halving where the equilibrium constant for reaction 4.1 was used as the objective function.

Comparison of the equilibrated gas composition results obtained with the second model were identical with the results obtained for the model employing the Newton-Raphson method for those gas compositions where a stable solution was obtained using the first model. Thus, the assumption that all Cl_2 and F_2 gases convert to HCl and HF appeared to be valid.

Once the equilibration gas composition had been determined, the equilibrium partial pressures for O_2, Cl_2, and F_2 were calculated from equations 4.2, 4.3, and the following:

$$CO_{(g)} + (1/2)O_{2(g)} = CO_{2(g)} \quad (4.4)$$

A program listing and sample printouts of the latter computer model are given in the Appendix.

4.6 Data Reduction

From the development of the chlorine (C_{Cl}) and fluorine (C_f) capacity functions presented in Chapter 3, the following equations are restated:

$$C_{Cl} = (\%Cl)^2 (P_{O2})^{1/2} / (P_{Cl2}) \quad (4.4)$$

$$C_f = (\%F)^2 (P_{O2})^{1/2} / (P_{F2}) \quad (4.5)$$

where:

%Cl = chloride assay in the equilibrated slag.
%F = fluoride assay in the equilibrated slag.
P_{O2} = equilibrium partial pressure of O_2 gas in the gas mixture.

P_{Cl2} = Equilibrium partial pressure of Cl_2 gas in the gas mixture.

P_{F2} = Equilibrium partial pressure of F_2 gas in the gas mixture.

The chlorine and fluorine assays were directly obtained from the analysis of the equilibrated slag samples. The equilibrium partial pressures of O_2, Cl_2, and F_2 were determined from the gas equilibration model discussed in the previous section.

V. RESULTS AND DISCUSSION

This chapter presents the results of the experimental work completed in the investigation of halogen solubility in an EAF slag produced by the Horsehead Flame Reactor.

5.1 Summary Of Experimental Runs Completed In This Investigation

A total of 25 experimental runs were completed in this investigation. A summary of the run conditions is given in Table 5.1 . For this study, all slag compositions were characterized in terms of a basicity ratio (R). The basicity ratio was defined as the mole percent ratio (basic oxides/acidic oxides) and is given below:

$$R = \frac{(\%MgO + \%CaO)}{(\%SiO_2 + \%Al_2O_3)} \qquad (5.1)$$

Two separate basicity values are given in Table 5.1 . Basicity values determined from mixed amounts of untreated slag with CaO and Al_2O_3 were termed the "calculated" basicity. Basicity values determined directly from the equilibrated slag composition were termed the "measured" basicity. A detailed discussion on the analysis of the

Table 5.1

Run Conditions

Run[1] (#)[4]	Temp. (°C)	Equil. Time (Hrs.)	Master Slag (Gms)	Additions Al_2O_3 (Gms)	Additions CaO (Gms)	Calc. Basicity (R)	Meas. Basicity (R)
121186-T 6	1380[2]	6	76.5	0	0	1.054	0.685
121186-T 7	1380[2]	6	76.5	0	5	1.644	0.756
121186-T10	1380[2]	6	76.5	0	10	2.244	0.697
121186-T12	1380	6	76.5	9.1	0	0.661	0.418
121186-T13	1380	6	76.5	9.9	5	1.001	0.437
121186-T15	1400	6	76.5	9.1	0	0.661	0.350
121186-T16	1400	4	76.5	9.9	5	1.001	0.626
121186-T17	1400	4	76.5	10.8	10	1.315	0.862
121186-T18	1400	4	76.5	11.7	15	1.608	0.756
121186-T19	1400	4	76.5	12.6	20	1.882	0.917
121186-T21	1420	4	76.5	12.6	20	1.882	0.798
121186-T22	1420	4	76.5	10.8	10	1.315	0.671
121186-T23	1420	4	76.5	9.1	0	0.661	0.360

(continued)

Table 5.1 (continued)

Run[1] (#)[4]	Temp. (°C)	Equil. Time (Hrs.)	Master Slag (Gms)	Additions Al_2O_3 (Gms)	Additions CaO (Gms)	Calc. Basicity (R)	Meas. Basicity (R)
121186-T24	1440	4	76.5	12.6	20	1.882	0.865
121186-T25	1440	4	76.5	10.8	10	1.315	0.698
121186-T26	1440	4	76.5	9.1	0	0.661	0.341
121186-T27	1460	4	76.5	10.8	10	1.315	0.642
121186-T28	1460	4	76.5	12.6	20	1.882	0.809
121186-T29	1480	4	76.5	10.8	10	1.315	0.685
121186-T30	1480	4	76.5	36.0	20	1.023	0.629
121186-T31	1500	4	76.5	10.8	10	1.315	0.783
121186-T32	1500	4	76.5	36.0	20	1.023	0.741
121186-T33	1500	4	76.5	40.3	30	1.271	0.739
121186-T34	1420	4	76.5	12.6	20	1.882	0.756
121186-T35[3]	1420	6	76.5	12.6	20	1.882	0.749

[1] Standard Gas Flow Rate except where noted (594 cc/min).
[2] Estimated Temperature (prior to thermocouple correlation).
[3] Enhanced Gas Flowrate (891 cc/min) [= standard gas flowrate • 1.5].
[4] Total Pressure was relative constant at 0.82 atm.

equilibrated slag sample and the shift in R is given later in this section.

A summary of the solubility data obtained and the calculated halogen capacities is given in Tables 5.2 and 5.3 respectively. Two analyses of the slag were done by HRD. These analyses are designated HRD(1) and HRD(2) or termed HRD first and second series respectively. An improved new analytical technique was employed by HRD for the second series of analyses. The $\log(P_{O2})$, $\log(P_{Cl2})$ and $\log(P_{F2})$ values required to calculate the halogen capacities were obtained from the gas equilibration model.

Table 5.4 summarizes the equilibrium gas compositions. The calculated equilibrium partial pressures for O_2, Cl_2, and F_2 are summarized in Table 5.5 . These values were generated from the gas equilibration model described in section 4.5 and were used in the calculation of the halogen capacities given in Table 5.3 .

Samples of equilibrated slag (HRI) at the completion of the project were analyzed for all of the major components. Table 5.6 summarizes the final slag composition for each run. Included in Table 5.6 are the optical basicity values for the analyzed slag samples. Refer to Chapter 2 for the calculation of optical basicity.

Table 5.2

Solubiliy Data

Run (#)	Temp. (°C)	% Cl			% F		
		HRI	HRD (1)	HRD (2)	HRI	HRD (1)	HRD (2)
121186-T 6	1380	0.08	0.11	0.16	0.53	0.42	0.47
121186-T 7	1380	0.03	0.13	0.15	0.52	0.35	0.51
121186-T10	1380	0.15	0.24	0.25	0.98	0.79	0.87
121186-T12	1380	0.24	0.18	0.18	0.48	0.47	0.47
121186-T13	1380	0.21	0.22	0.17	0.56	0.58	0.65
121186-T15	1400	0.31	0.28	0.23	0.50	0.64	0.50
121186-T16	1400	0.22	0.20	0.22	0.38	0.53	0.59
121186-T17	1400	0.42	0.32	0.32	0.84	0.72	0.72
121186-T18	1400	0.26	0.28	0.28	0.58	0.56	0.55
121186-T19	1400	0.28	0.30	0.29	0.75	0.67	0.72
121186-T21	1420	0.25	0.40	0.33	0.87	0.75	0.79
121186-T22	1420	0.18	0.34	0.26	0.85	0.75	0.74
121186-T23	1420	0.16	0.21	0.16	0.45	0.25	0.39

(continued)

Table 5.2 (continued)

Run (#)	Temp. (°C)	% Cl			% F		
		HRI	HRD (1)	HRD (2)	HRI	HRD (1)	HRD (2)
121186-T24	1440	0.20	0.35	0.27	0.71	0.63	0.68
121186-T25	1440	0.18	0.37	0.26	0.75	0.67	0.72
121186-T26	1440	0.06	0.21	0.09	0.32	0.21	0.25
121186-T27	1460	0.21	0.35	0.30	0.75	0.69	0.72
121186-T28	1460	0.22	0.36	0.32	0.72	0.92	0.78
121186-T29	1480	0.18	0.33	0.25	0.63	0.66	0.64
121186-T30	1480	0.10	0.24	0.21	0.53	0.82	0.57
121186-T31	1500	0.15	0.35	0.28	0.67	0.86	0.63
121186-T32	1500	0.09	0.19	0.21	0.53	0.79	0.54
121186-T33	1500	0.11	0.21	0.20	0.54	0.86	0.60
121186-T34	1420	0.36	--	0.22	0.57	--	0.65
121186-T35	1420	0.22	--	0.20	0.55	--	0.61

Table 5.3

Calculated Halogen Capacities

Run (#)	Temp. (°C)	Log (C_{Cl})			Log (C_F)		
		HRI	HRD (1)	HRD (2)	HRI	HRD (1)	HRD (2)
121186-T 6	1380	-2.52	-2.24	-1.91	9.97	9.79	9.88
121186-T 7	1380	-3.40	-2.09	-1.97	9.97	9.62	9.95
121186-T10	1380	-1.97	-1.56	-1.53	10.52	10.33	10.42
121186-T12	1380	-1.56	-1.81	-1.81	9.90	9.88	9.71
121186-T13	1380	-1.68	-1.64	-1.86	10.03	10.06	10.16
121186-T15	1400	-1.32	-1.40	-1.58	9.83	10.04	9.85
121186-T16	1400	-1.61	-1.70	-1.61	9.59	9.88	9.99
121186-T17	1400	-1.05	-1.29	-1.28	10.28	10.14	10.16
121186-T18	1400	-1.47	-1.40	-1.40	9.95	9.92	9.93
121186-T19	1400	-1.35	-1.34	-1.37	10.18	10.08	10.16
121186-T21	1420	-1.48	-1.07	-1.24	10.20	10.07	10.11
121186-T22	1420	-1.76	-1.21	-1.45	10.18	10.07	10.06
121186-T23	1420	-1.86	-1.63	-1.87	9.62	10.11	9.50
121186-T24	1440	-1.65	-1.17	-1.39	9.92	9.81	9.88
121186-T25	1440	-1.74	-1.12	-1.42	9.96	9.87	9.93
121186-T26	1440	-2.70	-1.61	-2.34	9.23	9.86	8.51

(continued)

Table 5.3 (continued)

Run (#)	Temp. (°C)	Log (C_{Cl})			Log (C_F)		
		HRI	HRD (1)	HRD (2)	HRI	HRD (1)	HRD (2)
121186-T27	1460	-1.59	-1.14	-1.28	9.86	9.84	9.83
121186-T28	1460	-2.70	-1.12	-1.22	9.82	10.04	9.90
121186-T29	1480	-1.70	-1.17	-1.56	9.61	9.64	9.62
121186-T30	1480	-2.21	-1.45	-1.54	9.46	9.84	9.52
121186-T31	1500	-1.84	-1.10	-1.30	9.57	9.79	9.51
121186-T32	1500	-2.28	-1.63	-1.54	9.36	9.71	9.38
121186-T33	1500	-2.11	-1.55	-1.59	9.40	9.79	9.47
121186-T34	1420	-1.19	--	-1.59	9.93	--	10.04
121186-T35	1420	-1.61	--	-1.67	9.90	--	9.99

Table 5.4

Equilibrium Compositions

Run (#)	Temp. (°C)	N_2 (Vol. %)	CO (Vol. %)	H_2O (Vol. %)	H_2 (Vol. %)	CO_2 (Vol. %)	HCl (Vol. %)	HF (Vol. %)
121186-T 6	1380	21.04	10.19	7.16	0.42	55.13	3.03	3.03
121186-T 7	1380	21.04	10.19	7.16	0.42	55.13	3.03	3.03
121186-T10	1380	21.04	10.19	7.16	0.42	55.13	3.03	3.03
121186-T12	1380	21.04	10.19	7.16	0.42	55.13	3.03	3.03
121186-T13	1380	21.04	10.19	7.16	0.42	55.13	3.03	3.03
121186-T15	1400	21.04	10.20	7.17	0.41	55.12	3.03	3.03
121186-T16	1400	21.04	10.20	7.17	0.41	55.12	3.03	3.03
121186-T17	1400	21.04	10.20	7.17	0.41	55.12	3.03	3.03
121186-T18	1400	21.04	10.20	7.17	0.41	55.12	3.03	3.03
121186-T19	1400	21.04	10.20	7.17	0.41	55.12	3.03	3.03
121186-T21	1420	21.04	10.21	7.18	0.40	55.11	3.03	3.03
121186-T22	1420	21.04	10.21	7.18	0.40	55.11	3.03	3.03
121186-T23	1420	21.04	10.21	7.18	0.40	55.11	3.03	3.03
121186-T24	1440	21.04	10.22	7.19	0.39	55.10	3.03	3.03
121186-T25	1440	21.04	10.22	7.19	0.39	55.10	3.03	3.03
121186-T26	1440	21.04	10.22	7.19	0.39	55.10	3.03	3.03

(continued)

Table 5.4 (continued)

Run (#)	Temp. (°C)	N_2 (Vol. %)	CO (Vol. %)	H_2O (Vol. %)	H_2 (Vol. %)	CO_2 (Vol. %)	HCl (Vol. %)	HF (Vol. %)
121186-T27	1460	21.04	10.22	7.19	0.38	55.10	3.03	3.03
121186-T28	1460	21.04	10.22	7.19	0.38	55.10	3.03	3.03
121186-T29	1480	21.04	10.23	7.20	0.37	55.09	3.03	3.03
121186-T30	1480	21.04	10.23	7.20	0.37	55.09	3.03	3.03
121186-T31	1500	21.04	10.24	7.21	0.37	55.08	3.03	3.03
121186-T32	1500	21.04	10.24	7.21	0.37	55.08	3.03	3.03
121186-T33	1500	21.04	10.24	7.21	0.37	55.08	3.03	3.03
121186-T34	1420	21.04	10.21	7.18	0.40	55.11	3.03	3.03
121186-T35	1420	21.04	10.21	7.18	0.40	55.11	3.03	3.03

Table 5.5

Equilibrium Gas Partial Pressures

Run (#)	Temp. (°C)	Log P_{O_2} (atm)	Log P_{Cl_2} (atm)	Log P_{F_2} (atm)
121186-T 6	1380	-7.36	-7.36	-18.22
121186-T 7	1380	-7.36	-7.36	-18.22
121186-T10	1380	-7.36	-7.36	-18.22
121186-T12	1380	-7.36	-7.36	-18.22
121186-T13	1380	-7.36	-7.36	-18.22
121186-T15	1400	-7.15	-7.28	-18.00
121186-T16	1400	-7.15	-7.28	-18.00
121186-T17	1400	-7.15	-7.28	-18.00
121186-T18	1400	-7.15	-7.28	-18.00
121186-T19	1400	-7.15	-7.28	-18.00
121186-T21	1420	-6.95	-7.20	-17.80
121186-T22	1420	-6.95	-7.20	-17.80
121186-T23	1420	-6.95	-7.20	-17.80
121186-T24	1440	-6.74	-7.03	-17.50
121186-T25	1440	-6.74	-7.03	-17.50
121186-T26	1440	-6.74	-7.03	-17.50

(continued)

Table 5.5 (continued)

Run (#)	Temp. (°C)	Log P_{O_2} (atm)	Log P_{Cl_2} (atm)	Log P_{F_2} (atm)
121186-T27	1460	-6.55	-7.04	-17.39
121186-T28	1460	-6.55	-7.04	-17.39
121186-T29	1480	-6.36	-6.97	-17.20
121186-T30	1480	-6.36	-6.97	-17.20
121186-T31	1500	-6.17	-6.90	-17.00
121186-T32	1500	-6.17	-6.90	-17.00
121186-T33	1500	-6.17	-6.90	-17.00
121186-T34	1420	-6.95	-7.20	-17.80
121186-T35	1420	-6.95	-7.20	-17.80

Table 5.6

Final Slag Composition

Run (#)	Temp. (°C)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	ZnO (%)	FeO (%)	MnO (%)	Na_2O (%)	CuO (%)	K_2O (%)	$CaCl_2$ (%)	CaF_2 (%)	CaO (%)	PbO (%)	Cr_2O_3 (%)	Total (%)	Measured Basicity (R)	Optical Basicity (Λ)
121186-T 6	1380	3.77	12.0	7.81	2.05	53.5	6.04	0.393	0.132	0.067	0.130	1.024	4.265	0.085	0.961	92.227	0.685	0.844
121186-T 7	1380	3.20	14.4	7.06	2.17	49.4	5.52	0.369	0.124	0.063	0.049	1.005	7.049	0.080	0.902	91.382	0.756	0.831
121186-T10	1380	3.03	19.4	6.36	1.53	45.8	4.94	0.348	0.117	0.059	0.245	1.894	7.365	0.075	0.850	91.939	0.697	0.815
121186-T12	1380	2.97	21.7	6.84	2.15	46.3	4.99	0.351	0.118	0.060	0.391	0.928	3.341	0.076	0.859	91.074	0.418	0.800
121186-T13	1380	2.44	27.8	5.18	1.69	35.6	3.83	0.329	0.110	0.056	0.342	1.102	5.391	0.071	0.804	84.745	0.437	0.768
121186-T15	1400	3.00	26.3	6.09	2.17	43.8	4.89	0.351	0.118	0.060	0.505	0.966	2.878	0.076	0.859	92.603	0.350	0.782
121186-T16	1400	2.76	22.6	6.39	2.16	41.4	4.67	0.329	0.110	0.056	0.359	0.735	7.665	0.071	0.804	90.109	0.626	0.796
121186-T17	1400	2.78	21.2	6.31	2.00	40.1	4.33	0.309	0.104	0.053	0.685	1.624	11.265	0.067	0.756	91.783	0.862	0.806
121186-T18	1400	2.31	28.9	5.56	1.73	35.4	3.86	0.291	0.098	0.050	0.424	1.121	12.738	0.063	0.712	93.267	0.756	0.779
121186-T19	1400	2.21	27.2	5.29	1.52	34.2	3.63	0.276	0.093	0.047	0.457	1.450	15.173	0.060	0.674	92.280	0.917	0.787
121186-T21	1420	2.09	31.8	4.52	1.45	33.0	3.53	0.276	0.093	0.047	0.408	1.682	14.419	0.060	0.674	94.049	0.798	0.775
121186-T22	1420	2.70	27.1	5.04	1.80	38.1	4.24	0.309	0.104	0.053	0.293	1.643	9.403	0.067	0.756	91.608	0.671	0.786
121186-T23	1420	3.16	27.2	5.96	2.29	44.6	4.88	0.351	0.118	0.060	0.261	0.870	3.000	0.076	0.859	93.685	0.360	0.782
121186-T24	1440	2.25	29.3	4.93	1.58	34.2	3.76	0.276	0.093	0.047	0.326	1.372	14.794	0.060	0.674	93.662	0.865	0.783
121186-T25	1440	2.46	26.4	5.41	1.84	36.7	4.05	0.309	0.104	0.053	0.293	0.563	10.228	0.067	0.756	89.223	0.698	0.785
121186-T26	1440	3.35	31.2	4.63	2.38	44.0	4.72	0.351	0.118	0.060	0.098	0.619	2.665	0.076	0.859	95.126	0.341	0.776

(continued)

Table 5.6 (continued)

Run (#)	Temp. (°C)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	ZnO (%)	FeO (%)	MnO (%)	Na_2O (%)	CuO (%)	K_2O (%)	$CaCl_2$ (%)	CaF_2 (%)	CaO (%)	PbO (%)	Cr_2O_3 (%)	Total (%)	Measured Basicity (R)	Optical Basicity (A)
121186-T27	1460	2.61	29.4	5.39	1.77	38.4	4.30	0.309	0.104	0.053	0.044	1.450	9.972	0.067	0.756	94.625	0.642	0.780
121186-T28	1460	1.95	28.5	4.29	1.29	27.2	3.28	0.276	0.093	0.047	0.046	1.392	13.214	0.060	0.674	82.312	0.809	0.770
121186-T29	1480	2.28	28.2	5.01	1.38	35.6	3.91	0.309	0.104	0.053	0.038	1.218	10.652	0.067	0.756	89.577	0.685	0.780
121186-T30	1480	1.84	36.7	3.86	1.42	25.0	3.02	0.226	0.076	0.039	0.021	1.024	12.408	0.049	0.555	86.239	0.629	0.744
121186-T31	1500	2.31	28.4	5.20	1.60	37.5	4.13	0.309	0.104	0.053	0.032	1.295	10.596	0.067	0.756	92.352	0.675	0.783
121186-T32	1500	1.95	39.7	4.36	1.65	26.1	3.10	0.227	0.076	0.039	0.019	1.024	13.508	0.049	0.555	92.357	0.626	0.741
121186-T33	1500	1.69	40.7	3.72	1.17	22.0	2.69	0.205	0.069	0.035	0.023	1.044	16.491	0.044	0.501	90.382	0.729	0.739
121186-T34	1420	1.89	33.5	4.43	1.54	27.3	3.23	0.279	0.094	0.048	0.498	1.171	13.010	0.060	0.683	87.733	0.693	0.756
121186-T35	1420	1.92	35.9	4.41	1.25	27.1	3.13	0.279	0.094	0.048	0.305	1.130	12.734	0.060	0.683	89.013	0.646	0.749

In comparing basicity values, it is obvious that there has been a significant shift in slag composition from the start to the end of an experiment. This is due to the extensive corrosion of the crucibles by the slag samples. Unfortunately, this effect has not only shifted the slag basicities to lower values but have decreased the range over which the basicities have been varied. These changes in basicity can be summarized as follows:

	High	Low	Difference
Old:	2.244	0.661	1.583
New:	0.917	0.341	0.576

5.2 Analysis Of The Solubility Data Using Chlorine and Fluorine Capacity Functions

The evaluation of the data tabulated in section 5.1 was achieved using the halogen capacity functions defined in Chapter 3. For each slag equilibration run, three capacity values 1 from HRI analytical data and 2 from HRD analytical data for both chlorine and fluorine were calculated (see Table 5.3). To determine which capacity values were to be used for further analysis, a series of figures were constructed which plotted the log capacity values (HRI) against both series of log capacity values (HRD). Each plot is accompanied by a 45^{o} line which represents the ideal relationship if all the given log capacity data from HRI and HRD are identical. This line serves as a measure of how far the actual data deviate from ideality. From these plots all data that deviated greatly were omitted from further analysis. The remaining points were averaged and plotted against reciprocal temperature for constant measured basicity values. Regression analyses were also performed for both reciprocal temperature plots.

Figures 5.1 and 5.2 show the log capacity plots using the different analytical data. In Figure 5.1 considerable scatter is observed in the plotted capacity values where the first series of HRD assay data are used. However, it is seen in Figure 5.2 that a majority of the capacity data give an excellant correlation with respect to the ideal line. Clearly, the second series HRD assay data, used in Figure 5.2, are more consistant with the independant HRI assay results. The open circles shown in Figure 5.2 represent the data points discarded on the basis of an excessive deviation from the ideal correlation line. The remaining HRI and HRD (second series) data were then averaged and are given in Table 5.7 .

The selected $Log(C_f)$ values in Table 5.7 are shown as a function of reciprocal temperature in Figure 5.3 . Table 5.8 summarizes all linear regression analysis results. The heat of solution can be calculated for the following reaction:

$$F_{2(g)} + O^{=}_{(slag)} = 2F^{-}_{(slag)} + (1/2)O_{2(g)} \qquad (5.2)$$

using the derivation given in Chapter 3.

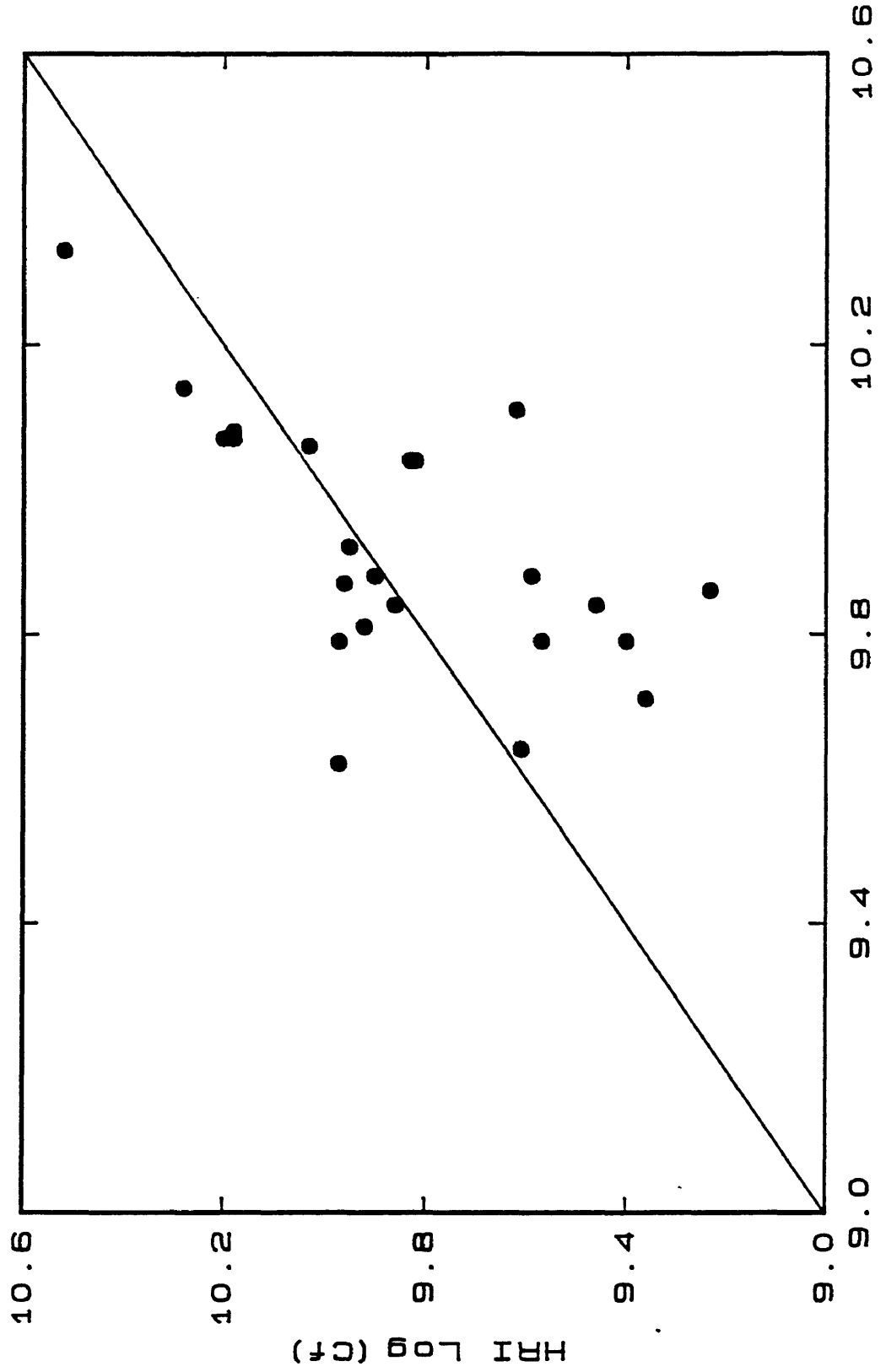

Figure 5.1 - Log Halogen Capacities for F_2.
HRI (C_f) / HRD (1st Series) (C_f)
Plot.

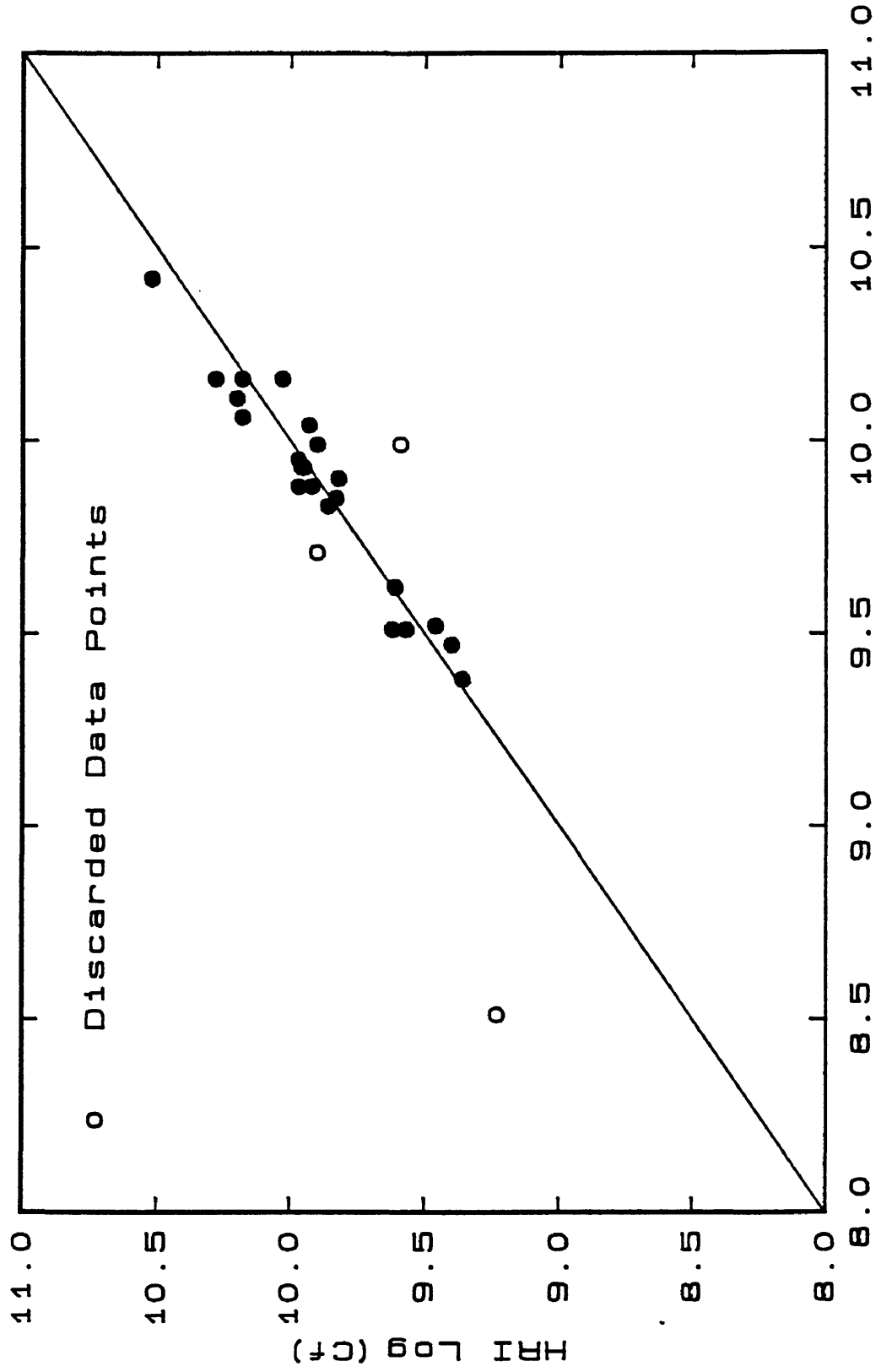

Figure 5.2 - Log Halogen Capacities for F_2.
HRI (C_f) / HRD (2nd Series) (C_f)
Plot.

TABLE 5.7

Averaged Log(C_f) Values From Figure 5.3

Run #	Log(C_f)	$10^4/T$ (K^{-1})
T6	9.93	6.05
T7	9.96	6.05
T10	10.47	6.05
T13	10.10	6.05
T15	9.84	5.98
T17	10.22	5.98
T18	9.44	5.98
T19	10.17	5.98
T21	10.16	5.91
T22	10.08	5.91
T23	9.56	5.91
T24	9.90	5.84
T25	9.95	5.84
T27	9.85	5.77
T28	9.86	5.77
T29	9.62	5.70
T30	9.49	5.70
T31	9.54	5.64
T32	9.37	5.64
T33	9.44	5.64
T34	9.99	5.91
T35	9.95	5.91

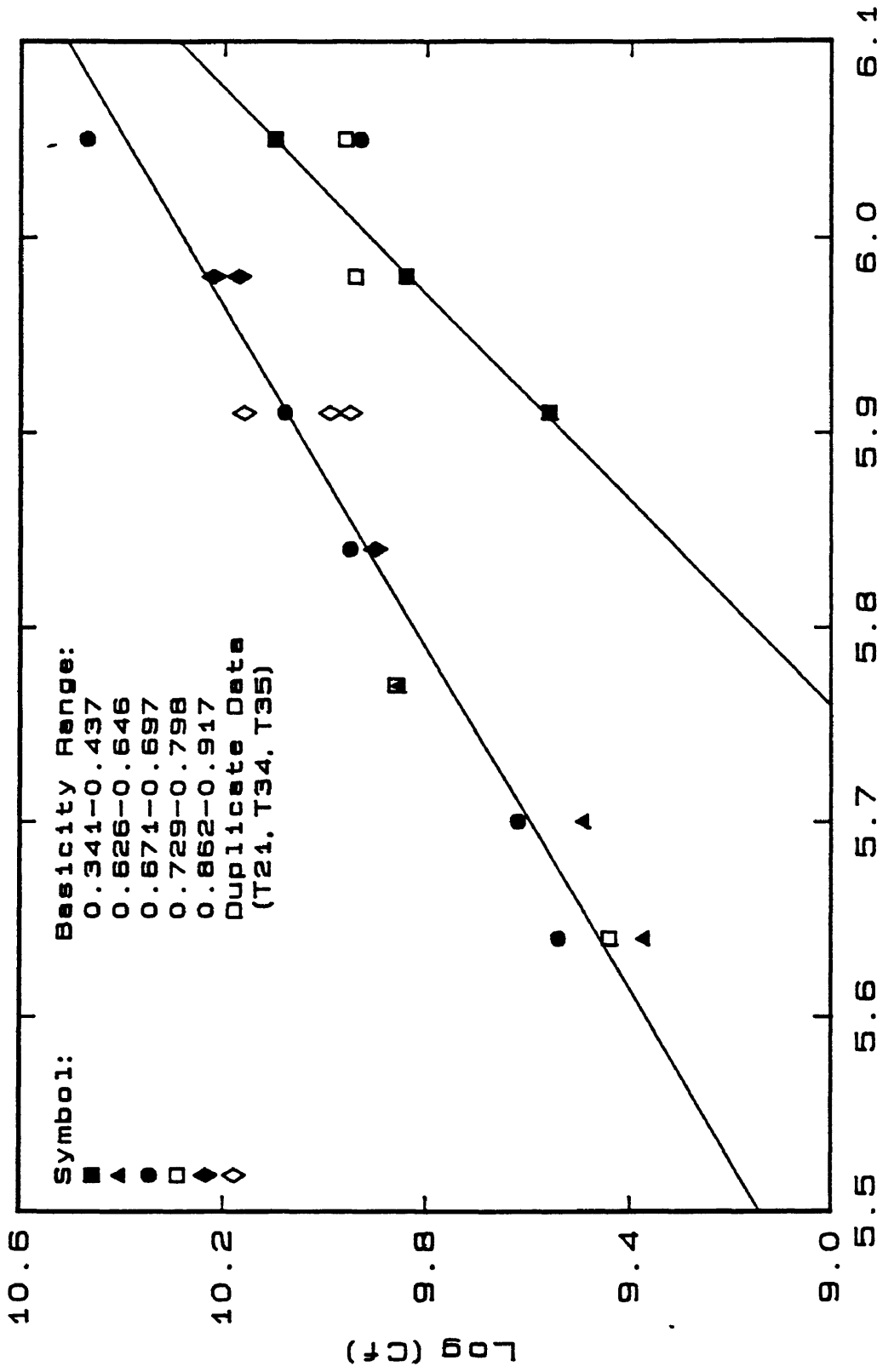

Figure 5.3 - Log(C_f) Versus Reciprocal Temperature

TABLE 5.8

Linear Regression Equations for Figures 5.3 and 5.6

Equation	r^2	ΔH°(Kcal)	Figure	Basicity Range
$\log(C_f)=(22785/T)-3.39$	0.94	-104	5.3	0.626-0.917
$\log(C_f)=(38654/T)-13.28$	1.0	-177	5.3	0.341-0.437
$\log(C_{Cl})=(5166/T)-4.52$	0.11	-23.6	5.6	0.626-0.917
$\log(C_{Cl})=(10003/T)-7.78$	0.80	-45.8	5.6	0.341-0.437

As stated earlier, since C_f is a function of the equilibrium constant, the activity of oxygen (A_o=), and the activity coefficient of fluorine (f_f), a linear relationship should be observed for a plot of log(C_f) against reciprocal temperature for a slag with constant basicity and the heat of reaction can be determined from the slope. Clearly, this trend is shown in Figure 5.3 . It is observed that for the lowest basicity range (solid squares) and for the balance of all other basicity ranges, two regressed lines were obtained with their corresponding heats of solution calculated. The fact that a straight line can be drawn through the combined highest basicity ranges is not suprising since such a narrow range (0.626-0.917) was involved. It should be noted that the ΔH^o values shown in Figure 5.3 for the 0.626-0.917 basicity range is based on the upper straight line. This line was obtained by least squares regression but does exclude the three lower data points that do correspond to the higher basicity range.

Figures 5.4 and 5.5 show the capacity plots based on the different analytical data for chlorine. In Figure 5.4 considerable scatter is observed in plotting log capacity

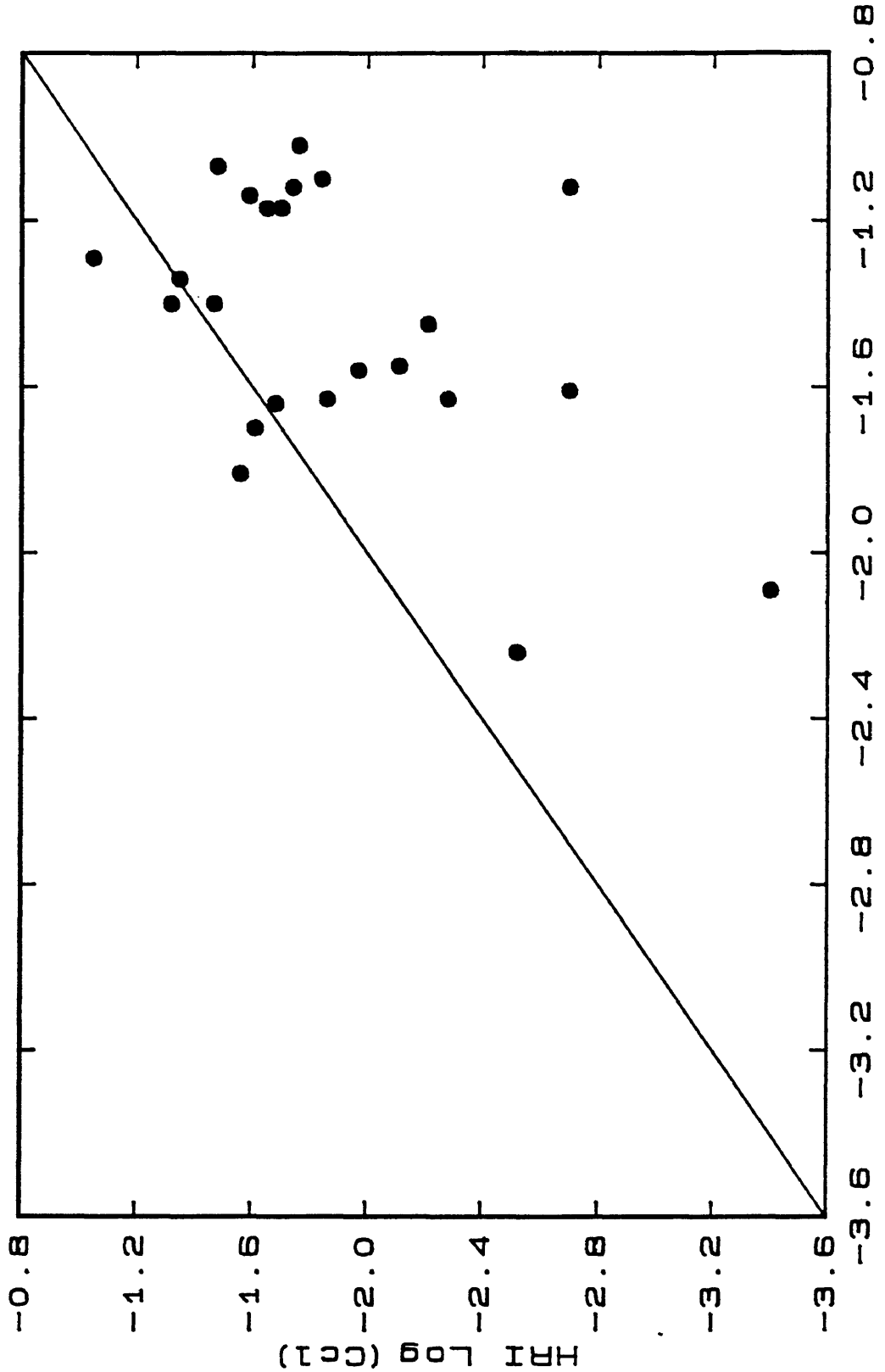

Figure 5.4 - Log Halogen Capacities for Cl_2.
HRI (C_{Cl}) / HRD (1st Series) (C_{Cl})
Plot.

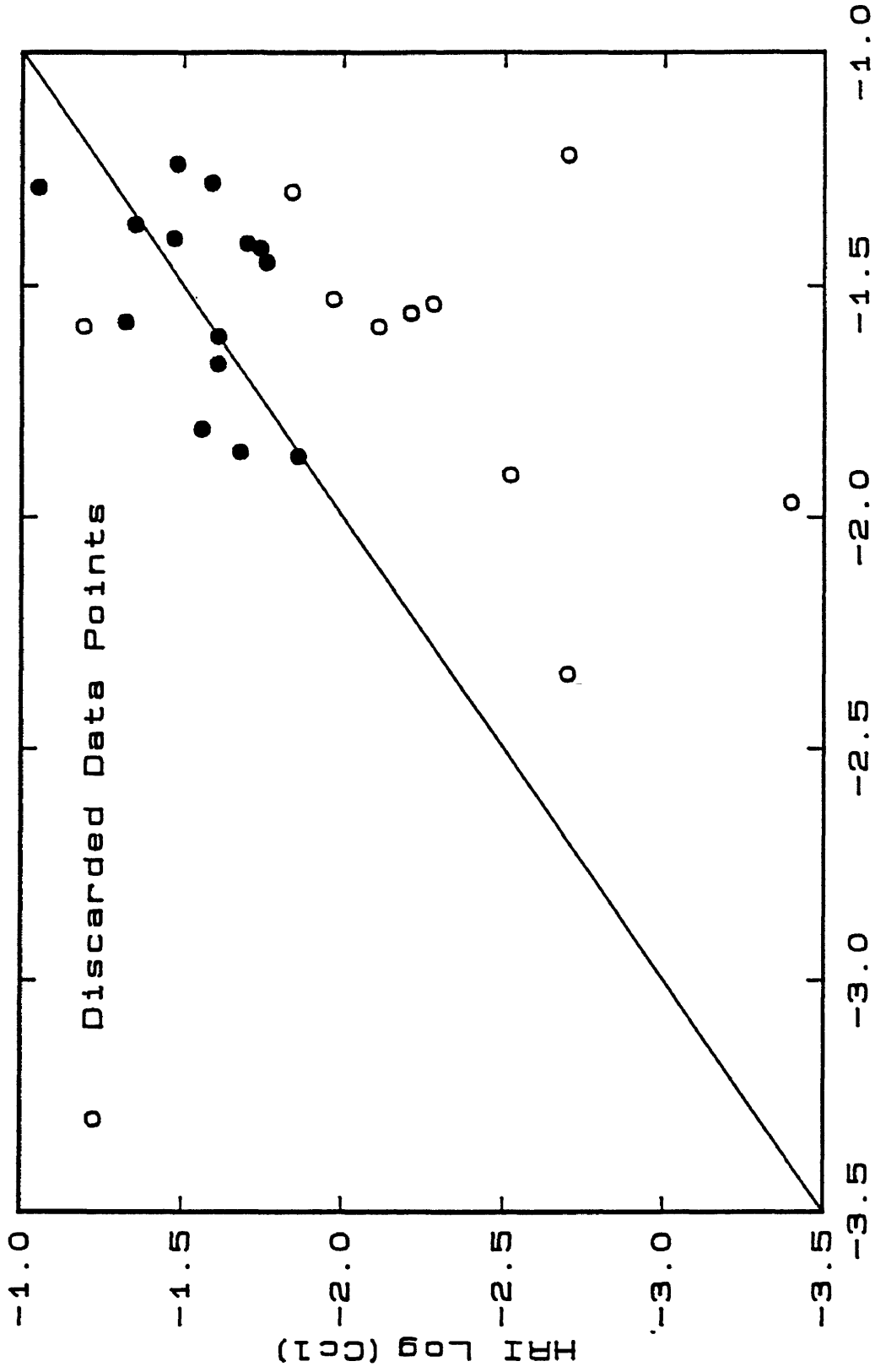

Figure 5.5 - Log Halogen Capacities for Cl_2. HRI (C_{Cl}) / HRD (2nd Series) (C_{Cl}) Plot.

values against the first series of HRD assay data. In Figure 5.5 considerable scatter is also present when plotting log capacity values against HRD second series data. However, the results are more uniformly distributed about the ideal line than the results in Figure 5.4 . Since the best correlation with the HRI independant data appears to be obtained for the data plotted in Figure 5.5, the analogous treatment used for the handling the fluorine data was applied to the HRI and HRD (second series) chlorine data. Again, the open circles represent the discarded data due to excessive deviation from the ideal correlation line. The remaining HRI and HRD (second series) $\log(C_{Cl})$ values were then averaged and are given in Table 5.9 .

The selected $\log(C_{Cl})$ values in Table 5.9 are shown as a function of reciprocal temperature in Figure 5.6 . Although the same trends are observed as in Figure 5.3, there is considerably more scatter in the chlorine results. It is suspected that systematic error inherant in the chlorine analysis procedures, used by both HRI and HRD, are the cause of the observed scatter. The heat of solution

TABLE 5.9

Averaged Log(C_{Cl}) Values For Figure 5.6

Run	Log(C_{Cl})	$10^4/T$ (K^{-1})
T12	-1.69	6.05
T13	-1.77	6.05
T15	-1.45	5.98
T16	-1.61	5.98
T17	-1.17	5.98
T18	-1.44	5.98
T21	-1.36	5.91
T22	-1.61	5.91
T24	-1.52	5.84
T25	-1.58	5.84
T26	-1.87	5.91
T27	-1.44	5.77
T29	-1.56	5.70
T34	-1.39	5.91
T35	-1.64	5.91

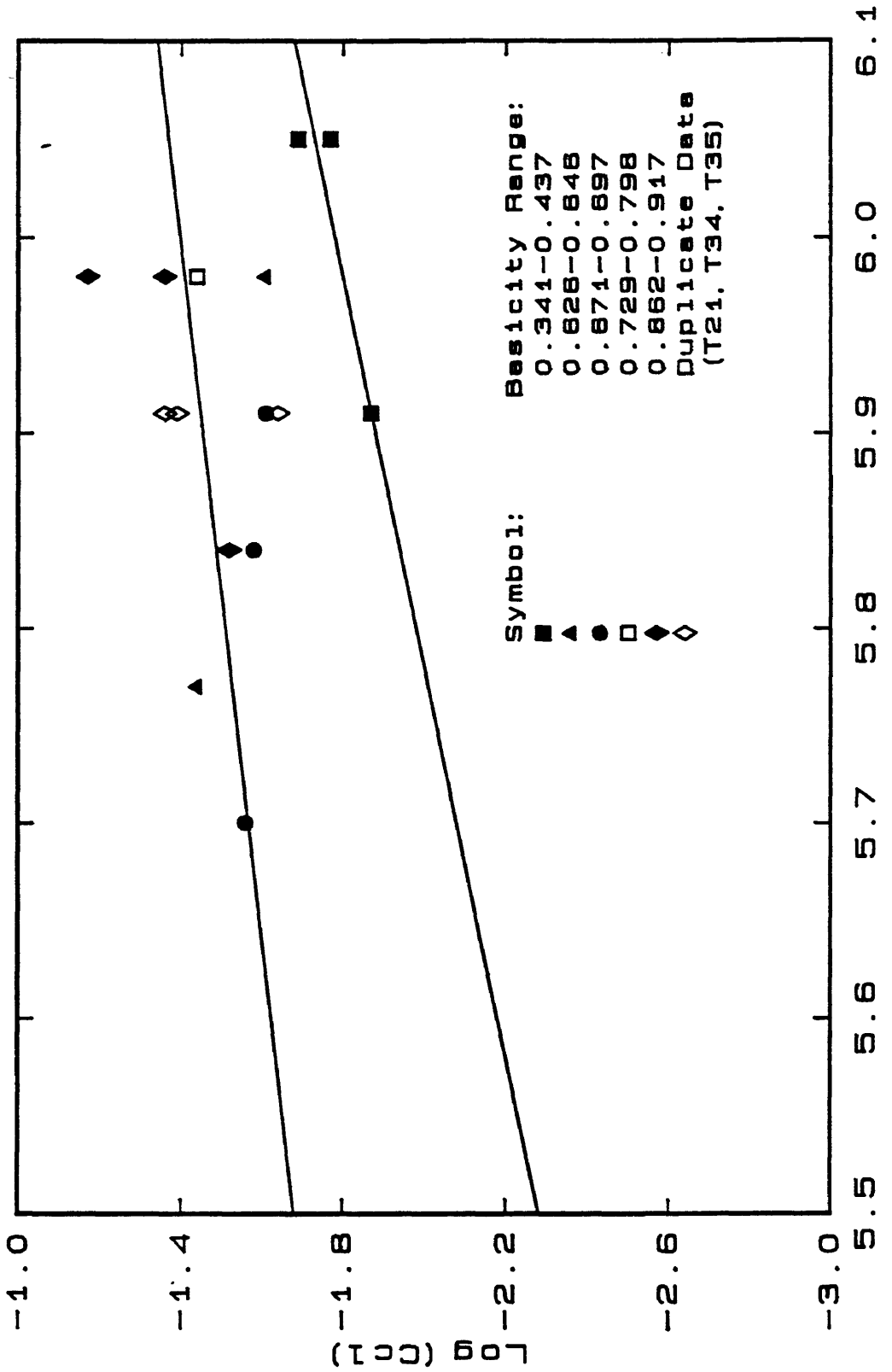

Figure 5.6 - Log (C_{cl}) Versus Reciprocal Temperature

shown in Figure 5.6 was calculated for the following reaction:

$$Cl_{2(g)} + O^{=}_{(slag)} = 2Cl^{-}_{(slag)} + (1/2)O_{2(g)} \qquad (5.3)$$

Plots of halogen capacities against measured basicity or optical basicity (at constant temperature) gave no correlation and are not reproduced here. This is not suprising since as stated above the halogen capacity functions have been shown to depend on the oxygen activity and halogen activity coefficients, and for the limited basicity ranges studied these should be constant.

The heats of solution derived form Figures 5.3 and 5.6 can be compared with the following reactions:

$$CaO_{(l)} + Cl_{2(g)} = CaCl_{2(l)} + (1/2)O_{2(g)} \qquad (5.4)$$

$$CaO_{(l)} + F_{2(g)} + CaF_{2(l)} + (1/2)O_{2(g)} \qquad (5.5)$$

Reactions 5.4 and 5.5 were choosen to approximate reactions 5.2 and 5.3 since calcium chloride and calcium fluoride are the most stable species that could be expected from the

slag. A comparison of these results is given in Table 5.10 . Reasonable agreement is observed between the enthalpy values measured in this study and with the data for the calculated reactions. It is seen that heats of solution for both solution reactions are less exothermic than for reactions 5.4 and 5.5 .

In summary, it is clear that the use of the fluorine capacity (C_f) and the chlorine capacity (C_{Cl}) functions are a effective method for correlation of the solubility data. This is not suprising because of the thermodynamic basis for the development of these functions. One clear advantage in developing correlations for these functions is that the %F and the %Cl in the slag can be computed using the values of (C_f) and (C_{Cl}) taken from the correlation plots.

Table 5.10

Heats of Reaction for Halogen Solubility Reactions

Reaction	Data Source	ΔH°(cal)
$Cl_{2(g)} + O^{=}_{(slag)} = 2\ Cl^{-}_{(slag)} + \frac{1}{2}\ O_2(g)$	This Study	- 23,600*
$Cl_{2(g)} + CaO_{(\ell)} = CaCl_{2(\ell)} + \frac{1}{2}\ O_{2(g)}$	JANAF	- 45,000
$F_{2(g)} + O^{=}_{(slag)} = 2\ F^{-}_{(slag)} + \frac{1}{2}\ O_{2(g)}$	This Study	-104,000*
$F_{2(g)} + CaO_{(\ell)} = CaF_{2(\ell)} + \frac{1}{2}\ O_{2(g)}$	JANAF	-145,000

*Data for Basicity Ranges (0.626-0.917)

5.3 Error Analysis

This section considers errors that would effect the experimental results. The errors considered were:

(i) Insufficient time for complete saturation.

(ii) Insufficient halogen available in the equilibrated gas mixture resulting in incomplete saturation over the time period of the experiments.

(iii) Analytical errors.

(iv) Errors in Temperature measurement.

(v) Uncertainties in gas composition.

If there is insufficient time for complete saturation to occur then a kinetic limitation on the system would exist. The effect would be a low halogen content in the equilibrated slag sample under conditions where sufficient chlorine and fluorine would be available. The corrective action would be to increase the equilibration time period.

Run 121186-T35 was designed to consider this error. A slag sample was equilibrated for a 6 hour period. Initial conditions used were the same as those for 121186-T21. No significant differences were observed in the results obtained. These two runs are identified by open diamonds

in Figures 5.3 and 5.6 . Although the points agree reasonably well it must be kept in mind that the lack of perfect agreement might be partially due to the fact that the basicity did vary slightly between these two runs. The good agreement obtained is taken as sufficient evidence that equilibrium saturation was obtained.

If insufficient halogen is available in the gas phase equilibration, then the slag would not be saturated for the calculated equilibrated gas composition. The resulting effect would be a lower halogen content for the given chlorine and fluorine potentials in the inlet gas mixture. This problem results from a stoichiometric limitation on the system. The corrective measure would be to increase the total gas volumetric flowrate while maintaining the same gas compostion.

Run 121186-T35 was also used to evaluate the possibility of insufficient halogen in the gas phase. The total gas flowrate was increased by 50% while the gas composition was kept identical to run 121186-T21. As stated above no significant difference was observed, and on this basis it was concluded that there was no gas phase limitation for equilibrium saturation.

If serious analytical errors are present, there will then be significant errors in the calculated halogen capacities. The data points shown in the above figures would be moved significantly.

When considering analytical data both random and systematic error may be present. Certainly, systematic error had to exist in the data given by HRD (first series). There appears to be a clear improvement in analytical results for the HRD (second series) data set. In the case of the fluorine, most random and systematic error appear to have been eliminated. However, considerable random error seems to be present in the chlorine assays as given by both HRI and HRD (second series). This is shown by the scatter in the data for all $\log(C_{Cl})$ plots. It would appear that work is needed to provide an analytical method that gives consistant chlorine analyses. Due to the recognized prescence of error of chlorine assays, the reliability of the chlorine capacity results is judged to be not as high as the flourine capacity results.

Another possible error that may be present would be incorrect temperature measurement. The effect of this error would be seen on the two reciprocal temperature plots. If the temperature measurement is incorrect, the points would be shifted horizontially. The resulting effect is an uncertainty in the ΔH^{o} for the solubilization reaction.

Thermocouple calibrations would be required frequently to ensure proper temperature readings. To minimize this problem, thermocouple calibration was made, new thermocouple beads were made on the measuring thermocouple for every other run, and the thermocouple was replaced from time to time. The problem could be further minimized if each thermocouple was calibrated before placing it into service.

Uncertainties in gas composition would effect the partial pressures of Cl_2, F_2, and O_2. This in turn create errors in the calculated halogen capacities. However, the uncertainties in gas composition are considered to be very low since stable and reproducible flowrates were obtained form the capillary flowmeters. Moreover, on two occasions the total gas flowrate was measured and compared with the sum of the individual flowrates. In both cases the agreement was within 5%.

VI. SUMMARY AND CONCLUSIONS

The technique used in this study overall was found to be effective for the measurement of halogen solubility in EAF slags. However, several problems were encountered in the course of this study that would have to be addressed in future work. Slag containment constituted the major problem. The use of alumina crucibles did provide slag containment, however, alumina dissolution into the slag decreased the range of basicity that could be considered. Another problem was the reliability of chlorine assays provided by both HRI and HRD. With poor chlorine assays, chlorine capacities cannot be calculated with any accuracy. This is further reflected in the reciprocal temperature plot for chlorine where the heat of solution is derived. In future work, improved chlorine assay procedures must be developed.

The use of chlorine and fluorine capacity functions did describe halogen solubilty as predicted by thermodynamics. This study was able to correlate C_{Cl} and C_f with temperature for a limited range of constant basicities. More experiments would be required to correlate C_{Cl} and C_f with slag composition.

The results show that the solubility reactions can be described as follows:

$$Cl_{2(g)} + O^{=}_{(slag)} = 2Cl^{-}_{(slag)} + (1/2)O_{2(g)} \quad (6.1)$$

$$F_{2(g)} + O^{=}_{(slag)} = 2F^{-}_{(slag)} + (1/2)O_{2(g)} \quad (6.2)$$

The heats of solution were determined for reactions 6.1 and 6.2 and were compared to the heats of solution for the following reactions:

$$CaO_{(l)} + Cl_{2(g)} = CaCl_{2(l)} + (1/2)O_{2(g)} \quad (6.3)$$

$$CaO_{(l)} + F_{2(g)} = CaF_{2(l)} + (1/2)O_{2(g)} \quad (6.4)$$

The good agreement between the two sets of heats of solution confirm the view that the principal form of the chlorine and fluorine in the slag is as $CaCl_2$ and CaF_2.

From the capacity data generated, by this study, the %F and %Cl that would be present in a flame reactor slag can be calculated from the correlations given below provided that the proposed slag is within the basicity ranges studied:

$$\log(C_{Cl}) = (10003/T) - 7.78 \qquad R = 0.341\text{-}0.437 \qquad (6.5)$$

$$\log(C_{Cl}) = (5166/T) - 4.52 \qquad R = 0.626\text{-}0.917 \qquad (6.6)$$

$$\log(C_f) = (38654/T) - 13.28 \qquad R = 0.341\text{-}0.437 \qquad (6.7)$$

$$\log(C_f) = (22785/T) - 3.39 \qquad R = 0.626\text{-}0.917 \qquad (6.8)$$

The results of this study show that for an EAF slag produced under flame reactor conditions, the halogen solubility is modest. The chlorine content was found to be 0.20-0.30%, and the fluorine content 0.5-0.8%. However, all the data were obtained for low (acidic) basicites, it is expected that as the slag is made more basic greater chlorine and fluorine solubility can be achieved. Results for the log halogen capacity - reciprocal temperature plots indicate improved solubility will be obtained with a decrease in temperature. For fluorine solubility, a decrease in temperature form 1527 ^{o}C to 1327 ^{o}C results in a 97% increase in fluorine capacity (C_f) (for R=0.626-0.917).

VII. SUGGESTIONS FOR FUTURE WORK

The following suggestions are made for the future study of halogen solubility in EAF slags:

1) The study of a larger range of basicities are required to allow correlation of halogen capacities with both slag composition and temperature.

2) A platinum crucible or some other suitable container will be required to control slag basicity without crucible contamination of the sample.

3) The development of a more reliable chlorine analysis technique is absolutely essential.

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APPENDIX

LISTING AND SAMPLE PRINTOUT OF GAS EQUILIBRATION PROGRAM

A computer program was developed to determine an equilibrated gas composition at reactor temperature given an unequilibrated gas mixture at room temperature. The description of the computer model was given in Chapter 4, Section 4.5 . The program was written in MS-Basic for use on the Texas Instruments Professional Computer.

A computer listing of the program is given below followed by a sample printout.

```
100  'This Program Calculates An Equilibrated Gas Composition
110  'Given Flowrates For a Given Gas Mixture
120  '
130  'This program is written for MT 701 by Ned Hall
140  '
150  'All Variables are defined double precision [DEFDBL]
160  '
170  DEFDBL C,S,F,W,X,K,M,P,T,Q,G,Y,A
180  '
190  DIM K(5),G(10),Y(10),Q(10),M(10)
200  KEY OFF:CLS:LOCATE ,,0
1150 '*****************************************************************
5000 'PRINT PROGRAM HEADER ***
5010 '
5020 LINE (10,10)-(700,275),1,BF
5030 LINE (20,20)-(685,260),6,BF
5040 PAINT (12,12),7,4
5050 COLOR 0,1,6,0
5060 LOCATE 5,29:PRINT " COLORADO SCHOOL OF MINES "
5070 COLOR 0,1,0,0
5080 LOCATE 8,23:PRINT " Dept. Of Metallurgical Engineering "
5090 COLOR 0,1,0,0
5100 LOCATE 10,37:PRINT " MT-701 "
5110 COLOR 0,1,0,0
5120 LOCATE 12,20:PRINT " DETERMINATION OF EQUILIBRATED GAS SPECIES "
5130 LOCATE 13,28:PRINT " FOR GAS METERING SYSTEM "
5140 COLOR 7,0,0,0
5150 COLOR 0,0,0,64
5160 LOCATE 20,40:PRINT " STRIKE SPACE BAR TO CONTINUE. "
5170 LOCATE 25,1
5180 COLOR 7,0,0,0
5190 X$=INKEY$:IF X$="" THEN 5190
5200 REM INPUT OF VARIABLES ***
5210 COLOR 7,0,0,0 :CLS
5220 LOCATE 12,15:INPUT "NAME: ",H1$
5230 LOCATE 14,15:INPUT "DATE: ",H2$
5240 LOCATE 16,15:INPUT "SUBJECT: ",H3$
5250 CLS:COLOR 6,0,0,0:IC=1
5260 LOCATE 9,15:PRINT "THIS SECTION ASKS FOR INITIAL GAS FLOWRATES [cc/min.]"
5270 COLOR 7,0,0,0
5280 LOCATE 12,15:INPUT "N2 IN OFF-GAS : ",Q(1)
5290 LOCATE 14,15:INPUT "H2  IN OFF-GAS: ",Q(2)
5300 LOCATE 16,15:INPUT "CO IN OFF-GAS : ",Q(3)
5310 LOCATE 18,15:INPUT "CO2 IN OFF-GAS: ",Q(4)
5320 LOCATE 20,15:INPUT "C12 IN OFF-GAS: ",Q(5)
5330 LOCATE 22,15:INPUT "F2 IN OFF-GAS : ",Q(6)
5340 CLS:COLOR 6,0,0,0
5350 LOCATE 9,15:PRINT "THIS SECTION ASKS FOR TEMP.(DEG. C) AND TOTAL PRESSURE(A
TM)"
5360 COLOR 7,0,0,0
5370 LOCATE 12,15:INPUT "TEMP.(DEG. C): ",T1
```

```
5380 LOCATE 14,15:INPUT "PRESSURE (ATM): ",PT
5385 T2=T1+273.15#
5390 '*************************************************************************
5400 'THIS SECTION CALCULATES THE UNEQUILIBRATED GAS COMPOSITION (VOL. %)
5410 QTOT=0#
5420 FOR I=1 TO 6
5430    QTOT=QTOT+Q(I)          'TOTAL FLOW RATE
5440 NEXT I
5450 '
5460 FOR J=1 TO 6
5470    G(J)=Q(J)/QTOT*100#     'ASSUMING 100 MOLES IN TOTAL GAS MIXTURE
5480 NEXT J
5490 G2=G(2):G3=G(3):G4=G(4)    'G(i) = MOLES GAS SPECIES i
5500 '*************************************************************************
6000 'CALCULATE K FOR H2(g) + CO2(g) = CO(g) + H2O(g)
6100 K=EXP((6868.96#-6.451#*T2)/(-1.987#*T2))
6200 '*************************************************************************
7000 'CALCULATION OF HF & HCl FORMED [100 % OF Cl2 & F2 REACT]
7010 G(7)=G(5)*2#  'HCl
7020 G(8)=G(6)*2#  'HF
7030 'CALCULATE REMAINING MOLES OF H2
7040 G(2)=G(2)-G(5)-G(6)
7050 '
7060 IF G(2) <=0 THEN 9000
7100 '*************************************************************************
7200 'H2(g) + Cl2(g) = 2HCl(g)
7210 K2=EXP(2#*(-22777#-1.357#*T2)/(-1.987#*T2))
7220 '
7230 'H2(g) + F2(g) = 2HF(g)
7240 K3=EXP(2#*(-65040#-.6338#*T2)/(-1.987#*T2))
7250 '
7255 'CO(g) + (1/2)O2(g) = CO2(g)
7256 K1=EXP((-66862.83#+20.249#*T2)/(-1.987#*T2))
7260 '*************************************************************************
8000 'THIS SECTION IS FOR INTERVAL HALVING
8010 '
8020 XMIN=0:XMAX=G(2)
8030 IF ABS(XMAX-XMIN) < 1E-08 THEN 8120
8040 XM=(XMIN+XMAX)/2#
8050 IC=IC+1
8060 KEST=((G(3)+XM)*XM)/((G(2)-XM)*(G(4)-XM))
8070 IF KEST > K THEN XMAX=XM
8080 IF KEST < K THEN XMIN=XM
8090 IF KEST =K THEN 8120
8100 LOCATE 22,32:PRINT ;IC
8110 GOTO 8030
8120 '*************************************************************************
8130 'FINAL UPDATE FOR ALL GAS SPECIES
8140 M(1)=G(1)    'N2
8150 M(2)=G(2)-XM 'H2
```

```
8160 M(3)=G(3)+XM 'CO
8170 M(4)=G(4)-XM 'CO2
8180 M(5)=0#      'Cl
8190 M(6)=0#      'F2
8200 M(7)=G(7)    'HCl
8210 M(8)=G(8)    'HF
8215 M(9)=XM      'H2O
8220 '
8230 'CALCULATE TOTAL MOLES
8240 MT=0#
8250 FOR I=1 TO 9
8260   MT=MT+M(I)
8270 NEXT I
8280 'VOL. % EQUILIBRATED FLOWMETER GAS [EFG]
8290 FOR J=1 TO 9
8300    EFG(J)=M(J)/MT*100#
8310 NEXT J
8320 '
8400 'CALCULATE MOLES AND PARTIAL PRESSURES OF Cl2, F2, O2 GASES
8410 MCL2=(M(7)^2)/(M(2)*K2)
8420 FCL2=MCL2/MT*100
8430 PCL2=(FCL2/100)*PT
8440 '
8450 MF2=(M(8)^2)/(M(2)*K3)
8460 FF2=MF2/MT*100
8470 PF2=(FF2/100)*PT
8480 '
8490 PO2=(M(4)/(M(3)*K1))^2
8500 '
8510 GOTO 10000
8999 '*****************************************************************************
9000 'ALL H2 HAS BEEN USED UP FORMING HCl & HF THEREFORE NO SOLUTION **
9010 CLS:LOCATE 20,10:PRINT "ALL H2 HAS BEEN USED, NO SOLUTION MAY BE FOUND"
9020 LOCATE 25,40:PRINT "HIT F2 KEY TO RE-RUN PROGRAM"
9030 END
10000 '*****************************************************************************
10010 '   PRINTOUT RESULTS [LINE PRINTER AND MONITOR] *****
10020 '   MONITOR PRINTOUT **
10030 CLS
10040 LOCATE 12,10:PRINT "CHOOSE EITHER MONITOR OR LINE PRINTER TO OUTPUT RESULT
S"
10050 PRINT :LOCATE 14,10:PRINT "TYPE -1- FOR MONITOR OR -2- FOR LINE PRINTER"
10060 LOCATE 15,10:PRINT "BE SURE LINE PRINTER IS TURNED ON!"
10070 A$=INKEY$:IF A$="" THEN 10070
10080 IF A$="2" THEN 10270
10090 CLS:COLOR 0,1,0,0
10100 LOCATE 5,4:PRINT "EQUILIBRATED GAS COMPOSITION [VOL. %]"
10110 COLOR 0,7,0,0
10120 LOCATE 7,30:PRINT USING "& ##.###";"N2  :",EFG(1)
10130 LOCATE 8,30:PRINT USING "& ##.###";"CO  :",EFG(3)
10140 LOCATE 9,30:PRINT USING "& ##.###";"H2O :",EFG(9)
```

```
10150 LOCATE 10,30:PRINT USING "& ##.###";"H2  :",EFG(2)
10160 LOCATE 11,30:PRINT USING "& ##.###";"CO2 :",EFG(4)
10170 LOCATE 12,30:PRINT USING "& ##.###";"C12 :",EFG(5)
10180 LOCATE 13,30:PRINT USING "& ##.###";"HC1 :",EFG(7)
10190 LOCATE 14,30:PRINT USING "& ##.###";"F2  :",EFG(6)
10200 LOCATE 15,30:PRINT USING "& ##.###";"HF  :",EFG(8)
10210 COLOR 0,6,0,0
10220 LOCATE 18,30:PRINT USING "& ####.# &";"TEMPERATURE: ";T1;"DEG. CELSIUS"
10230 LOCATE 19,30:PRINT USING "& ##.## &";"TOTAL PRESSURE: ";PT;"ATM."
10240 COLOR 7,0,0,0:PRINT "HIT SPACE BAR TO CONTINUE."
10250 X$=INKEY$:IF X$="" THEN 10250
10260 CLS:LOCATE 7,30:PRINT "MINOR SPECIES"
10261 LOCATE 7,30:PRINT USING "& ##.#####^^^^";"C12 % ",PCL2
10262 LOCATE 8,30:PRINT USING "& ##.#####^^^^";"F2  % ",PF2
10263 LOCATE 10,30:PRINT USING "& ##.#####^^^^";"PC12 (atm): ",PCL2
10264 LOCATE 11,30:PRINT USING "& ##.#####^^^^";"PF2 (atm):  ",PF2
10265 LOCATE 12,30:PRINT USING "& ##.#####^^^^";"PO2 (atm):  ",PO2
10266 X$=INKEY$:IF X$="" THEN 10266
10267 GOTO 11000
10270 REM LINE PRINTOUT OF RESULTS. ******
10280 LPRINT "*********************************************************************"
10290 LPRINT "*                                                                   *"
10300 LPRINT "*                 COLORADO SCHOOL OF MINES                          *"
10310 LPRINT "*          Dept. Of Metallurgical Engineering                       *"
10320 LPRINT "*                       MT 701                                      *"
10330 LPRINT "*                                                                   *"
10340 LPRINT "*       FLOWMETER EQUILIBRATED GAS CALCULATIONS                     *"
10350 LPRINT "*                    Version:2.1                                    *"
10360 LPRINT "*               Written By: Ned Hall                                *"
10370 LPRINT "*********************************************************************"
10380 LPRINT :LPRINT
10390 LPRINT USING "&& && &&";"NAME: ",H1$,"DATE: ",H2$,"SUBJECT: ",H3$
10400 LPRINT :LPRINT :LPRINT
10410 LPRINT "***************** SUMMARY OF INPUT DATA ************************"
10420 LPRINT
10430 LPRINT "               UNEQUILIBRATED GAS FLOWRATES  [cc/min]"
10440 LPRINT USING "& ###.###&";"           N2                    ",Q(1);" cc/mi
n"
10450 LPRINT USING "& ###.###&";"           H2                    ",Q(2)
10460 LPRINT USING "& ###.###&";"           CO                    ",Q(3)
10470 LPRINT USING "& ###.###&";"           CO2                   ",Q(4)
10480 LPRINT USING "& ###.###&";"           C12                   ",Q(5)
10490 LPRINT USING "& ###.###&";"           F2                    ",Q(6)
10500 LPRINT
10510 LPRINT USING "& ####.# &";"TEMPERATURE: ",T1,"DEG. CELSIUS.":LPRINT
10520 LPRINT USING "& ####.##";"TOTAL FLOW RATE (cc/min): ";QTOT:LPRINT
10530 LPRINT USING "& ##.## &";"TOTAL PRESSURE: ",PT,"ATM."
10540 LPRINT :LPRINT
10550 LPRINT "               UNEQUILIBRATED GAS VOLUME %":LPRINT
10560 LPRINT USING "& ##.###&";"          N2                     ",G(1);"%"
10570 LPRINT USING "& ##.###&";"          H2                     ",G2;"%"
```

```
10580 LPRINT USING "& ##.####&";"          CO                    ",G3;"%"
10590 LPRINT USING "& ##.####&";"          CO2                   ",G4;"%"
10600 LPRINT USING "& ##.####&";"          C12                   ",G(5);"%"
10610 LPRINT USING "& ##.####&";"          F2                    ",G(6);"%"
10620 LPRINT
10630 LPRINT "***************** SUMMARY OF RESULTS ****************************"
10640 LPRINT
10650 LPRINT "               EQUILLIBRATED GAS COMPOSTION [VOL. %]" :LPRINT
10660 LPRINT USING "& ##.####&";"          N2                     ",EFG(1);"%"
10670 LPRINT USING "& ##.####&";"          CO                     ",EFG(3);"%"
10680 LPRINT USING "& ##.####&";"          H2O                    ",EFG(9);"%"
10690 LPRINT USING "& ##.####&";"          H2                     ",EFG(2);"%"
10700 LPRINT USING "& ##.####&";"          CO2                    ",EFG(4);"%"
10710 'LPRINT USING "& ##.####&";"          C12                    ",EFG(5);"%"
10720 LPRINT USING "& ##.####&";"          HCl                    ",EFG(7);"%"
10730 'LPRINT USING "& ##.####&";"          F2                     ",EFG(6);"%"
10740 LPRINT USING "& ##.####&";"          HF                     ",EFG(8);"%"
10750 LPRINT CHR$(12):LPRINT
10760 LPRINT "  *Calculated Concentrations of Minor Species*  "
10770 LPRINT
10780 LPRINT USING "& ##.####^^^^";"% Cl2 :",FCL2
10782 LPRINT USING "& ##.####^^^^";"%  F2 :",FF2
10784 LPRINT
10786 LPRINT  "   *Calculated Potentials* ":LPRINT
10788 LPRINT USING "& ##.####^^^^&";"PO2  = ";PO2; " atm"
10790 LPRINT USING "& ##.####^^^^&";"PCl2 = ";PCL2; " atm"
10792 LPRINT USING "& ##.####^^^^&";"PF2  = ",PF2; " atm"
10794 LPRINT CHR$(12)
11000 '******************** FURTHER PROGRAM SELECTIONS ************************
11010 CLS
11020 LOCATE 9,32:COLOR 2,0,0,96:PRINT "#SELECTION MENU#"
11030 LOCATE 12,22:COLOR 0,7,0,0:PRINT "PLEASE MAKE THE FOLLOWING SELECTION:"
11040 PRINT :PRINT
11050 LOCATE 15,24:COLOR 6,0,0,32:PRINT "TYPE 1 FOR MENU OR 2 FOR SYSTEM"
11060 LOCATE 16,24:PRINT "OR 3 TO RUN PROGRAM AGAIN"
11070 COLOR 7,0,0,0
11080 X$=INKEY$:IF X$="" THEN 11080
11090 IF X$="1" THEN RUN"MENU"
11100 IF X$="2" THEN SYSTEM
11110 '
11120 GOTO 200
11130 END
```

```
*****************************************************************
*                                                               *
*                COLORADO SCHOOL OF MINES                       *
*           Dept. Of Metallurgical Engineering                  *
*                      MT 701                                   *
*                                                               *
*       FLOWMETER EQUILIBRATED GAS CALCULATIONS                 *
*                   Version:2.1                                 *
*                Written By: Ned Hall                           *
*****************************************************************

NAME: NED HALL DATE: 8/5/88 SUBJECT: EQUILIBRATION TRIALS AT 1500 C


***************** SUMMARY OF INPUT DATA *************************

              UNEQUILIBRATED GAS FLOWRATES  [cc/min]
          N2                    125.000 cc/min
          H2                     63.000
          CO                     18.000
          CO2                   370.000
          Cl2                     9.000
          F2                      9.000

TEMPERATURE:  1500.0 DEG. CELSIUS.

TOTAL FLOW RATE (cc/min):   594.00

TOTAL PRESSURE:   0.82 ATM.


              UNEQUILIBRATED GAS VOLUME %

          N2                    21.044%
          H2                    10.606%
          CO                     3.030%
          CO2                   62.290%
          Cl2                    1.515%
          F2                     1.515%

***************** SUMMARY OF RESULTS ****************************

              EQUILIBRATED GAS COMPOSTION [VOL. %]

          N2                    21.044%
          CO                    10.240%
          H2O                    7.209%
          H2                     0.366%
          CO2                   55.080%
          HCl                    3.030%
          HF                     3.030%
```

Calculated Concentrations of Minor Species

% Cl2 : 1.5511D-05
% F2 : 1.2236D-15

Calculated Potentials

PO2 = 6.7490D-07 atm
PCl2 = 1.2719D-07 atm
PF2 = 1.0034D-17 atm

BIOGRAPHICAL NOTE

The author was born to Bill and Mary Hall in Burnaby, British Columbia, Canada on March 16, 1956.

The author received a Diploma of Technology in the Chemical and Metallurgical program at the British Columbia Institute of Technology, Burnaby, B.C. in May, 1978. Following graduation, the author worked as a metallurgical technologist for Newmont Mines, Similkameen Div., Princeton, B.C. from 1978-1981.

The author received his Bachelor of Science degree in Metallurgical Engineering from the Colorado School of Mines, Golden, CO, June, 1986. In August, 1986 the author commenced working towards his Master of Science degree in Metallurgical Engineering.

The author is a member of the Metallurgical Society of AIME, the National Association of Corrosions Engineers (NACE), Applied Science Technologists of B.C., and registered as an E.I.T., Professional Engineering Association of British Columbia.