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**DISPOSITION OF CHLORINE-CONTAINING SPECIES
IN AN MHD COAL-FIRED FLOW FACILITY**

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Shuying Wang
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ABSTRACT

Chlorine-containing species in an MHD Coal-Fired Flow Facility (CFFF) could decrease plasma conductivity, release chloride gas emission, and cause fouling and corrosion of downstream components.

Therefore, this thesis work has been conducted to characterize the disposition of chlorine-containing species under CFFF conditions; to identify parameters affecting gas phase chloride emission; to propose possible reaction pathways in the CFFF system; and to rationalize chlorine mass balance across CFFF.

To achieve the above-mentioned objectives of this research work, extracted gas samples and bulk solid samples were taken at certain major MHD downstream components. Equilibrium concentrations of chlorine-containing species in CFFF were calculated using NASA-SP 273 computer code. Bench Scale experiments were then carried out by simulating MHD downstream test conditions.

The results of the test sampling, the theoretical calculations, and the bench scale experiments were compared. Based on the comparison results, possible disposition and chlorine-containing species in the CFFF system were given in this thesis. An overall chlorine mass balance in the CFFF was also attempted.

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CHAPTER 1

INTRODUCTION

1.1 MHD Background

A typical system consists of an MHD topping cycle for direct conversion of kinetic energy of plasma into electrical energy, combined with a steam bottoming cycle for generating electricity with a steam turbine. In the topping cycle, potassium in the form of K_2CO_3 is added to the fuel before the combustor to increase the electrical conductivity of the combustion-derived gases. The potassium salt used is called seed. The seeded coal is burned fuel-rich in a primary combustor. The electrically conducting plasma produced then passes through a converging/diverging section surrounded by a strong MHD magnetic field at high velocity. In the steam generation stage and superheat stages, the combustion gases are cooled from more than 2200 K to less than 422 K to recover the thermal energy. A secondary combustion is carried out to burn the remaining CO and H_2 in the gas derived from the fuel-rich primary combustion. Steam generated from the hot combustion gases can be then used to drive a turbine/generator set to produce additional electrical power. A combined-cycle MHD system has the potential of increasing the overall plant efficiency to more than 50 % [1].

One of the main objectives of the integrated MHD bottoming cycle program is to develop and evaluate technologies on emission control, fouling, corrosion prevention required for scale up to commercial plants [2]. Those objectives are being accomplished at the Coal-Fired Flow Facility (CFFF) located at the University of Tennessee Space Institute (UTSI) under contract from the U.S. Department of Energy (DOE).

A schematic of the 28 Mwt MHD CFFF bottoming cycle system located at The University of Tennessee Space Institute is shown in Figure 1-1. This system consists of upstream and downstream components. The upstream includes an oxidant preheater (vitiation heater), a primary combustor, a supersonic nozzle, aerodynamic duct, and a diffuser to simulate gas flowing conditions of the topping cycle. The downstream includes the radiant furnace, secondary combustor, superheater, air heater, Baghouse (BH), dry electrostatic precipitator (ESP), venturi scrubber/cyclone system, and a stack. The near future plans include replacing the venturi scrubber/cyclone system with a wet ESP.

1.2 Chlorine Occurrences in CFFF Feedstock

Chlorine-containing species are possibly present in the CFFF feedstock from three different sources: coal, oil, and the seed. The chlorine occurrences in these feed materials are discussed as follows.

Chlorine generally occurs in fuel in a form that is very easily decomposed or vaporized during combustion. Cox et al. have presented a hypothesis [3] that a coal sample contained a total of 0.52 wt% Cl, of which 83% was in inorganic salt form, 17% chlorine was held by an ion exchange mechanism, and none was covalently bonded chlorine. However, researches during the 1950's showed that only a minor amount occurs as NaCl, with the most of the chlorine being weakly bonded chloride ions distributed over the surface of the organic part of the coal [4], while Pearce and Hill postulated that the chlorine is present in one form uniformly distributed and linked ionically to the coal substance but sufficiently labile to be evolved mainly as hydrogen chloride at temperatures above about 170 °C and that it has no particular relationship with sodium or other alkali/alkaline earth metals [5].

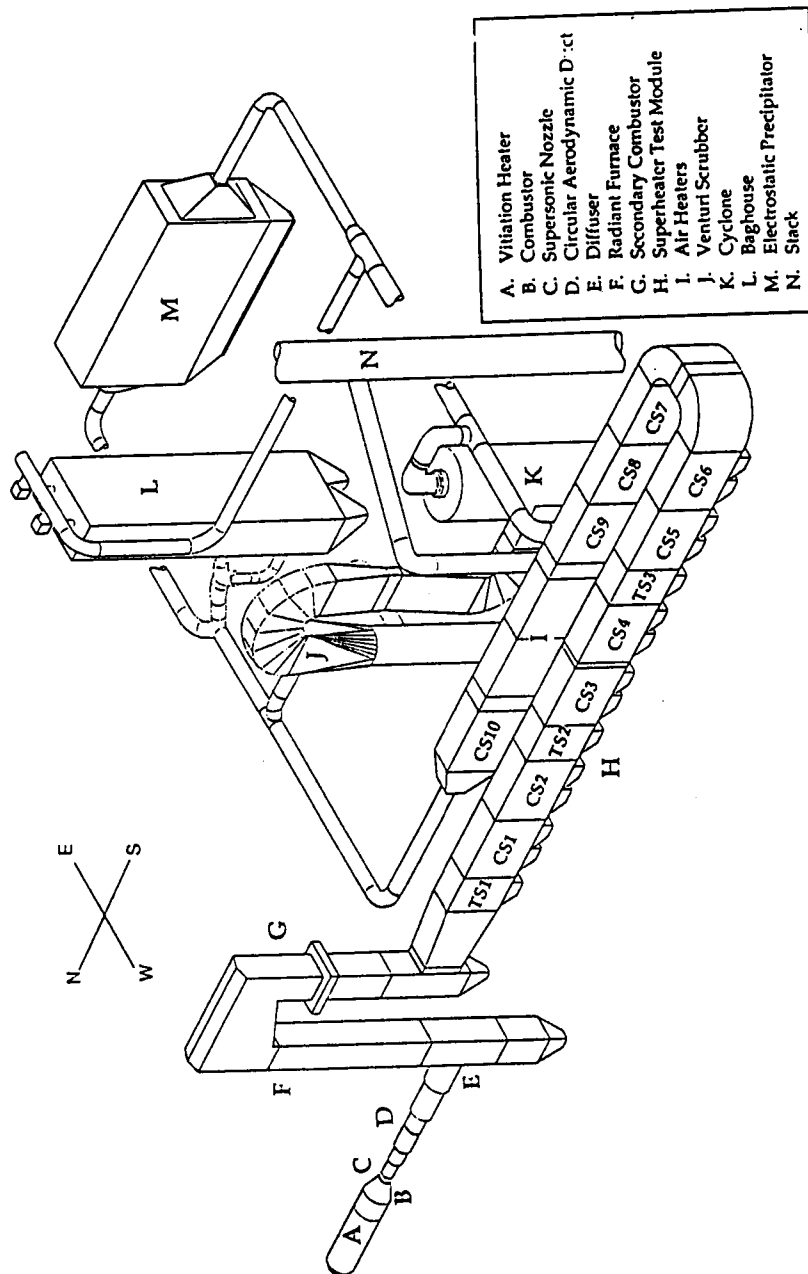


Figure 1-1. Coal-Fired Low-Mass Flow Facility at UTSI

Based on analyses of over 6000 samples of U.S. coal, it is believed that western U.S. coal basins average less than 200 ppm chlorine. While the Illinois No.5 and No.6 coals from the Illinois Basin have a chlorine content varying from about 100 ppm to 8000 ppm (dry basis). The chlorine content in Illinois coal reserves increases with the depth of the coal seams at about 2000 ppm per 100 m [4]. Two coals used at the CFFF in previous tests were Illinois No. 6 and Montana Rosebud, with chlorine concentrations about 0.2 % and 0.1 % respectively.

In contrast to coal, the chlorine in heavy oils is present as NaCl. Some of this salt is originally present in the oil-field brines and another source could be the seawater contamination during shipment. The highest levels reported have been about 150 ppm by weight [4].

Chlorine in fresh (or make-up) seed can occur mainly as chlorides of potassium and sodium. In the mineral grade K_2SO_4 supplied by Great Salt Minerals and Chemicals Corporation, chloride is reported to vary from 0.05 to 0.25%. From our analysis of the fresh K_2CO_3 (supplied as dense, anhydrous, granular, more than 99.5 % pure by Continental Industrial Chemicals Company) used as seed material in the CFFF, we have found that the chloride level is about 54 ppm [6].

During the tests conducted at the CFFF in UTSI, fuel oil is first burnt with oxygen-enriched air in vitiation heater to raise the temperature of the oxidizer. The vitiated oxidizer is then mixed with the mixture of K_2CO_3 seed and pulverized coal to get the fuel-rich feedstock of the primary combustor. For the previous Low Mass Flow (LMF) MHD tests on Illinois # 6 coal, the chlorine level in the fuel/seed mixture was between 0.1 % to 0.25 % weight percentage.

1.3 Effect of Chlorine-Containing species on MHD System

It has been recognized that chlorine in coal can contribute to the formation of a corrosive atmosphere during combustion and most of the chlorine can be driven off as HCl while heating the coal in air at 473 K, irrespective of the initial form of the chlorine [1,7]. 0.2 % - 0.3 % Cl by mass is recommended as the maximum level that should be present in routine combustion procedures [8,9]. Many corrosion problems have been observed in coal-fired utility systems and in coal conversion process equipments [10-12]. Chlorine-containing fuels are reported to have caused fireside corrosions whether in a conventional boiler, fluidized-bed unit, or a waste incinerator [4,13,14]. Moreover, in a lime/limestone-based Flue Gas Desulfurization (FGD) system, high chloride levels are generally thought to be detrimental to the SO₂ removal efficiency [15-17].

Components of the MHD bottoming cycle are basically identical to those of a steam plant. However, much higher temperature exists in the combustion process and there is a significant difference in the gas chemistry of the combustion gases due to the presence of potassium in the MHD system. Therefore, it is inappropriate to extrapolate completely from whatever is known about the effects of chlorine in the conventional power generation system to advanced MHD system.

First, potassium salts used as seed material in the coal-fired MHD system are recovered, regenerated and recycled for economic and environmental reasons. Such recovery/regeneration operations with MHD spent seed materials raise a potential problem of causing coal-derived chloride build-up in the MHD seed system after recycling many times. Ash deposition, corrosion, fouling, heat transfer and particulate collection in MHD downstream can be affected significantly if the seed material is recycled without controlling/removing chlorides [1].

Being an electro-negative atom, chlorine also traps free electrons and, thus, reduces the plasma conductivity [6]. Sheth et al. have identified several options to control the build-up of chlorine-containing impurities in the recycled seed [18].

Second, as a result of the Clean Air Act amendment of 1990 based on the municipal solid waste incineration the emission of HCl (hydrochloric acid) gas/aerosol from a continuous source must be reduced from 17 tons/year to less than 10 tons annually [19]. This criterion is equal to about 19.03 g/min, on a basis of 365 days/year of continuous HCl emission. From the samples taken from the MHD LMF4 series tests conducted in the CFFF, we found that the HCl-emission levels of some tests, which used Illinois No. 6 coal as fuel and low potassium-to-sulfur (K_2/S) ratio, appeared to be far beyond this proposed criterion of the EPA regulation. For example, during Test LMF4-U, the emission level of HCl was 36.26 g/min, which is about 19.06 ton/year on a continuous emission basis. In this case, the emission level of HCl was about 90.6 % higher than the proposed criterion of New Clean Air Act amendment.

1.4 Objective and Approach

The current study aims at evaluating the disposition of chlorine-containing species in the CFFF, which will provide valuable information for the determination of acceptable level of chloride in the MHD system and for the evaluation of the effects of chlorine-containing species on the performance of various MHD bottoming cycle components. Related objectives include understanding the chloride chemistry for the CFFF, analyzing the different factors affecting the chloride emission from the coal-fired open cycle MHD power generation system, and reaching a reasonable overall chlorine mass balance in the CFFF.

Three major approaches have been used in this project. Extracted gas

samples were taken at certain MHD downstream components, equilibrium chloride concentration profiles in the CFFF were calculated using the NASA SP-273 computer code, and a controlled bench scale experiments were also carried out by simulating the test conditions for the MHD downstream particulate control device. Temperature, potassium-to-sulfur ratio, and the stoichiometric ratio used in the MHD tests are the major parameters investigated in the above-mentioned approaches. The stoichiometric ratio of oxygen in a combustion process is defined as the weight ratio of oxygen actually used to oxygen theoretically needed to convert the combustible elements contained in the fuel into their stable oxides.

The results of the test sampling, the theoretical calculations, and the experimental results have been compared. Based on this information, an overall chloride chemistry profile in certain MHD downstream components was developed. A sensitivity analysis of the different factors affecting chlorine emission from the CFFF was carried out. An overall chlorine mass balance in the CFFF was also attempted.

CHAPTER 2

CHLORIDE MEASUREMENTS FROM CFFF

2.1 Sampling Locations and Methods

2.1.1 Extracted Gas Samplings

Extracted gas samples were taken at the outlets of superheater test module (SHTM), baghouse, and ESP. The SHTM outlet samples served as the inlet sample for the baghouse and ESP.

These samples were collected using a sampling flow train consisting of a stainless steel nozzle, in-stack primary and backup filters, heated stainless steel probe, glass tubing used to transport the sample through the heated section of the sample case, four 250 ml impingers and an EPA Method 17 control unit. The first impinger contained 100 ml of 0.1 N H_2SO_4 solution. The second and third impingers contained 100 ml each of 0.1 N NaOH. The fourth impinger contained 200 grams of silica gel. Data collected at the CFFF indicate that measured Cl_2 concentrations are below our detection limits. Therefore, all gas phase chlorine data are assumed to be as HCl, although it is recognized that there may be some Cl_2 present. A schematic of the flow train and related control unit are shown in Figure 2-1.

2.1.2 Condensed Phase Chloride Sampling

Grab samples of bulk solids were taken at Feed Tank, Baghouse, and ESP outlets every two hours. A Feed Tank sample is a mixture of pulverized coal and seed being fed to the primary combustor, therefore, Feed Tank chloride level

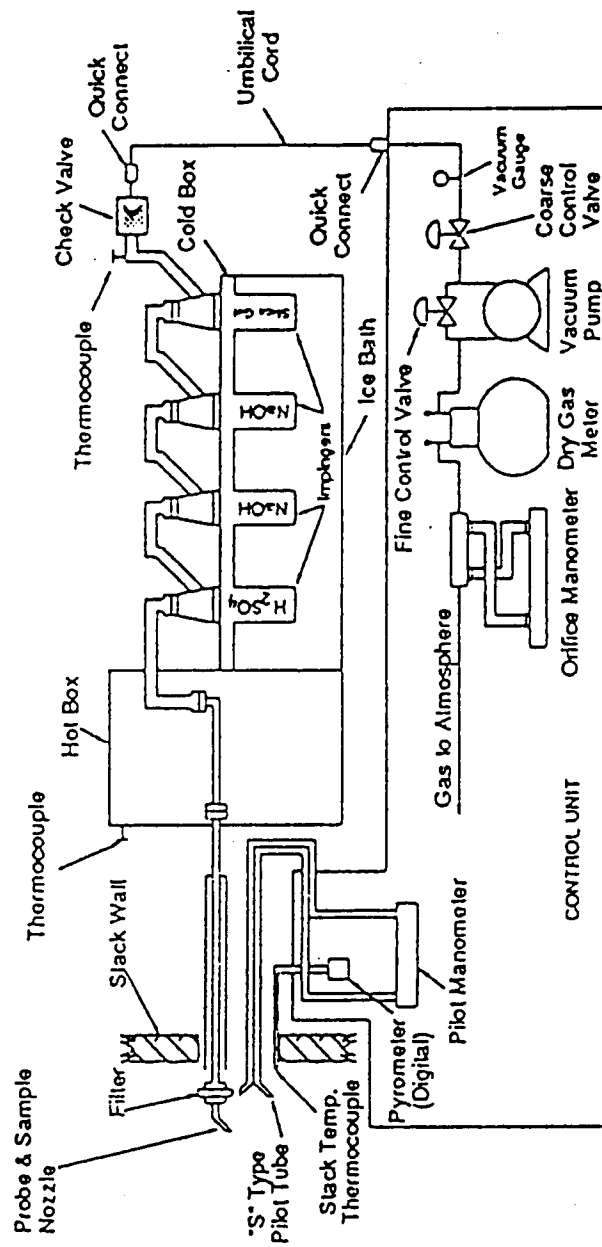


Figure 2-1. Schematic of HCl/Cl₂ Sampling Train

basically represents the total chlorine input level to CFFF. In the LMF Series tests carried out so far, since no recycled seed material is used, the Feed Tank chloride level would not show the effect of chloride build-up.

Besides the bulk solid samples mentioned above, composite samples were also taken from the Superheater Ash, Air Heater Ash, and the Radiant Furnace slag. Particulate samples of the entrained material at SHTM outlet were also obtained by collecting the filter cakes from the sampling probe described earlier.

2.2 Analysis of Gas Sampling Results

2.2.1 HCl-Emission Dependency on Temperature and K_2/S Ratio

All gas phase chloride measurements for LMF4-Q to LMF4-T tests were carried out using the UTSI HCl/Cl₂ sampling train providing mass loading data along with the chloride concentration (PPM) data. Results of these measurements are shown in Figures 2-2 to Figure 2-7.

From Figures 2-2 to 2-4, it is shown that higher gas temperatures result in higher concentrations of gas phase chloride at each sampling location. Whereas, Figures 2-5 to 2-7 show that the emission level is inversely proportional to molar K_2/S ratio, with the concentrations decreasing sharply at K_2/S above 1.0.

The average gas temperatures at SHTM outlet, BH outlet and ESP outlet are summarized in Table 2-1 along with the related HCl-emissions.

From Table 2-1, it is evident that the average temperatures are in a sequence of SHTM Outlet > ESP Outlet > BH Outlet. However, the HCl concentrations appear to follow a pattern of BH Outlet > ESP Outlet > SHTM Outlet. This is completely opposite of the trends shown in Figure 2-2 to Figure 2-4. This

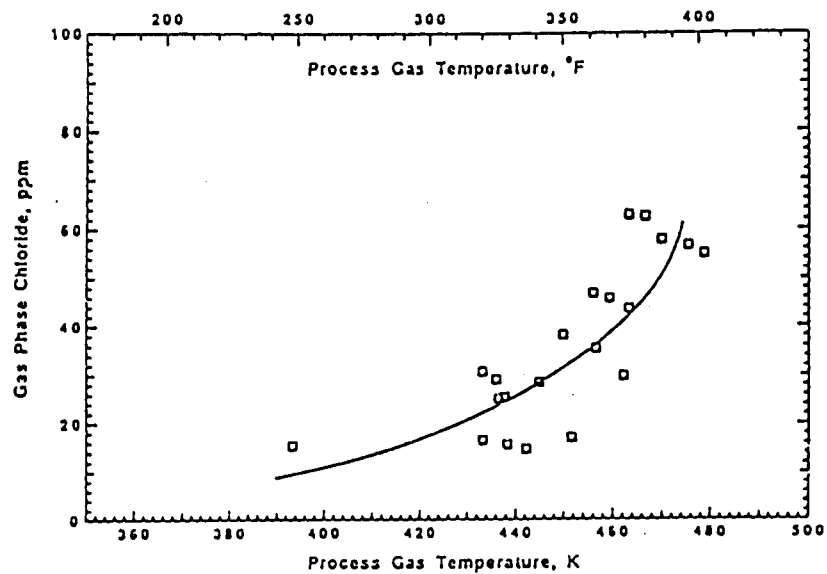


Figure 2-2. Effect of Gas Temperature on Measured Chloride Concentration at the SHTM Outlet

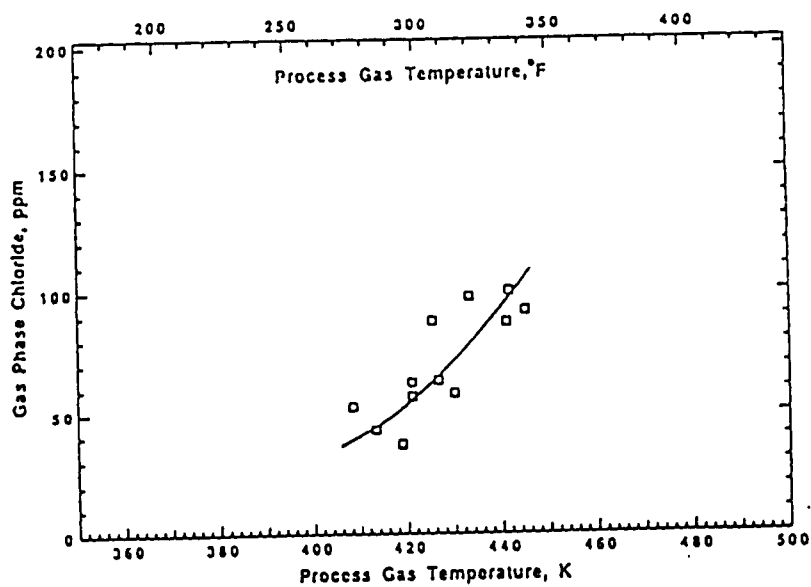


Figure 2-3. Effect of Gas Temperature on Measured Chloride Concentration at the ESP Outlet

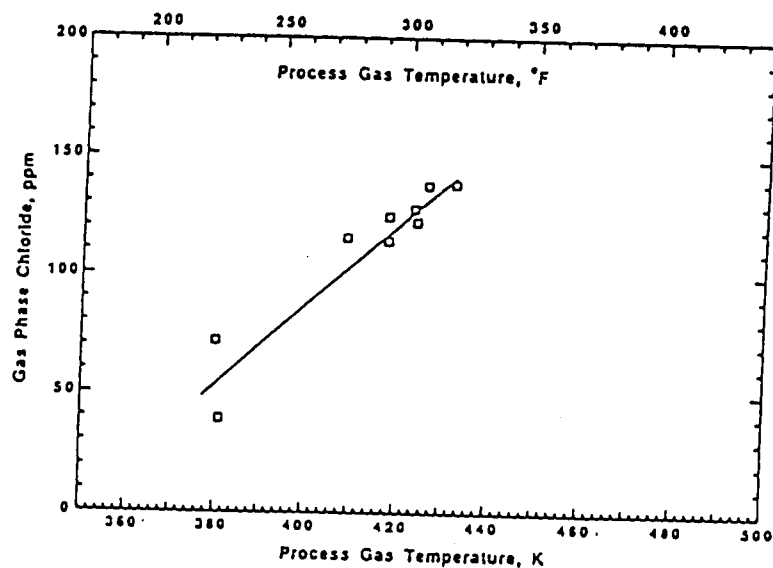


Figure 2-4. Effect of Gas Temperature on Measured Chloride Concentration at the BH Outlet

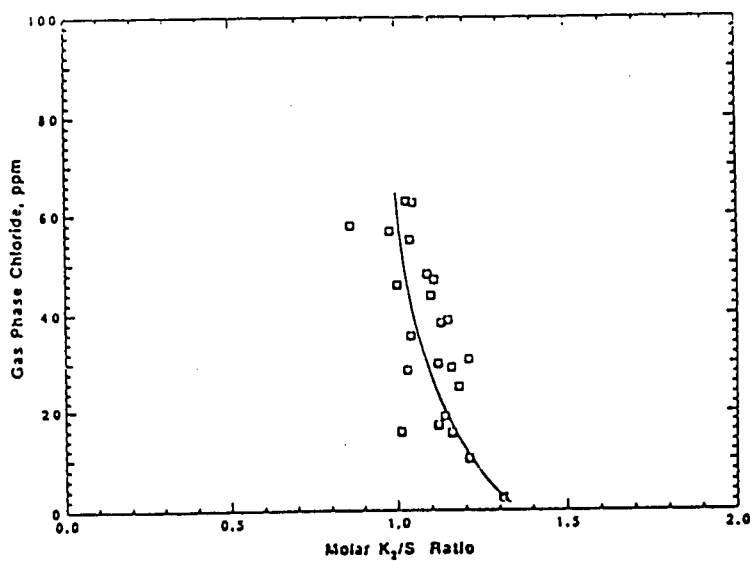


Figure 2-5. Effect of K₂/S Ratio on Measured Chloride Concentration at the SHTM Outlet

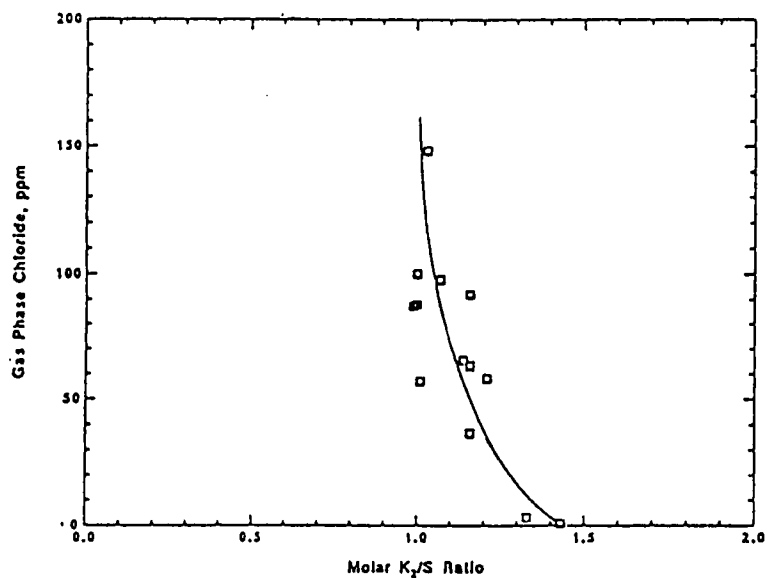


Figure 2-6. Effect of K_2/S Ratio on Measured Chloride Concentration at the ESP Outlet

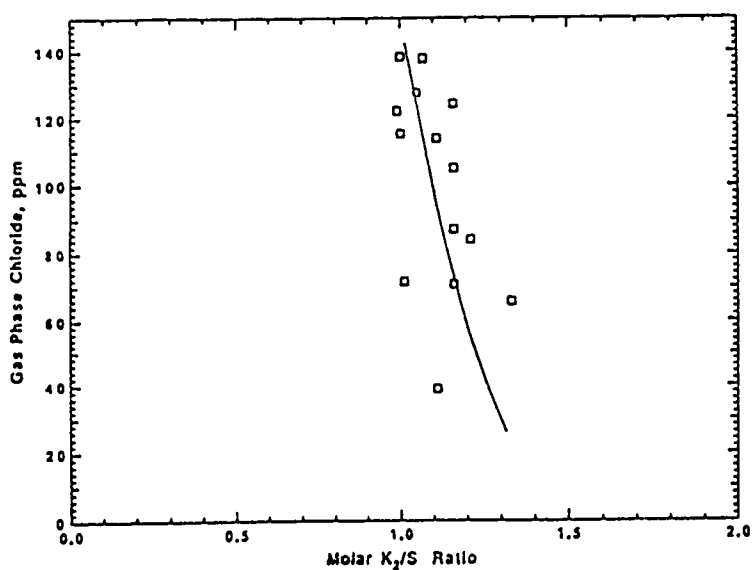


Figure 2-7. Effect of K_2/S Ratio on Measured Chloride Concentration at the BH Outlet

**Table 2-1. Temperature and HCl Concentration
at Selected Gas Sampling Locations**

Sampling Location	Temperature (K)	HCl Concentration (PPM)
SHTM Outlet	460	50
ESP Outlet	440	94
BH Outlet	420	127

apparent discrepancy further shows the necessity of investigating the chloride chemistry in BH and ESP. Therefore, controlled bench scale experiments were carried out to study the chemical reactions possibly takes place inside BH/ESP by simulating the BH test conditions. The results and analysis of these experimental data are given in Chapter 5.

2.2.2 HCl-Emission Level from MHD System and the Related EPA Criterion

Based on the municipal solid waste (MSW) incineration, the Clean Air Act amendment of 1990 requires that the emission of HCl gas/aerosol from a continuous source must be no higher than 10 tons/year. HCl-emission measurements from the LMF4-U and LMF4-V tests are converted to the unit of tons/year on a basis of 365 days/year continuous operation. Comparisons of these converted data and the proposed EPA criterion for MSW incinerations are then given in Tables 2-2 and 2-3.

Table 2-2 shows that the average HCl-emissions from LMF4-U Test on an annual basis is about 90.6 % above the New Clean Air Act amendment. Therefore, it is important to pursue research studying the factors responsible for MHD HCl-emissions and then developing appropriate options to control the

**Table 2-2. Comparison of LMF4-U HCl-Emissions and
the Proposed EPA Criterion**

Test	BH Outlet	ESP Outlet	Total CFFF	Proposed EPA	Difference
Date	(g/min)	(g/min)	Emissions (tons/year)	Criterion (tons/year)	%
8/02/90	21.15	15.91	19.48	10	94.9
8/01/90	17.01	13.57	16.07	10	60.7
8/05/90	16.53	24.13	21.37	10	113.7
8/11/90	18.84	17.92	19.32	10	93.2
Average			19.06	10	90.6

**Table 2-3. Comparison of LMF4-V HCl-Emissions and the
Proposed EPA Criterion**

Test	BH Outlet	ESP Outlet	Total CFFF	Proposed EPA	Difference
Date	(g/min)	(g/min)	Emissions (tons/year)	Criterion (tons/year)	%
11/06/90	11.28	8.39	10.34	10.00	3.4
11/07/90	19.63	10.07	15.61	10.00	56.1
11/08/90	12.29	8.40	10.87	10.00	8.7
Average	14.40	8.95	12.27	10.00	22.7
11/11/90	2.87	0.77	1.91	10.00	-80.9
11/12/90	1.71	0.80	1.32	10.00	-86.8
11/14/90	1.26	0.59	0.97	10.00	-90.3
Average	1.95	0.72	1.40	10.00	-86.0

HCl-emissions from the MHD system.

Table 2-3 shows that the HCl-Emissions from LMF4-V Test are much lower than LMF4-U test. During the eastern coal burning period, the average HCl-emission is 22.7 % above the EPA criterion. If western coal is used, the average HCl-emission is only 1.40 tons/year, which is much lower than the EPA limit.

2.3 Sampling Results for Condensed Phase Chlorides

2.3.1 Results for Feed Tank Coal Samples

Composite samples of feed tank coals were analyzed for the LMF4-U, LMF4-V, and LMF4-T tests. The analytical results are shown in Table 2-4.

Table 2-4 shows that chloride input levels for LMF4-U and LMF4-V tests are quite close, which are 2223 ppm and 2107 ppm respectively. However, the K_2/S ratios for the two tests are significantly different (i.e. 1.05 and 1.10, respectively). This difference may explain why LMF4-U and LMF4-V tests had different HCl-emission on the yearly basis (see Tables 2-2 and 2-3).

2.3.2 Results for Radiant Furnace (RF) Slag and Superheater/Air Heater (SH/AH) Ash

In Table 2-5, TS1, TS2, and TS3 refer to the test sections 1 to 3, TDM refers to the test drum module, and CS1 to CS10 refer to the cooling sections 1 to 10 in the CFFF, respectively. This table provides the data that can be used later on for the overall chlorine mass balance across the CFFF.

Table 2-4. Chloride Analysis for Feed Tank Coal

Test No.	Sample No.	K2/S	Cl (ppm)
LMF4-U	FC 90390	0.98	2136
	FC 90391	1.09	2288
	FC 90392	1.10	2228
	FC 90393	1.04	2240
	Average	1.05	2223
LMF4-V	FC 90400	1.01	2223
	FC 90533	1.15	1981
	FC 90536	1.14	2034
	Average	1.10	2107

**Table 2-5. Chloride Analysis for Composite RF Slag
and SH/AH Ash Samples (LMF4-V)**

Location	Average Cl Concentration (ppm)	Total Weight (lb)
RF Slag	49	55160
AH Ash	2136	6128
TS1, TS2, TS3	77	2427
Transition Section	69	1196
Ash/Slag Hopper	192	6631
TDM	1096	2078
CS1 - CS10	2012	17830

2.3.3 Condensed Phase Chloride in Solids from Outlets of SHTM, BH, and ESP

Table 2-6 shows that the average Cl concentration in the condensed phase follows an order of BH Outlet < ESP Outlet < SHTM Outlet. The measured gas phase Cl concentration, however, behaves in the opposite way as BH Outlet > ESP Outlet > SHTM Outlet (Shown in Table 2-1). This will be explained later based on the bench scale results and equilibrium calculations.

**Table 2-6. Condensed Phase Chloride Concentrations
at Different Sampling Locations**

Composite Sample No.	SHTM Solids (ppm)	BH Solids (ppm)	ESP Solids (ppm)
1	1525	1141	1367
2	2845	1283	1470
3	2464	1246	2045
4	1945	1503	1700
Average	2195	1418	1646

CHAPTER 3

EQUILIBRIUM CALCULATIONS

3.1 NASA SP-273 Equilibrium Code

A theoretical distribution of chlorine-containing species and potassium species in the CFFF was studied by using NASA SP-273 Equilibrium Code [20]. The equilibrium composition was established by minimizing the total Gibbs free energy of the system.

The Gibbs free energy per kilogram of mixture for a multicomponent system is represented by a summation over the mixture chemical species,

$$g = \sum_{j=1}^N n_j \mu_j \quad (3.1)$$

where n_j is the number of kilogram-moles of species j per kilogram of mixture, μ_j is the chemical potential per kilogram mole of species j . To reach chemical equilibrium of the mixture, the minimization of the mixture's Gibbs free energy, g , is usually subject to certain constraints such as the following mass balance constraints:

$$\sum_{j=1}^N a_{ij} n_j - b_i^0 = 0 \quad i = 1, \dots, l \quad (3.2)$$

or

$$b_i - b_i^0 = 0 \quad i = 1, \dots, l \quad (3.3)$$

where the coefficient $a_{i,j}$ is the number of kilogram-atoms of element i per kilogram-mole of species j , b_i^0 is the assigned number of kilogram-atoms of

element i per kilogram of total reactants (fuel and oxidant), and

$$b_i = \sum_{j=1}^N a_{i,j} n_j \quad i = 1, \dots, l \quad (3.4)$$

is the number of kilogram-atoms of element i per kilogram of mixture.

Defining a term G to be

$$G = g + \sum_{i=1}^l \lambda_i (b_i - b_i^0) \quad (3.5)$$

where λ_i is Lagrangian multiplier, the condition for equilibrium then becomes

$$\begin{aligned} \delta G &= \sum_{j=1}^N (\mu_j + \sum_{i=1}^l \lambda_i a_{i,j}) \delta n_j + \sum_{i=1}^l (b_i - b_i^0) \delta \lambda_i \\ &= 0 \end{aligned} \quad (3.6)$$

Treating the variations δn_j and $\delta \lambda_i$ as independent of each others gives

$$\mu_j + \sum_{i=1}^l \lambda_i a_{i,j} = 0 \quad j = 1, \dots, N \quad (3.7)$$

and also the mass balance equation (3.3).

By assuming all gases to be ideal and the interactions among the phases being negligible, the equation of state for the mixture is

$$PV = nRT \quad (3.8)$$

where P is pressure (N/m^2), V specific volume (m^3/kg), n moles (kg-mole/kg), T temperature (K), and R gas constant ($R=8314.3 \text{ J/(kg-mole)(K)}$). This equation is assumed to be correct even when small amounts of condensed species (up to several percent by weight) are present, since the volume of condensed species is very small.

Based on the above assumptions, the chemical potential of species j may be written as

$$\mu_j = \mu_j^0 + RT \ln(n_j/n) + RT \ln(P_{atm}) \quad j = 1, \dots, N_g \quad (3.9)$$

where N_g is the number of gas species and pressure P_{atm} in the above equation must be in units of atmospheres. The unit of pressure must be the same as that used in defining μ_j , at the standard state. The μ_j is defined at 1 atm in the data set used for thermodynamic properties.

For condensed species ($j > N_g$),

$$\mu_j = \mu_j^0 \quad j = N_g + 1, \dots, N \quad (3.10)$$

where μ_j^0 is the chemical potential in the standard state.

In this paper, we will assign temperature and pressure to specify the thermodynamic status of the mixture. The given temperature and pressure together with equations (3.3), (3.7), (3.9), (3.10) will thus permit the determination of compositions of the mixture. The output of the NASA SP-273 gives the mole fractions for each species in both condensed phase and gaseous phase. The mole fraction is defined as

$$x_j = \frac{n_j}{n} \quad (3.11)$$

Output has different n for equations (3.8) and (3.11). In equation (3.8), only total moles of gas species are included. In equation (3.11), sum of all moles, including condensed species, are included.

It should be also noticed that an iteration procedure is generally required to obtain the solutions of the above-mentioned equations. In the iteration proce-

dures involved in the program, it will be convenient to treat n as an independent variable.

3.2 Parameter Determination

To set up the input data in the required format for NASA SP-273 Code, a FORTRAN Program named Coal [21] was developed at UTSI. The modified form of the Coal program [22] has been used in this paper. Besides the coal analysis data, this modified Coal reads in: (1) fuel oil analysis data based on ASTM standard; (2) fuel oil-to-coal ratio (by mass flow rate); (3) K_2/S ratio, which reflects the stoichiometric amount of seed needed to convert all the sulfur into potassium-sulfur compound, such as K_2SO_4 ; (4) primary stoichiometry ratio (SR1) and secondary stoichiometry ratio (SR2), which will be defined later in this section.

The equilibrium calculations were carried out under the typical LMF4-U test conditions shown in Table 3-1 and Table 3-2.

In these two tables, stoichiometric ratio of oxygen in a combustion process is the weight ratio of oxygen actually used over the theoretical oxygen required to convert the combustible elements contained in the fuel into their stable oxides, such as CO_2 , H_2O , and SO_2 . The theoretical amounts of oxygen needed can be calculated from the flow rate (by weight) of combustible elements (C, H, S) and the stoichiometry of the complete oxidization of these elements. At CFFF, the primary stoichiometric ratio (SR1) is generally less than one, providing the primary combustion with reducing conditions. On the other hand, the secondary stoichiometric ratio (SR2) is generally greater than one, making the secondary combustion under oxidizing conditions.

**Table 3-1. Typical Operating Conditions for Primary Combustion
from Individual Run Schedule for LMF4-U Test**

Parameter	Value
Peak Temperature (K)	3000
Pressure (atm)	1.0
Stoichiometric Ratio	0.85
K ₂ /S (molar ratio)	0.85–1.30
Coal/seed/moisture(lb/sec)	0.90*
Fuel oil(lb/sec)	0.40
Air(lb/sec)	3.5
O ₂ (lb/sec)	1.5
Upstream Purge N ₂ (lb/sec)	0.10

*Where K₂/S ratio is about 1.

**Table 3-2. Typical Operating Conditions for Secondary Combustion
from Individual Run Schedule for LMF4-U Test**

Parameter	Value
Peak Temperature(K)	1500
Pressure (atm)	1.0
Secondary Air(lb/sec)	2.2
Secondary Air Temperature(K)	590
K ₂ /S Ratio	1.0
Secondary Stoichiometry	1.05 - 1.10
Downstream Purge N ₂ (lb/sec)	0.30

In the calculations, temperature, K_2/S ratio and stoichiometric ratio are chosen to be the major variable parameters. The situations before and after secondary combustion were considered respectively by assigning different set of parameter ranges. Two sets of parameters used in the calculations under conditions corresponding to LMF4-U test data are shown in Table 3-3 and Table 3-4.

In both Tables 3-3 and 3-4, ROC is defined as the weight ratio of oil to coal. In Table 3-3, a temperature range of 1500 - 2400 (K) is chosen to cover the normal CFFF test operation conditions before the secondary combustion. SR1 is selected from 0.80 to 0.95 in steps of 0.05, and K_2/S ratio is from 0.75 to 1.3 in also the steps of 0.05. In Table 3-4, the temperature range of 350 - 1500 (K) is chosen to cover the normal CFFF test operation conditions after the secondary combustion. SR2 is selected from 1.05 to 1.30 in steps of 0.05 and the K_2/S ratios remain the same as those in Table 3-3. Besides the major variable parameters (Temperature, K_2/S ratio, SR1, SR2) used in the calculations, the actual analysis data of coal, ash, and fuel oil from LMF4-U test were also included in the input file of program Coal. The weight ratio of oil to coal (ROC) was calculated using the LMF4-U test data [23], and a value of 0.564 was introduced into the Coal program. The analysis data of coal, ash and oil are shown in Table 3-5 and Table 3-6.

It should be noted that the actual chloride level used in our calculations with the NASA SP-273 was 2506 ppm obtained from the composite sample analysis of the feed tank coal.

In addition to those above-mentioned parameters, the effects of nitrogen purge and potassium loss were also considered in the calculations. Based on the earlier UTSI study, seventy percent of the raw coal ash is assumed to be

removed from the radiant furnace as slag, and 10 % of the seed potassium is considered to be lost as K_2O in the slag [22].

Table 3-3. Major Parameters Before Secondary Combustion

Parameter	Value
Coal	Illinois # 6
Fuel Oil	Fuel Oil # 2
Seed	K_2CO_3
Temperature (K)	1500 - 2400
Pressure	1 atm
K_2/S Ratio	0.75 - 1.30
SR1	0.80 - 0.95
Oil/Coal (Wt, ROC)	0.564

Table 3-4. Major Parameters After Secondary Combustion

Parameter	Value
Coal	Illinois # 6
Fuel Oil	Fuel Oil # 2
Seed	K_2CO_3
Temperature (K)	350 - 1500
Pressure	1 atm
K_2/S Ratio	0.75 - 1.30
SR1	0.85
SR2	1.05 - 1.30
Oil/Coal (Wt, ROC)	0.564

Table 3-5. Coal and Ash Analysis for Test LMF4-U

Proximate and Ultimate Analysis		Coal Ash Analysis	Wt %
Carbon (wt %)	66.60	SiO ₂	50.15
Hydrogen (wt %)	4.43	Al ₂ O ₃	20.67
Nitrogen (wt %)	1.67	Fe ₂ O ₃	12.85
Sulfur (wt %)	2.39	TiO ₂	1.03
Moisture (wt %)	3.30	CaO	3.27
Ash (wt %)	10.11	MgO	.89
Heating Value (BTU/LB)	11,032	Na ₂ O	0.51
Chlorine (ppm)	2569	K ₂ O	6.67
		SO ₃	4.13

Table 3-6. Fuel Oil Analysis for Test LMF4-U

Component	Wt (%)
Carbon	86.89
Hydrogen	12.92
Nitrogen	0.15
Sulfur	0.17
Heating Value BTU/LB	19,900

3.3 Na-K-Cl Species Considered in Equilibrium Calculations

In this paper, the equilibrium release of alkali metal species is also considered in order to investigate the disposition of chlorine-containing species. Tables 3-7, 3-8, and 3-9 show the potassium-containing species, the sodium-containing species and the chlorine-containing species which have been included in the equilibrium calculations.

The thermodynamic data for the species listed in Table 3-7 to Table 3-9 are included in the data base of NASA code. The calculated results and related analysis are presented in the next chapter.

Table 3-7. K Species Considered in Equilibrium Calculations

K	KO	KOH	KCl
K ₂	K (s)	K (l)	KCN (s)
KCN (l)	KCN	KH	KOH
KOH(s)	KOH(l)	KNO ₂ (s)	KHCO ₃ (s)
KHSO ₄ (s)	KNO ₃ (s)	KNO ₃ (s)	KNO ₃ (l)
KO ₂ (s)	K ₂ CO ₃ (s)	K ₂ CO ₃ (l)	K ₂ C ₂ N ₂
K ₂ O(s)	K ₂ O ₂ (s)	K ₂ O ₂ H ₂	K ₂ SO ₄ (s)
K ₂ SO ₄ (s)	K ₂ SO ₄ (l)	K ₂ SO ₃ (l)	K ₂ SO ₃ (s)
K ₂ S(l)	K ₂ S(s)	K ₂ SiO ₃ (s)	K ₂ SiO ₃ (l)

Table 3-8. Cl Species Considered in Equilibrium Calculations

TiCl	TiCl ₂ (s)	TiCl ₂	TiCl ₃
TiCl ₃ (s)	TiCl ₄ (l)	TiCl ₄	TiOCl
TiOCl ₂	AlCl	AlCl ₂	AlCl ₃ (s)
AlCl ₃ (l)	AlCl ₃	AlOCl	Al ₂ Cl ₆
CCl	CCl ₂	CCl ₃	CCl ₄
CH ₃ Cl	COCl	COCl ₂	C ₂ Cl ₂
CaCl	CaCl ₂ (s)	CaCl ₂ (l)	CaCl ₂
Cl	ClCN	ClO	ClO ₂
Cl ₂	Cl ₂ O	FeCl	FeCl ₂ (s)
FeCl ₂ (l)	FeCl ₂	FeCl ₃ (s)	FeCl ₃ (l)
FeCl ₃	Fe ₂ Cl ₄	HCl	KCl(s)
KCl(l)	K ₂ Cl ₂	MgCl	MgCl ₂ (s)
MgCl ₂ (l)	MgCl ₂	NOCl	NO ₂ Cl
NaCl(s)	NaCl(l)	Na ₂ Cl ₂	SO ₂ Cl ₂
SiCl	SiCl ₂	SiCl ₃	SiCl ₄
SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl	KCl
NaCl			

Table 3-9. Na Species Considered in Equilibrium Calculations

Na	NaO	NaOH	Na ₂
NaCl	Na(s)	Na(l)	NaCN(s)
NaCN(l)	NaCN	NaH	NaOH(s)
NaOH(l)	NaO ₂ (s)	Na ₂ CO ₃ (s)	Na ₂ CO ₃ (s)
Na ₂ CO ₃ (l)	Na ₂ C ₂ N ₂	Na ₂ O(s)	Na ₂ O(s)
Na ₂ O(l)	Na ₂ O	Na ₂ O ₂ (s)	Na ₂ O ₂ (s)
Na ₂ O ₂ H ₂	Na ₂ S(l)	Na ₂ S(s)	NaSO ₄

CHAPTER 4

CALCULATED RESULTS AND ANALYSIS

4.1 Potassium, Sodium and Chlorine Containing Species at Equilibrium

Under the typical LMF4-U test conditions, the equilibrium distribution of potassium-, sodium- and chlorine-containing species in the CFFF was calculated. The results are presented as molar percentage of each species over the total amount of their total inputs.

The original output form of NASA SP-273 equilibrium code is in molar fractions of species over total moles of gas and condensed phase species. Modifications have been made in the Subroutine OUT of the NASA code. In Subroutine OUT, possible potassium-, sodium- and chlorine-containing species are searched first. Total moles of potassium-, sodium- and chlorine-containing species are then calculated. Dividing moles of a particular chlorine-containing species by total moles of chlorine-containing species gives the molar percentage of that particular species. Similarly, molar percentages of other species are calculated. In the same Subroutine, the molar ratios of total chlorine-containing species and potassium-containing species in gas phase and in condensed phase are also calculated.

It is noted that the term molar percentage mentioned above is better to be referred as atomic percentage because some species such as chlorine could exist in diatomic forms. Therefore, atomic percentage(s) is used throughout the following text.

The following subsections will demonstrate the prevailing potassium-, sodium- and chlorine-containing species existing in CFFF at equilibrium as a result of the

NASA code calculations. The typical CFFF operating conditions before and after the secondary combustion are both included in the equilibrium calculations. The parameters chosen for temperature, potassium-to-sulfur ratio, and the stoichiometries are shown in the tables contained in the following subsections. It should be noted that the gas phase species are listed just by their molecular formulae, while the condensed phase species are listed by their molecular formulae followed by parentheses, in which the state of the species is given. For example, KCl represents gas phase potassium chloride, whereas KCl(s), KCl(l), and KCl(c) represent liquid, solid and condensed state of potassium chloride, respectively.

4.1.1 Potassium-Containing Species at Equilibrium

Tables 4-1 and 4-2 list the atomic percentages of potassium-containing species at equilibrium before and after the secondary combustion, respectively. A chlorine content of 2506 ppm based on the feed coal analysis is used as the chlorine input in the calculations. It is of interest to know whether the compounds of potassium will be present in the aerosol/vapor phase or in the condensed phase at different temperatures under the typical CFFF operating conditions.

From the above calculated results, a relative distribution of potassium-containing species between the gas/aerosol and the condensed phase can be seen. Before the secondary combustion, the gas phase potassium species consist primarily of KOH, K, and KCl. When the temperature is above 1900 K, potassium compounds are completely in gas phase. But as the temperature drops to 1800 K, $K_2SiO_3(l)$ is formed and remains at about the same level. K_2CO_3 reveals in the condensed phase only after the temperature has lowered down to 1300 K. This is shown in Figure 4-1 (a).

**Table 4-1. Atomic Percentages of Potassium-Containing Species
Before Secondary Combustion ($K_2/S=1.00$, $SR1=0.85$)**

Species	Atomic Percentage (%)						
	2200 K	2000 K	1800 K	1700 K	1600 K	1500 K	1300 K
K	41.95	34.76	18.63	15.77	12.88	10.06	4.76
KO	0.08	0.02	0.00	0.00	0.00	0.00	0.00
KOH	54.17	61.27	47.89	50.72	53.59	56.40	55.46
KCl	3.77	3.94	4.00	4.02	4.04	4.04	4.01
KH	0.03	0.02	0.01	0.01	0.01	0.00	0.00
K ₂ CO ₃ (l)	0.00	0.00	0.00	0.00	0.00	0.00	6.09
K ₂ O ₂ H ₂	0.00	0.00	0.00	0.00	0.01	0.02	0.19
K ₂ SiO ₃ (l)	0.00	0.00	29.47	29.48	29.48	29.48	29.49

**Table 4-2. Atomic Percentage of Potassium-Containing Species After
Secondary Combustion ($K_2/S=1.00$, $SR1=0.85$, $SR2=1.10$)**

Species	Atomic Percentage (%)						
	1500 K	1300 K	1100 K	900 K	700 K	500 K	400 K
K	0.02	0.00	0.00	0.00	0.00	0.00	0.00
KOH	11.28	0.17	0.00	0.00	0.00	0.00	0.00
KCl	4.69	3.92	0.27	0.00	0.00	0.00	0.00
K ₂ SO ₄ (s)	0.00	95.91	99.73	100.00	100.00	100.00	100.00
K ₂ SO ₄ (l)	48.81	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ SiO ₃ (l)	35.20	0.00	0.00	0.00	0.00	0.00	0.00

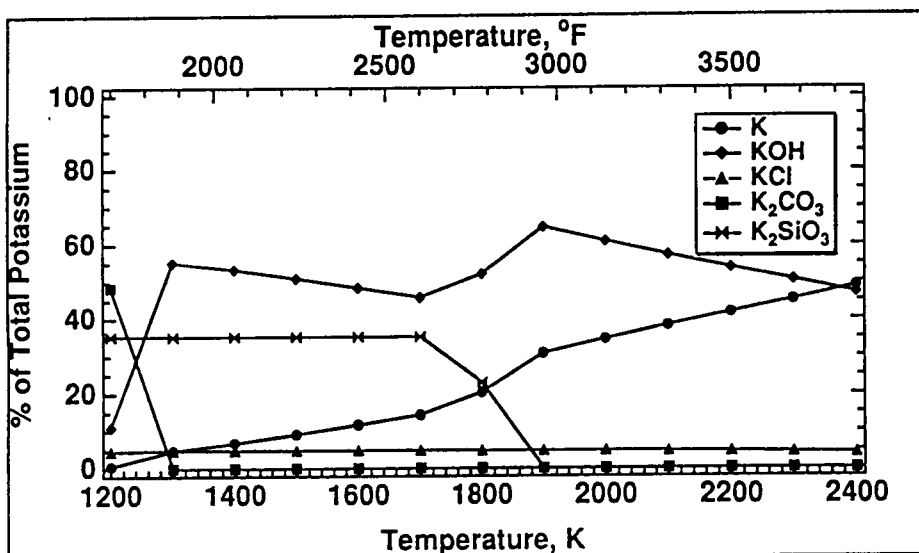
After the secondary combustion, if K_2/S ratio is equal to 1, potassium species mainly exist in the condensed phase. Here $K_2SO_4(c)$ dominates and reaches about 100 % after the temperature decreases to 900 K. Above 900 K, low levels of K, KOH, and KCl still exist in the gas phase. Meanwhile, if K_2/S ratio is greater than 1.06, condensed phase KCl(s) also exist, making up of about 5 % of the total potassium species at temperatures below 900 K. This is shown in Figure 4-1 (b).

4.1.2 Sodium-Containing Species at Equilibrium

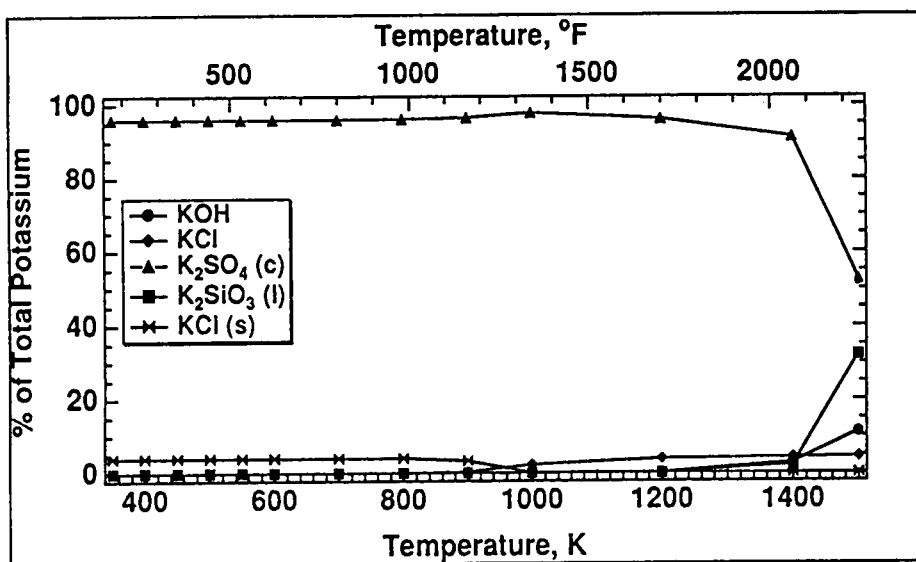
Table 4-3 shows that before secondary combustion, sodium-containing species are completely in gas phase. NaOH and Na prevail the distribution with more than 95 %, whereas NaCl takes about 2 - 5.5 %. The distribution of sodium-containing species after secondary combustion is shown in Table 4-4. The gas phase mainly consists of NaOH and NaCl in 1500-1400 K temperature range. Then NaCl and K_2SO_4 dominate the gas phase in 1400-900 K temperature range. Dichloride of sodium (Na_2Cl_2) is also formed at temperature between 1200-900 K. Table 4-4 also shows that as temperature drops to 700 K, sodium-containing species are converted completely into condensed phase as of NaCl(s).

4.1.3 Chlorine-Containing Species at Equilibrium

According to Table 4-5, KCl dominates the chloride distribution with 92 - 99 % of the total chlorine-containing species before secondary combustion, and the low levels of HCl, NaCl, Cl, and K_2Cl_2 make up the rest. No condensed form of chlorides is revealed before the secondary combustion. This is shown in Figure 4-2 (a).



(a)

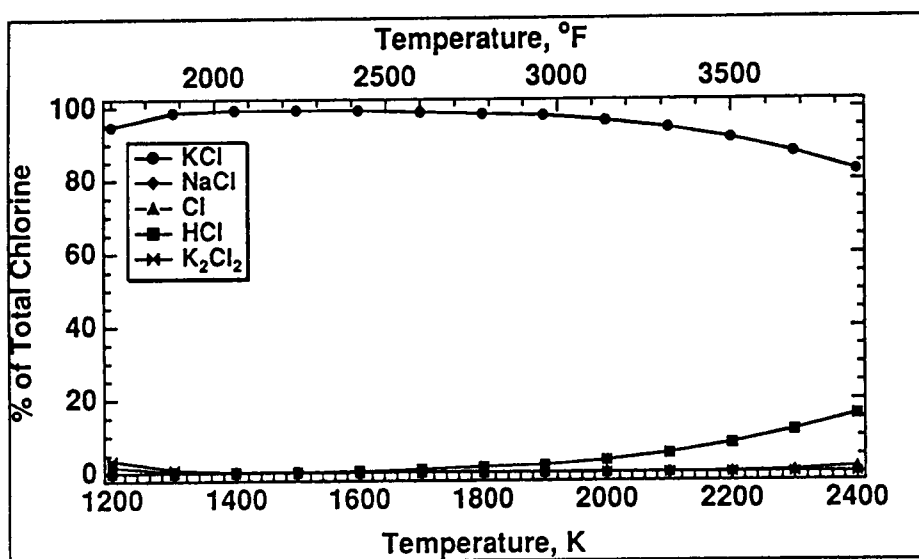


(b)

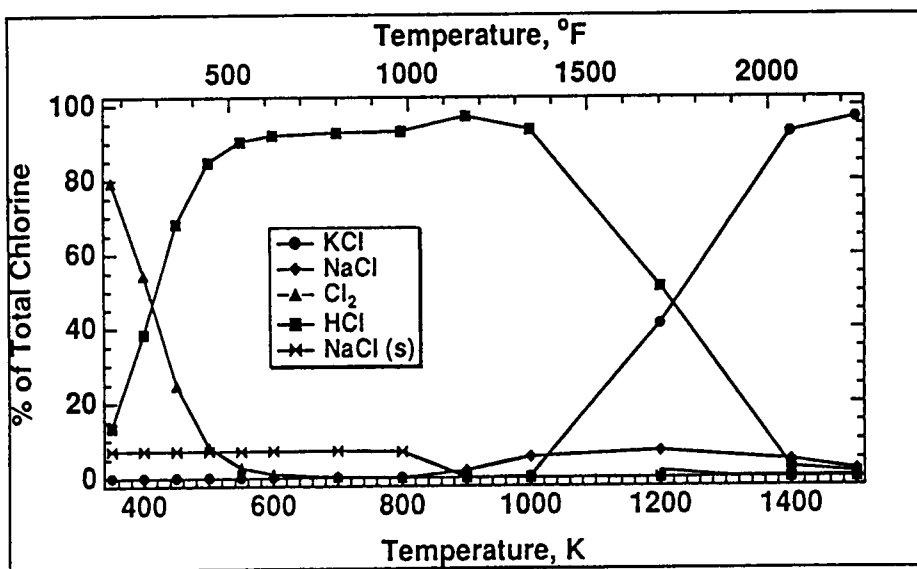
Figure 4-1. Atomic Percentage of Major Potassium Species:

(a). Before Secondary Combustion, $K_2/S=1.0$, $SR1=0.85$

(b). After Secondary Combustion, $K_2/S=1.1$, $SR1=0.85$, $SR2=1.10$



(a)



(b)

Figure 4-2. Atomic Percentage of Major Chloride Species:

(a). Before Secondary Combustion, $K_2/S=1.0$, $SR1=0.85$

(b). After Secondary Combustion, $K_2/S=1.0$, $SR1=0.85$, $SR2=1.10$

**Table 4-3. Atomic Percentage of Sodium-Containing Species
Before Secondary Combustion ($K_2/S=1.00$, $SR1=0.85$)**

Species	Atomic Percentage (%)						
	2200 K	2000K	1800 K	1700 K	1600 K	1400 K	1300 K
Na	67.40	62.50	55.73	51.44	46.89	35.78	29.65
NaO	0.12	0.03	0.01	0.00	0.00	0.00	0.00
NaOH	30.16	34.95	40.78	44.23	48.56	59.10	64.89
NaCl	2.24	2.44	3.43	4.29	4.51	5.09	5.43
NaH	0.07	0.07	0.06	0.05	0.04	0.03	0.02

**Table 4-4. Atomic Percentage of Sodium-Containing Species After
Secondary Combustion ($K_2/S=1.00$, $SR1=0.85$, $SR2=1.10$)**

Species	Atomic Percentage (%)						
	1500 K	1400 K	1200 K	1000 K	900K	700K	500 K
Na	0.56	0.10	0.00	0.00	0.00	0.00	0.00
NaO	0.02	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	70.89	35.25	0.36	0.01	0.00	0.00	0.00
NaCl	27.79	63.21	99.07	76.82	25.90	0.01	0.00
Na ₂ SO ₄	0.73	1.06	0.28	13.95	59.06	0.01	0.00
NaCl(s)	0.00	0.00	0.00	0.00	0.00	99.99	100.00
Na ₂ Cl ₂	0.00	0.01	0.29	9.22	15.03	0.00	0.00

**Table 4-5. Atomic Percentage of Chlorine-Containing Species
Before Secondary Combustion ($K_2/S=1.00$, $SR1=0.85$)**

Species	Atomic Percentage (%)						
	2200 K	2000 K	1800 K	1700 K	1600 K	1500 K	1300 K
KCl	92.87	95.29	98.36	98.99	99.33	99.46	98.73
NaCl	0.14	0.14	0.22	0.23	0.25	0.26	0.33
Cl	0.21	0.08	0.00	0.00	0.00	0.00	0.00
HCl	6.78	4.49	1.41	0.76	0.38	0.18	0.03
K ₂ Cl ₂	0.00	0.00	0.01	0.02	0.04	0.10	0.92

The distribution of chlorine-containing species after the secondary combustion appears very interesting as shown in Table 4-6. The condensed phase consists of only NaCl(s) which is formed as temperature drops to about 800 K. On the other hand, the composition of gas phase is more complicated. KCl dominates the distribution in 1300-1500 K temperature range, while NaCl maintains a significant level at 900-1500 K temperature range. HCl increases to a prevailing level when temperature decreases to 1100 K and the same pattern maintains until temperature drops to 500 K. A significant level of Cl₂ is present at about 500 K, and increases dramatically and remains dominant at 400 K. This can be seen clearly from Figure 4-2 (b).

In the following sections, systematic studies to evaluate the effects of major operating parameters, such as temperature, K_2/S ratio and stoichiometric ratio, on the concentration of potassium- and chlorine-containing species of interest are carried out. More emphasis will be applied to chlorine-containing species such as KCl, HCl, and Cl₂ since these species are the most important from the standpoint of chloride distribution and/or HCl-emissions.

**Table 4-6. Atomic Percentage of Chlorine-Containing Species
After Secondary Combustion ($K_2/S=1.00$, $SR1=0.85$)**

Species	Atomic Percentage (%)						
	1500 K	1300 K	1100 K	900 K	700 K	500 K	400 K
KCl	96.69	80.72	5.47	0.00	0.00	0.00	0.00
NaCl	1.98	6.78	6.93	1.87	0.00	0.00	0.00
Cl	0.01	0.04	0.05	0.00	0.00	0.00	0.00
Cl ₂	0.00	0.00	0.00	0.02	0.18	8.16	54.41
HCl	1.25	12.03	87.39	97.03	92.69	84.71	38.46
K ₂ Cl ₂	0.07	0.44	0.04	0.00	0.00	0.00	0.00
NaCl(s)	0.00	0.00	0.00	0.00	7.13	7.13	7.13
Na ₂ Cl ₂	0.00	0.00	0.12	1.08	0.00	0.00	0.00

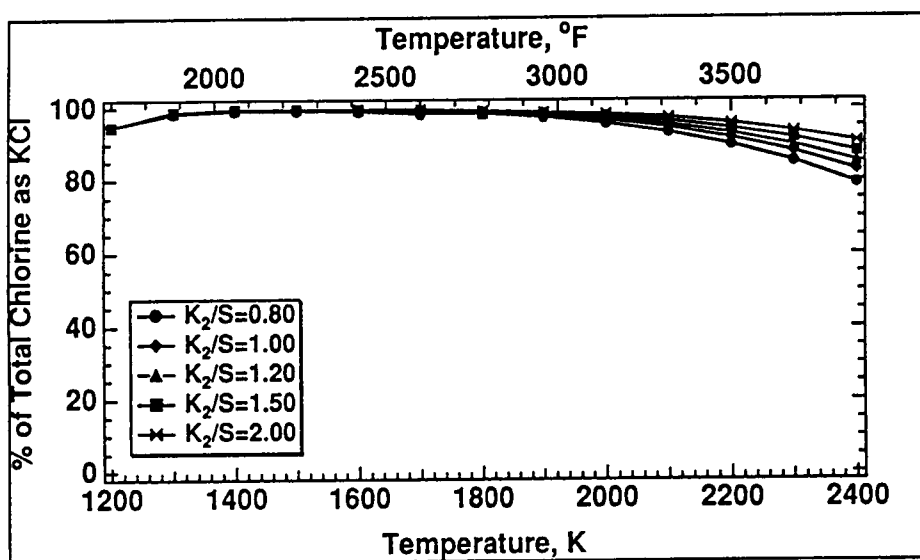
4.2 Distribution of Chloride Species Before Secondary Combustion

4.2.1 KCl Behavior

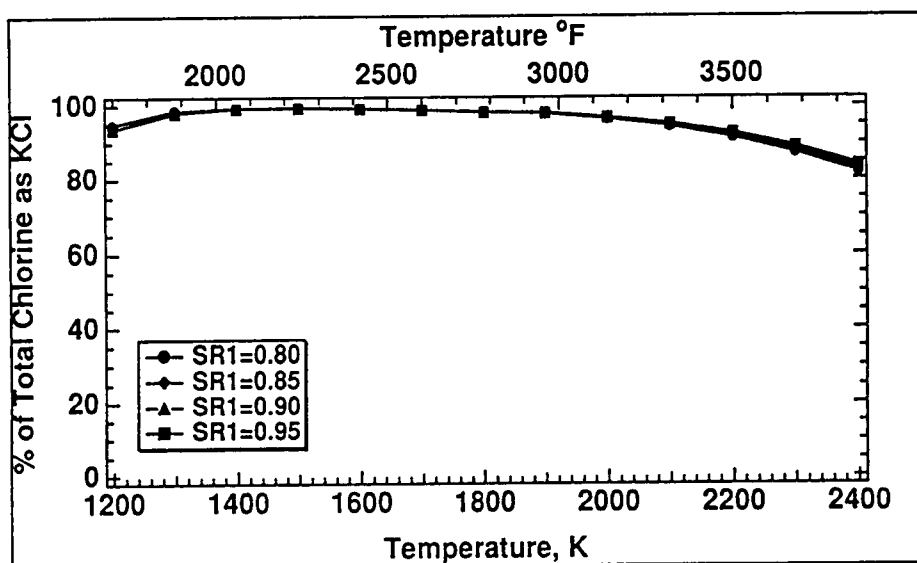
As described in Section 4.1, KCl is the dominant chloride species before secondary combustion across the entire temperature range. It comprises of about 90 % or higher of the total chloride species present in this region. This indicates that chloride has a very strong affinity for potassium radicals/species in the topping cycle of an MHD system.

Figure 4-3 shows the effects of K_2/S ratio and primary stoichiometric ratio, $SR1$, on the KCl atomic percentage of total chloride species. According to Figure 4-3 (a), KCl atomic percentage increases slightly with K_2/S ratio at temperatures above 2000 K, and remains independent of the K_2/S ratio at temperatures below 2000 K because most of the chlorine may have been converted to KCl.

According to Figure 4-3 (b), the primary stoichiometric ratio has no effect on the KCl atomic percentage.



(a)



(b)

Figure 4-3. Effect of K_2/S Ratio and SR1 on KCl Atomic Percentage of Total Chloride Species Before Secondary Combustion

(a). At Different K_2/S Ratios, SR1=0.85

(b). At Different SR1's, $K_2/S=1.0$

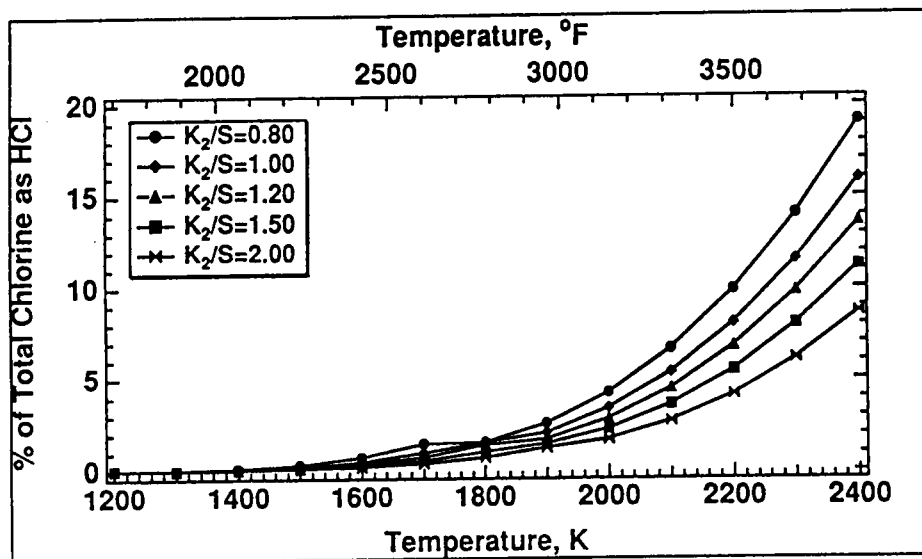
4.2.2 HCl Behavior

HCl is the second important chloride species before secondary combustion. From Figure 4-2 (a), it can be seen that HCl atomic percentage decreases with temperature from about 20 % of the total chloride species at 2400 K to about 5 % at 2000 K, and drops further to zero if temperature keeps decreasing.

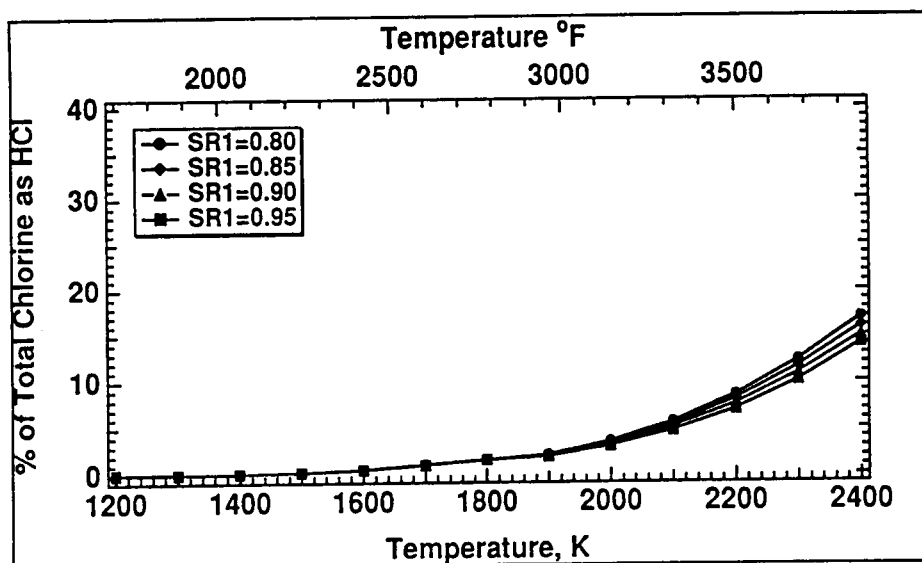
Figure 4-4 shows the relationship between HCl atomic percentage of total chloride species and K_2/S ratio and SR1. According to Figure 4-4 (a), the higher the K_2/S ratio, the lower the HCl fraction will be, provided that the temperature is above 2000 K. If however, the temperature is below 2000 K, the HCl atomic percentage becomes so small that the effects of K_2/S ratio can then be neglected. Similar to Figure 4-3 (b), it can be seen from Figure 4-4 (b) that SR1 has no significant effect on the HCl atomic percentage.

4.3 Distribution of Chloride Species After Secondary Combustion

As pointed out in Section 4.1, the compositions of chloride species after secondary combustion are more complicated. Both gas phase and condensed phase species exist simultaneously. Interactions between potassium species and chloride species, as well as between chloride species and other species such as sulfur and carbon species, may well be taking place at this stage. In this section, six chloride species, namely, KCl, KCl(s), HCl, Cl_2 , NaCl, and NaCl(s), which are the major chloride species in terms of the amount and reaction pathways, are discussed. Their dependence on performance parameters such as temperature, K_2/S ratio, and secondary stoichiometric ratio SR2, are also fully investigated.



(a)



(b)

Figure 4-4. Effect of K_2/S Ratio and $SR1$ on HCl Atomic Percentage of Total Chloride Species Before Secondary Combustion

(a). At Different K_2/S Ratios, $SR1=0.85$

(b). At Different $SR1$'s, $K_2/S=1.0$

4.3.1 KCl Behavior

Figure 4-5 shows the effects of temperature, K_2/S ratio, and SR2 on KCl atomic percentage. According to this figure, temperature has a profound impact on KCl atomic percentage. The KCl atomic percentage drops quickly from about 95 % at 1500 K to zero at 800 - 1000 K, depending upon the K_2/S ratio. This indicates that a major chloride redistribution or a phase transition reaction must be taking place in this temperature range.

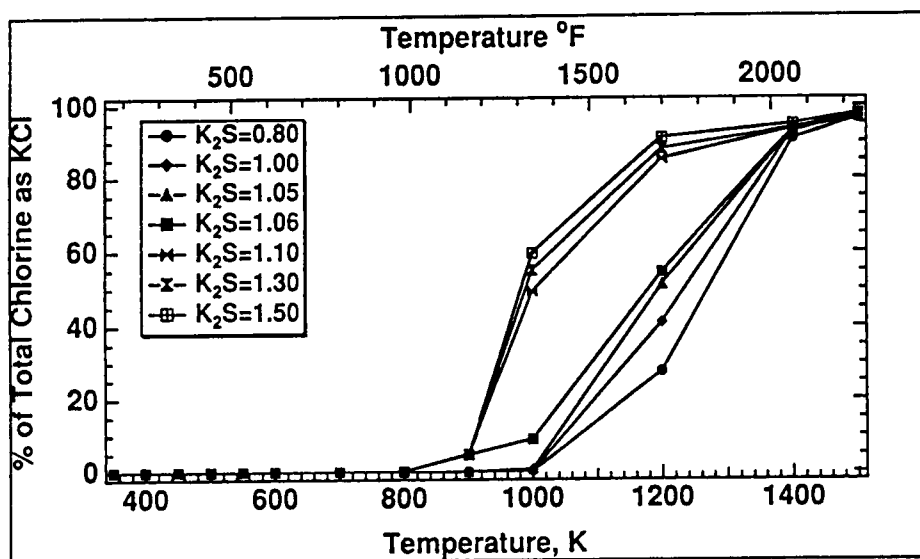
According to Figure 4-5 (a), it can be seen that KCl atomic percentage increases with K_2/S ratio, but not linearly. K_2/S ratio of 1.06 is a critical value in view of the variation in the atomic percentage. Across this critical value, there is a significant jump/drop of KCl atomic percentage with respect to K_2/S ratio.

According to Figure 4-5 (b), the secondary stoichiometric ratio SR2 has no effect on the KCl atomic percentage.

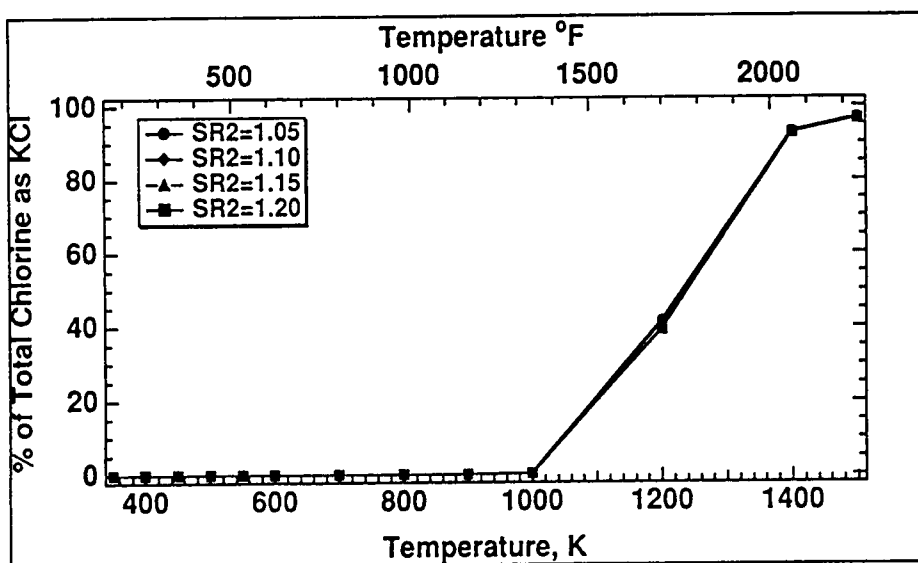
4.3.2 KCl(s) Behavior

As indicated in the previous subsection, if K_2/S is greater than 1.06, KCl(s) will also appear in the chloride species after secondary combustion. Figure 4-6 shows the effects of K_2/S ratio and SR1 on KCl(s) atomic percentage. According to Figure 4-6 (a), KCl(s) atomic percentage increases with the K_2/S ratio and is very sensitive to the K_2/S ratio. KCl(s) exists only at K_2/S ratio equal to or above 1.06, and becomes the exclusive chloride species at K_2/S ratio of about 1.15 or higher. This indicates that KCl(s) is the most stable chloride species if K_2/S ratio is above certain value.

According to Figure 4-6 (b), the secondary stoichiometric ratio SR2 has no effect on the KCl(s) atomic percentage.

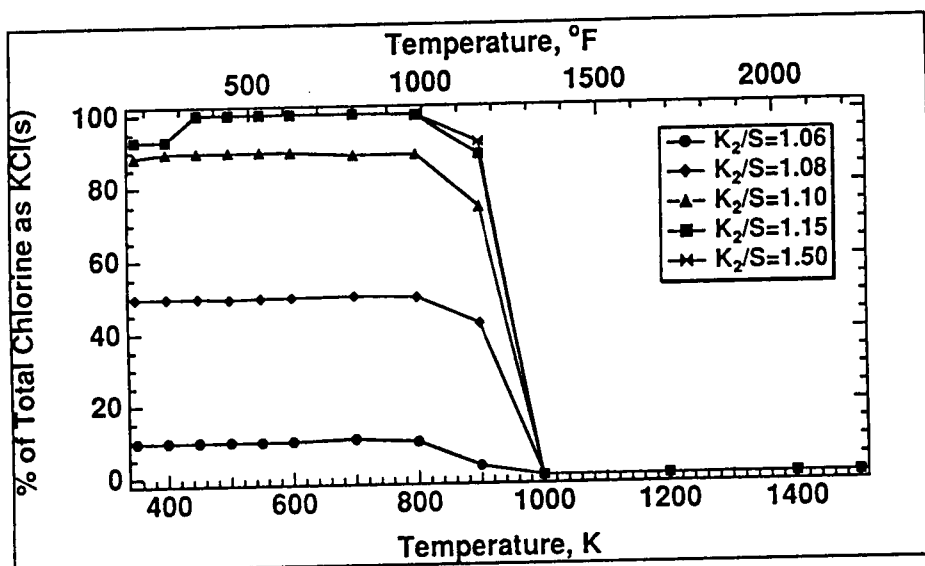


(a)

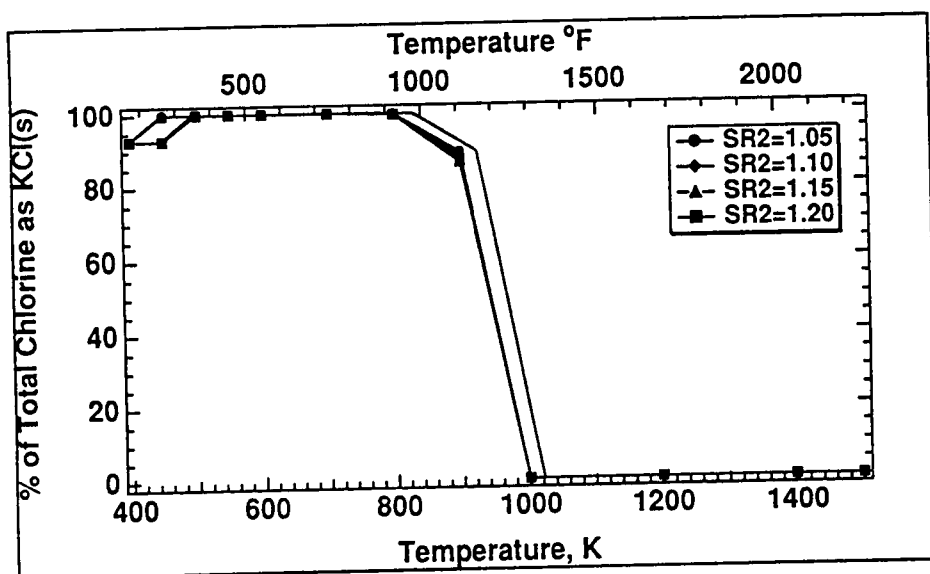


(b)

Figure 4-5. Effect of K_2/S Ratio and SR2 on KCl Atomic Percentage of Total Chloride Species After Secondary Combustion
 (a). At Different K_2/S Ratios, $SR1=0.85$, $SR2=1.10$
 (b). At Different $SR2$'s, $K_2/S=1.0$, $SR1=0.85$



(a)



(b)

Figure 4-6. Effect of K_2/S Ratio and SR_2 on KCl(s) Atomic Percentage of Total Chloride Species After Secondary Combustion

(a). At Different K_2/S Ratios, $SR_1=0.85$, $SR_2=1.10$

(b). At Different SR_2 's, $K_2/S=1.0$, $SR_1=0.85$

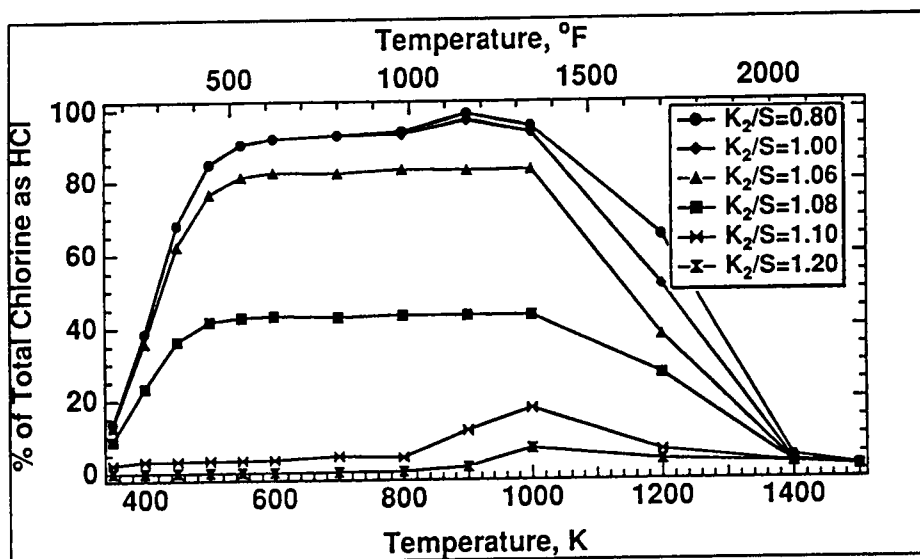
4.3.3 HCl Behavior

HCl is a major chloride species after secondary combustion. The effects of major parameters (T , K_2/S , SR_2) on HCl atomic percentage of total chloride species are shown in Figure 4-7.

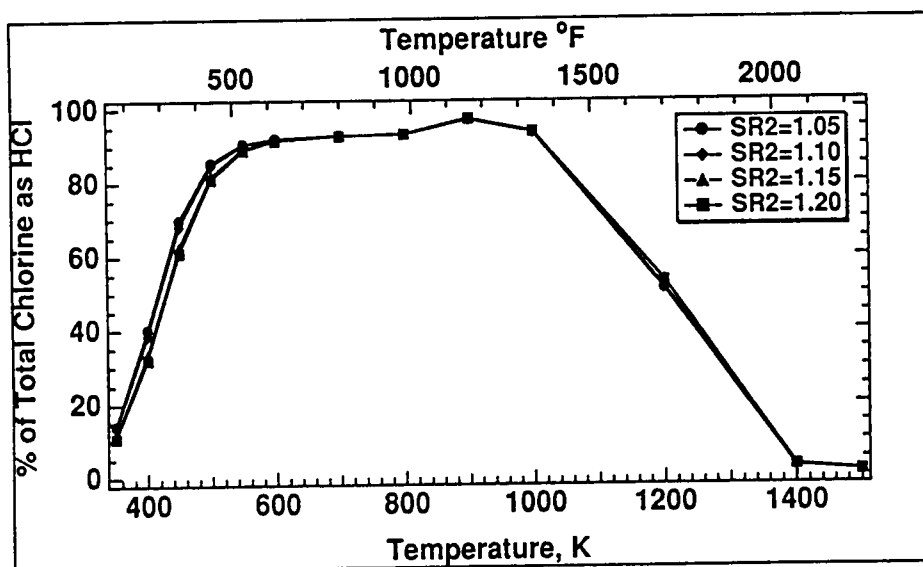
The effect of temperature on HCl concentration can be distinguished in three ranges. First, as temperature drops from 1400 K to about 1000 K, HCl fraction increases quickly from zero to its maximum value. Second, at temperatures between 1000 K and 600 K, HCl fraction remains unchanged. Third, as temperature drops further from 600 K to 350 K, HCl fraction decreases sharply. This indicates that chlorine redistribution reactions, if there are any, most likely will occur in the first and the third temperature range. As it will become clear in the following discussion, such chlorine redistribution reactions may not necessarily occur if K_2/S ratio exceeds a certain value.

Also according to Figure 4-7 (a), K_2/S ratio has a strong impact on HCl atomic percentage. HCl concentration remains relatively unchanged at K_2/S ratio below 1.06. In contrast, as K_2/S ratio increases from 1.06, HCl atomic percentage decreases dramatically. At K_2/S ratio of about 1.20 or higher, HCl atomic percentage approaches to zero and the above mentioned three distinguished temperature ranges disappear. Combining with the discussion of Subsection 4.3.2, it is clear that under high K_2/S ratio, $KCl(s)$ is the only stable chloride species. This indicates that a phase transition reaction of KCl to $KCl(s)$ is more important than any other chemical reactions at certain K_2/S values. However, the possibility that this $KCl(s)$ is converted from other potassium salts of weaker acid, e.g. $K_2CO_3(s)$, should not be ruled out.

According to Figure 4-7 (b), SR_2 has no effect on HCl atomic percentage.



(a)



(b)

Figure 4-7. Effect of K_2/S Ratio and $SR2$ on HCl Atomic Percentage of Total Chloride Species After Secondary Combustion
 (a). At Different K_2/S Ratios, $SR1=0.85$, $SR2=1.10$
 (b). At Different $SR2$'s, $K_2/S=1.0$, $SR1=0.85$

4.3.4 Cl₂ Behavior

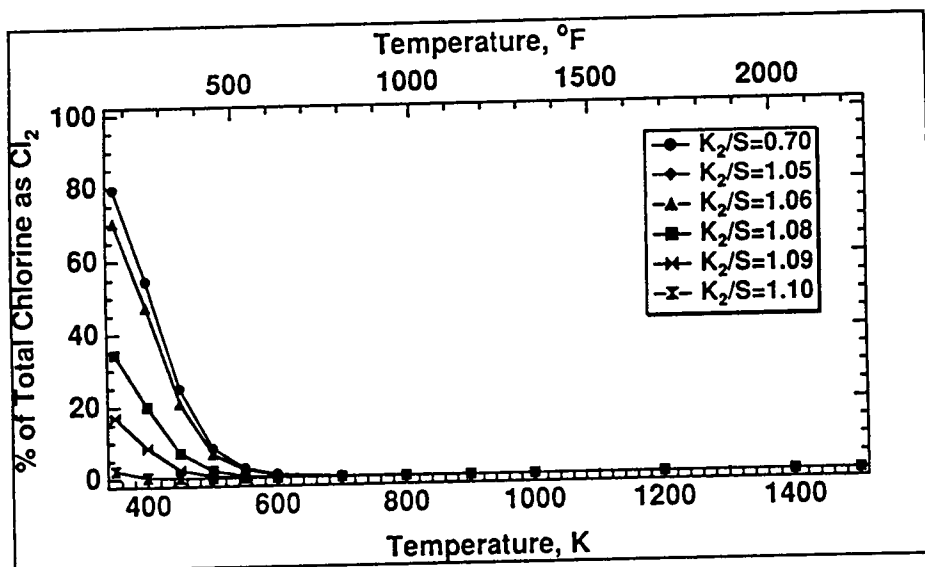
Following up the discussion of the previous subsection, Cl₂ appears only in the third distinguished temperature range of 600 - 400 K (see Figure 4-8 (a) and (b)). The lower the temperature, the higher the Cl₂ atomic percentage, provided that the K₂/S ratio is less than 1.1.

According to Figure 4-8 (a), Cl₂ atomic percentage is also very sensitive to the K₂/S ratio. At K₂/S ratios below 1.06, Cl₂ atomic percentage is independent of the K₂/S ratio. In contrast, as K₂/S ratio increases from 1.06, Cl₂ atomic percentage drops quickly. Similar to HCl, Cl₂ atomic percentage also becomes zero if K₂/S ratio is above 1.15.

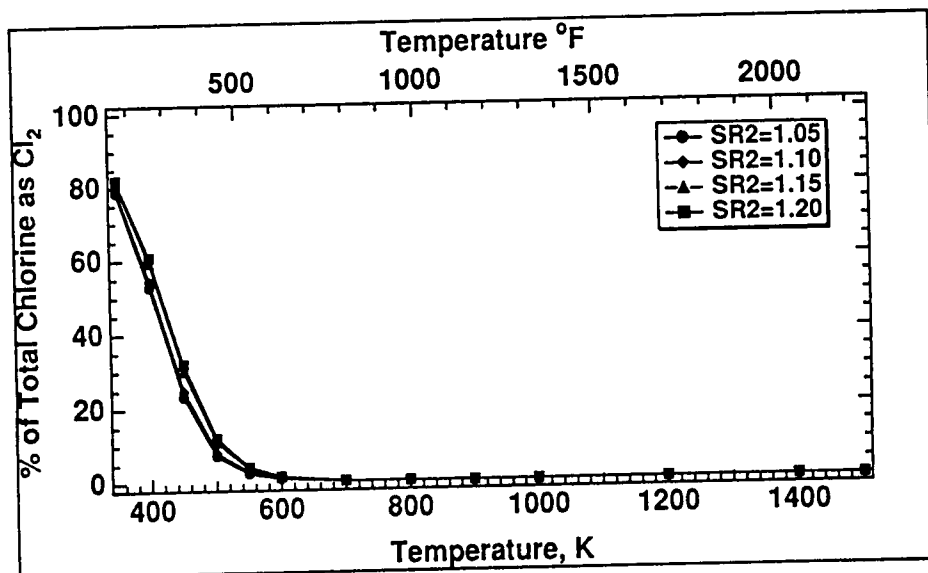
According to Figure 4-8 (b), SR2 has no effect on Cl₂ atomic percentage.

4.3.5 NaCl, NaCl(s) Behavior

Although sodium species are not of any concern of the present study, NaCl and NaCl(s) are involved in chlorine disposition chemistry and of major concern in the fouling of the downstream equipment. Therefore, the behavior of these two species is also briefly studied here. According to Figure 4-2 (b), NaCl and NaCl(s) account for about 7 % of the total chloride species at low K₂/S ratio. A phase transition reaction is expected for NaCl species. As shown earlier, KCl(s) is the only chloride species possible if K₂/S ratio is about 1.15 and higher. Therefore, it can be seen that NaCl(s) is a more stable species than K₂SO₄(s), and KCl(s) is a more stable species than NaCl(s) under the conditions considered here.



(a)



(b)

Figure 4-8. Effect of K_2/S Ratio and SR_2 on Cl_2 Atomic Percentage of Total Chloride Species After Secondary Combustion

(a). At Different K_2/S Ratios, $SR_1=0.85$, $SR_2=1.10$

(b). At Different SR_2 's, $K_2/S=1.0$, $SR_1=0.85$

4.4 Selected Potassium Species Before and After Secondary Combustion

4.4.1 KCl Behavior Before Secondary Combustion

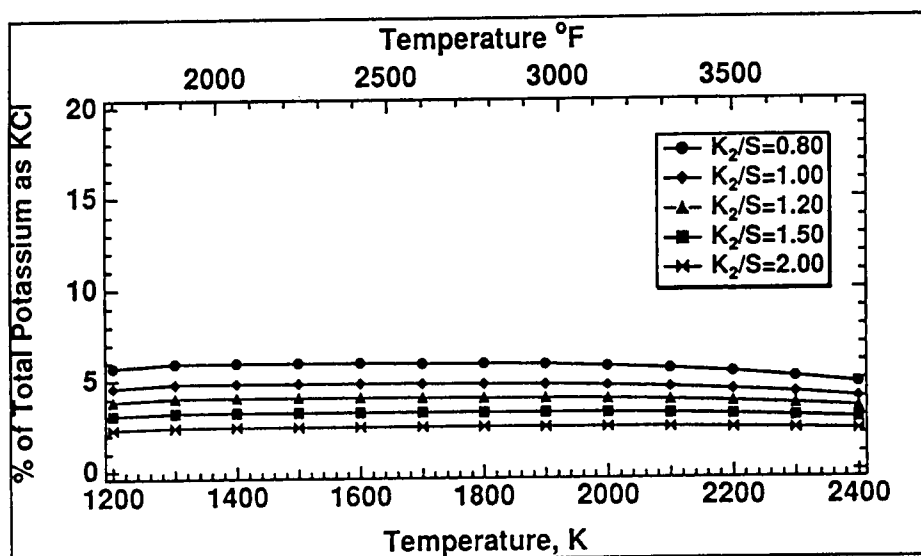
KCl comprises only a small portion (about 5 %) of the potassium species. Figure 4-9 shows the relationship between the KCl concentration expressed as atomic percentage of the total potassium species and the temperature, K_2/S ratio and SR1. According to Figure 4-9 (a), temperature has no effect on KCl atomic percentage before secondary combustion. This is also in agreement with the results given in the subsection 4.2.1, indicating that chlorine has a strong affinity for potassium radicals/species.

Also according to Figure 4-9 (a), the KCl atomic percentage decreases as K_2/S ratio increases. This is because that chlorine content is very low compared to potassium content, and it can not catch up with the increase in potassium content as K_2/S ratio increases. Hence, the existence of this excess potassium content would reduce the KCl atomic percentage.

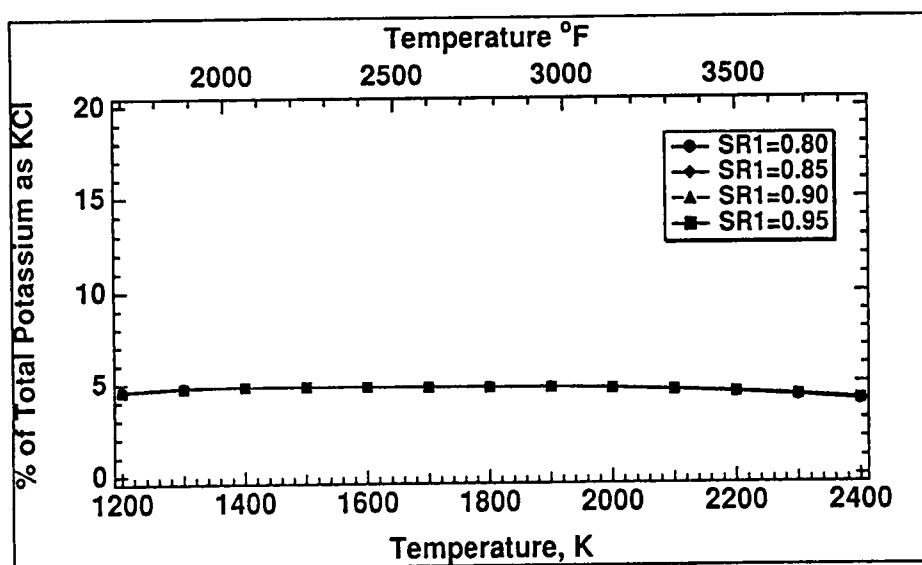
According to Figure 4-9 (b), primary stoichiometric ratio SR1 has no effect on the KCl atomic percentage.

4.4.2 K and KOH Behavior Before Secondary Combustion

K and KOH are the major potassium species before secondary combustion, comprising of more than 90 % of the total potassium species. Referring to Figures 4-10 and 4-11, it can be seen that as temperature decreases, K atomic percentage decreases while KOH atomic percentage increases accordingly. This indicates that there is a potassium transformation reaction from K to KOH taking place before secondary combustion. If temperature is below 1400 K, both K



(a)

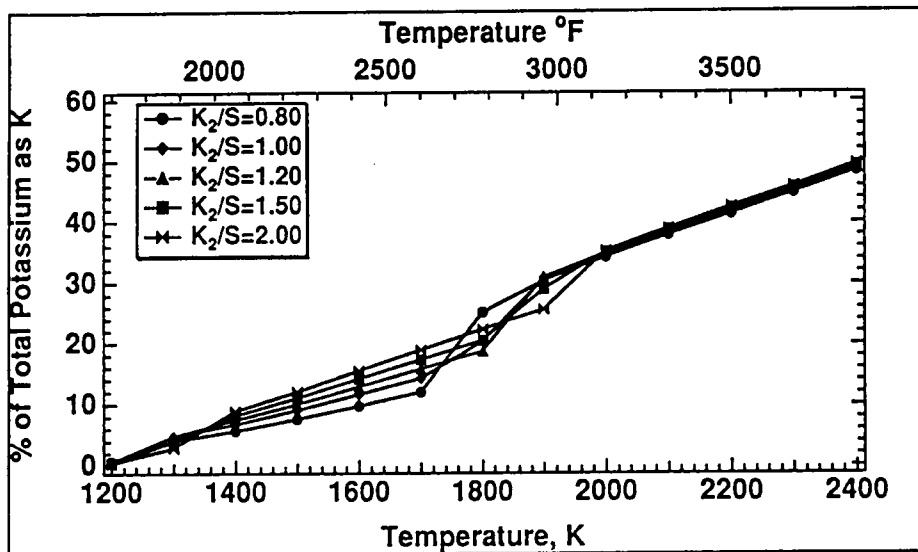


(b)

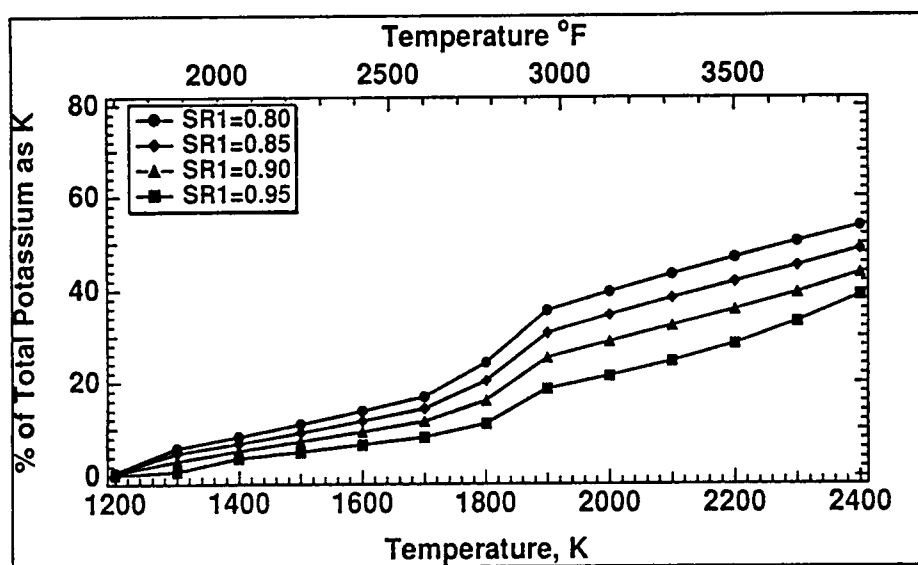
Figure 4-9. Effect of K_2/S Ratio and $SR1$ on KCl Atomic Percentage of Total Potassium Species Before Secondary Combustion

(a). At Different K_2/S Ratios, $SR1=0.85$

(b). At Different $SR1$'s, $K_2/S=1.0$



(a)

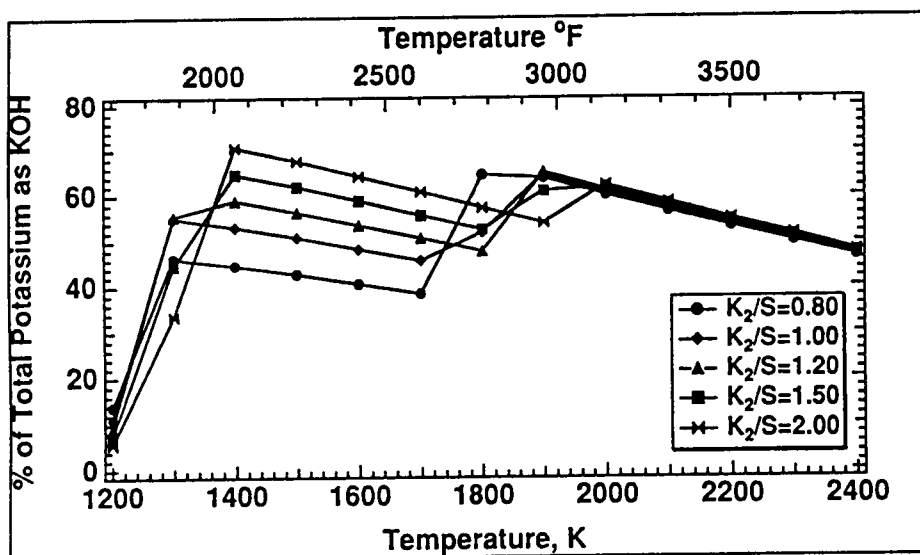


(b)

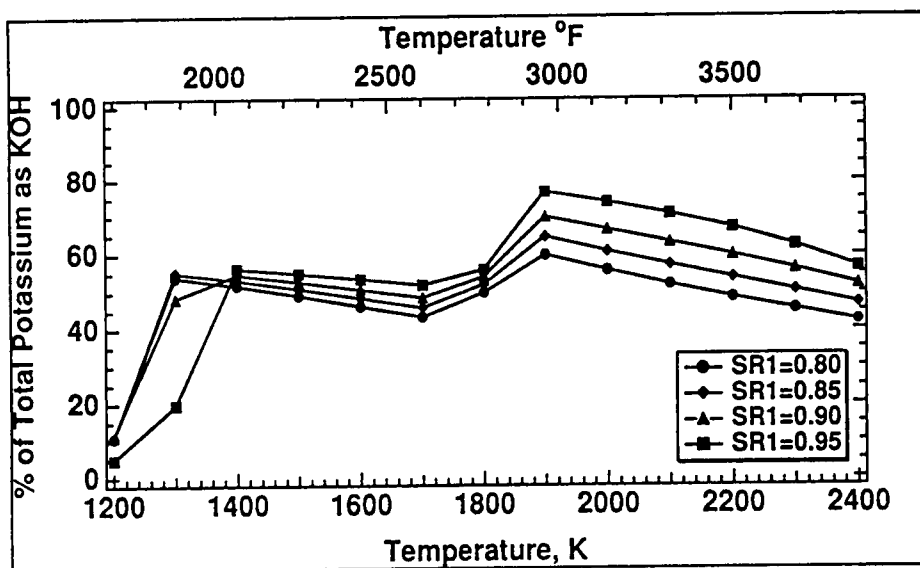
Figure 4-10. Effect of K_2/S Ratio and $SR1$ on K Atomic Percentage of Total Potassium Species Before Secondary Combustion

(a). At Different K_2/S Ratios, $SR1=0.85$

(b). At Different $SR1$'s, $K_2/S=1.0$



(a)



(b)

Figure 4-11. Effect of K_2/S Ratio and SR1 on KOH Atomic Percentage of Total Potassium Species Before Secondary Combustion

(a). At Different K_2/S Ratios, SR1=0.85

(b). At Different SR1's, $K_2/S=1.0$

and KOH atomic percentages drop to zero and potassium will be in the form of K_2CO_3 or $K_2CO_3(s)$.

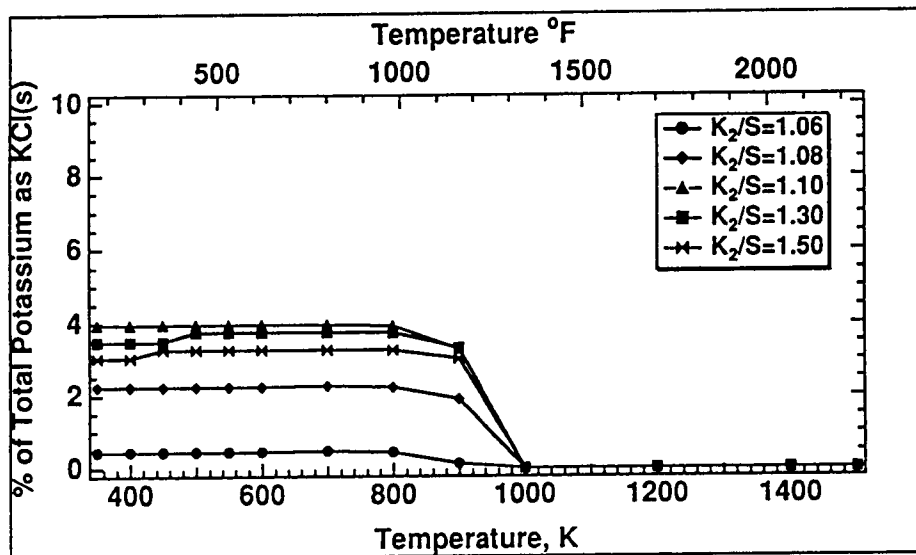
According to Figures 4-10 (a) and 4-11 (a), K_2/S ratio has negligible effect on K and KOH atomic percentage either above 1800 K or below 1400 K. However, at temperatures between 1800 K and 1400 K, both K and KOH fractions increase with the K_2/S ratio even though the K_2/S ratio affects the K atomic percentage less than the KOH's. Moreover, the impact of K_2/S ratio on K and KOH atomic percentages varies with its value, that is the K_2/S ratio has a relatively stronger impact on K and KOH atomic percentage when K_2/S ratio is less than 1.

According to Figures 4-10 (b) and 4-11 (b), SR1 has a stronger impact on K and KOH atomic percentages at high temperatures (above 1800 K). The higher the SR1 ratio, the lower the K atomic percentage, and the higher the KOH atomic percentage. This again indicates that the potassium conversion reaction of K to KOH is taking place under the conditions considered. Combining with the results shown in Figures 4-10 (a) and 4-11 (a), it can be seen that the potassium conversion reaction takes place at temperatures between 2400 and 1400 K.

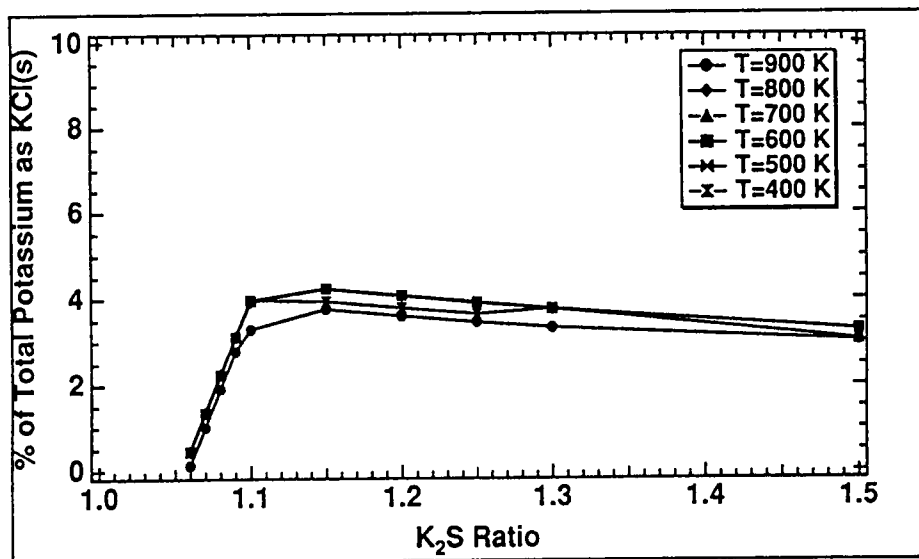
4.4.3 KCl (s) Behavior After Secondary Combustion

As discussed before, KCl(s) appears at temperature below 1000 K. If K_2/S ratio is greater than 1.06, KCl(s) will remain constant independent of temperature. This is also shown in Figure 4-12.

According to Figure 4-12 (a), KCl (s) comprises at most about 5 % of total potassium species. If K_2/S ratio is greater than 1.06, then KCl(s) atomic percentage is independent of temperature (below about 900 K). It is interesting to note the K_2/S ratio effect on KCl(s) atomic percentage. When K_2/S ratio increases from 1.06 to 1.1, KCl(s) atomic percentage also increases from about 1 % to



(a)



(b)

Figure 4-12. Effect of K_2/S Ratio and Temperature on KCl(s) Atomic Percentage of Total Potassium Species After Secondary Combustion

(a). At Different K_2/S Ratios, SR1=0.85, SR2=1.10

(b). At Different Temperature's, SR1=0.85, SR2=1.10

5 % of the total potassium species. In contrast, when K_2/S ratio is increased from 1.1 to 1.5, $KCl(s)$ is reduced from about 5 % to 3 %. It seems that there is a particular K_2/S ratio value that leads to the highest $KCl(s)$ atomic percentage. This is more clearly shown in Figure 4-12 (b). According to this figure, all the six curves are very close to each other, meaning that temperature has very little effect on $KCl(s)$ atomic percentage. The K_2/S ratio that leads to the maximum $KCl(s)$ atomic percentage is about 1.15. This indicates that when K_2/S reaches 1.15, the $KCl(s)$ atomic percentage reaches its maxima. Continued increase of K_2/S ratio above 1.15 only adds more potassium species to the system, thereby reducing the atomic percentage of $KCl(s)$ of total potassium species.

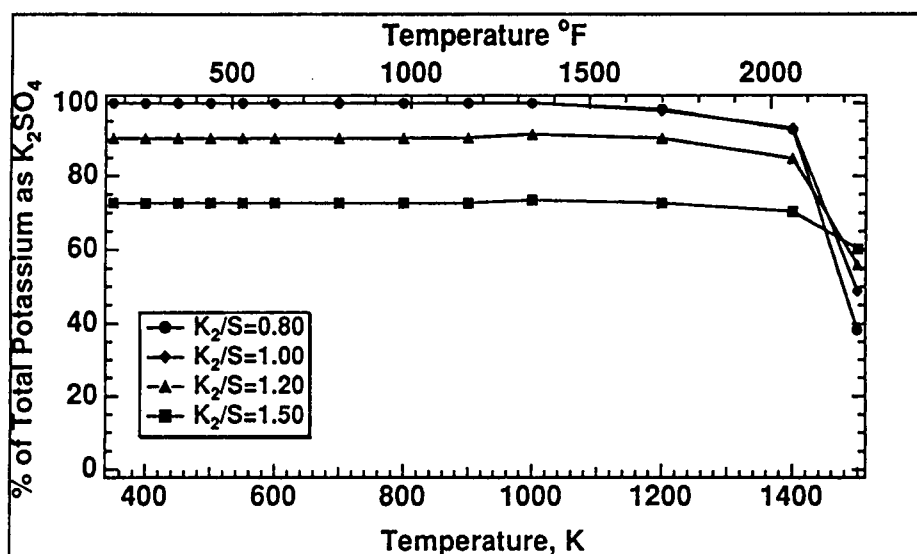
Calculations showed that SR2 has no effect on the $KCl(s)$ atomic percentage.

4.4.4 $K_2SO_4(c)$ Behavior After Secondary Combustion

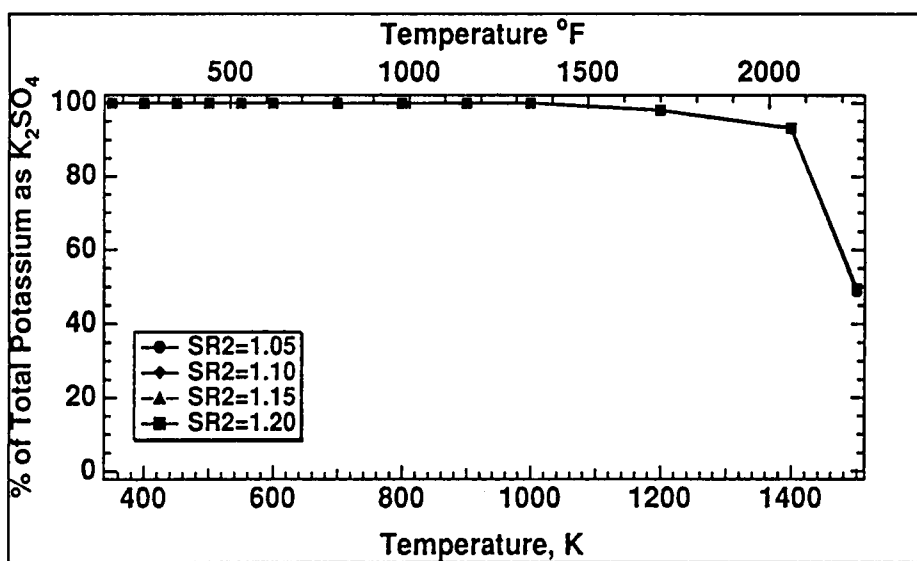
Figure 3-13 shows the effect of K_2/S ratio and SR2 on the $K_2SO_4(c)$ atomic percentage. As shown in this figure, $K_2SO_4(c)$ is the dominant potassium species after secondary combustion. It starts to form at temperature about 1600 K, and then quickly attains its equilibrium concentration at about 1400 K, and remains constant throughout the rest of the downstream region.

According to Figure 4-13 (a), $K_2SO_4(c)$ is the exclusive potassium species at K_2/S ratio equal to or less than 1. As K_2/S ratio increases, the $K_2SO_4(c)$ atomic percentage decreases because other potassium species such as $K_2SiO_3(c)$, $K_2CO_3(c)$, $KCl(s)$ start to form. This indicates that thermodynamically $K_2SO_4(c)$ is the most favorable potassium product.

According to Figure 4-13 (b), it is clear that the secondary stoichiometric ratio has no effect on the $K_2SO_4(c)$ atomic percentage.



(a)



(b)

Figure 4-13. Effect of K_2/S Ratio and SR2 on K_2SO_4 (c) Atomic Percentage of Total Potassium Species After Secondary Combustion

(a). At Different K_2/S Ratios, SR1=0.85, SR2=1.10

(b). At Different SR2's, $K_2/S=1.0$, SR1=0.85

CHAPTER 5

CONTROLLED BENCH SCALE EXPERIMENTS

From the measured CFFF results discussed in Chapter 2, a discrepancy appears between the dependence of gas phase chloride concentration on gas temperature at one sampling location and the gas phase chloride concentrations at different MHD downstream particulate control components. Figures 2-1 to 2-6 show that the measured gas chloride (ppm) levels are in an order of BH outlet > ESP outlet > SHTM outlet, whereas the temperature at these locations follows a sequence of BH outlet < ESP outlet < SHTM outlet. However, both the measured data from any one of the sampling locations and the calculated results from Chapter 4 indicate that the HCl concentration will increase as the temperature goes up. In order to explain the discrepancy and investigate the possible interactions between the gas phase and condensed phase chlorides within BH/ESP, bench scale experiments were carried out by simulating MHD test operation conditions at the BH.

5.1 Experiment Set-up

Figure 5-1 shows the bench scale experiment set-up used to simulate the MHD test conditions at the Baghouse.

The experiments aimed at examining the possible interactions between the flowing gas and the solid phase material while the gas stream from SHTM outlet passes through BH/ESP. From the left end of the experiment set-up, dry gas supply includes N₂, O₂, CO₂, and SO₂ cylinders. Each gas cylinder has a flow meter installed at the outlet to control the composition of the gas mixture as required. A calibrated metering pump is used to provide the input gas stream

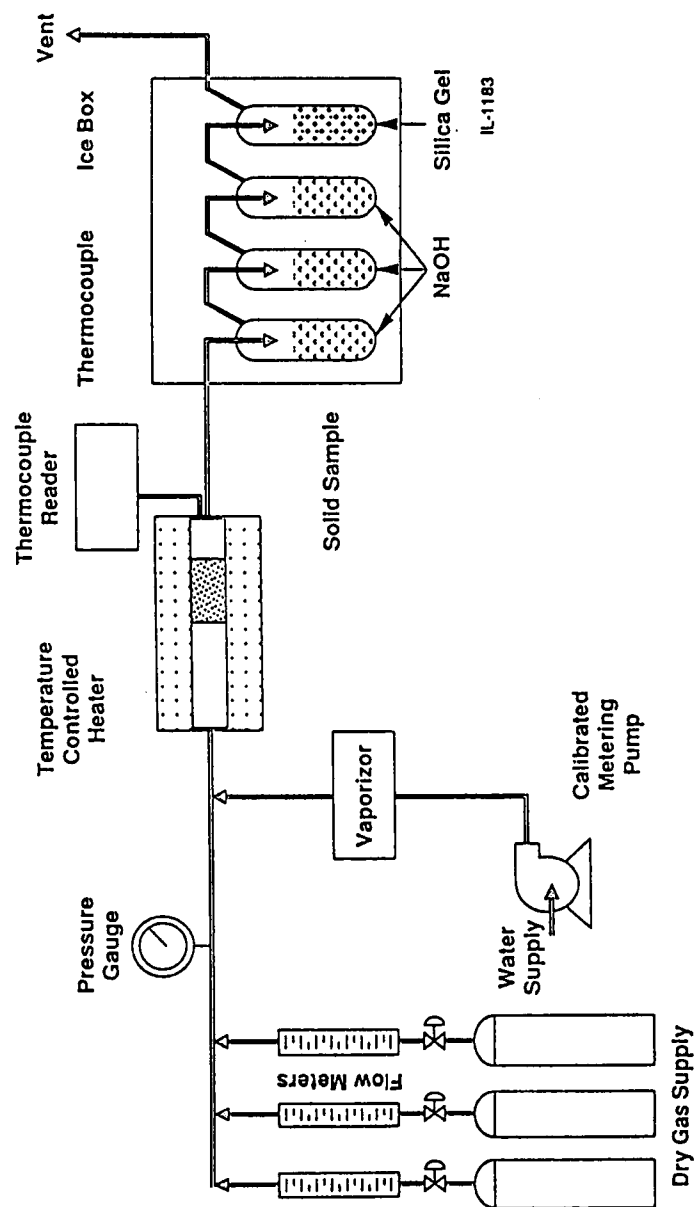


Figure 5-1. Proposed Bench Scale Chloride Reaction Apparatus

with moisture similar to that of the SHTM outlet gas stream. A temperature controlled tube furnace with three heating sections was used in the experiments.

The first section of the tube furnace is used as the vaporizer of the pumped water, the second section is used as the preheater of the moisturized gas stream, and a two inch stainless steel reaction chamber with filters at both ends is placed in the third section of the tube furnace. Solid samples consisting of K_2SO_4 , KCl , and/or K_2CO_3 were placed inside the reaction chamber to be interaction with the passing gas mixture. A separate electronic temperature controller was used to control the temperature of each furnace section, and a thermocouple reader would indicate the temperatures set for the experiments. The gas stream out of the reaction chamber will then enter the sampling train which contains four 250 ml impingers. The first three impinger contained 100 ml each of 0.1 N NaOH solution, and the fourth impinger contained 200 grams of silica gel. The four impingers are held in an ice bath and the NaOH solution in the first three impingers would extract the HCl from the gas samples. The collected NaOH extract samples were then analyzed in the chemistry laboratory.

5.2 Test Parameters

Test variables used for the bench scale experiment included gas composition, composition of potassium-containing solid samples, gas phase temperature, and reaction time. The parameter ranges are shown in Table 5-1.

For all the other test parameters listed in Table 5-1, except the gas phase composition, the bench scale experiments were carried out by flowing gas mixture composed of 61% N_2 , 20 % CO_2 , 0.04% SO_2 , 4.96% O_2 , and 14% H_2O . This gas composition was chosen to simulate the gas composition at BH/ESP inlet during MHD LMF tests. According to the equilibrium calculations in Chapter

4, major potassium-containing species after the secondary combustion within the BH/ESP operating temperature range will be $K_2SO_4(s)$, $KCl(s)$, and $K_2CO_3(s)$. Among which, $K_2CO_3(s)$ start forming only when K_2/S greater than 1.06. So the variation of $K_2CO_3(s)$ level in the solid samples in the reaction chamber will enable us to see the effect of K_2/S on the interaction between gas mixture and the solid samples. The gas phase temperature range is selected to cover the normal BH and ESP LMF test operation conditions, and the reaction time range is chosen to cover the residence time of solids in BH/ESP during the normal MHD test.

Table 5-1. Test Parameters for the Bench Scale Chloride Experiments

Parameters	Range
Gas phase SO_2 (%)*	0 - 0.04
Gas phase CO_2 (%)	0 - 24.4
Gas phase O_2 (%)	0 - 4.65
Gas phase N_2 (%)	0 - 70.91
Gas phase moisture (%)	0 - 30
$K_2CO_3(s)$ in solid samples (%)**	0 - 20
$KCl(s)$ in solid samples (%)	0.5 - 20
$K_2SO_4(s)$ in solid samples (%)	80 - 95.5
Gas phase temperature (K)	400 - 600
Gas flow rate (ml/min)	2000

* volume percentage ** weight percentage

5.3 Test Results and Analysis

To investigate the possible interactions taking place in the reaction chamber, a number of experiments were carried out. Results of these experiments were then used to evaluate the influence of different parameters discussed in the previous section on the chloride conversion from the solid sample to the gas phase stream.

5.3.1 Composition of Input Gas Mixture

A set of experiments were designed to test the influence of different input gas compositions on the interactions between the gas stream and the solid samples inside the reaction chamber. These experiments were carried out at 450 °F, 2000 ml/min gas flow rate, 14% (vol.) gas moisture, and 2 hour sampling time. All the solid samples used in this series of experiments were composed of 20% KCl, and 80% K₂SO₄. The analysis from UTSL chemistry laboratory of the results were originally reported as Cl [mg/l], which were then converted into number of moles Cl collected during the sampling time. Table 5-2 shows results at different input gas compositions. Chloride conversions from solid sample to the gas flowing out are also given in Table 5-2.

Table 5-2 shows that conversions of chloride from solid samples to gas phase remained the same for Runs G11 and G13. Run G11 had N₂, 14% H₂O as input gas composition and G13 included 5% O₂ besides N₂. From Table 5-2, it is also obvious that Run G5 has higher chlorine conversion than Run G13, which suggests that presence of CO₂ in the incoming gas flow will increase the chlorine conversion from solid sample to the gas phase. From Table 5-2, outlet gas chloride level for Run G6 is much higher than that of G5. This suggests that

inclusion of SO₂ in G6 gas stream significantly increased the chloride conversion from solid sample to the gas phase.

Gas moisture levels were also varied in another set of experiments. Parameters used for this set of experiments include 450 °F reaction temperature, 2000 ml/min gas flow rate, 2 hour sampling time, and 80 (wt)% K₂SO₄, 20 (wt)% KCl as solid samples. The test results from this set are given in Table 5-3. Chlorine conversion used in Table 5-3 is defined the same as in Table 5-2.

From Table 5-3, both Run G11 and G14 had N₂ as input gas, but with higher moisture level, G14 has significant increase in chlorine conversion. Both Run G15 and G16 had the same dry gas inlet composition, similar to CFFF BH/ESP Inlet gas composition. Again with higher moisture level, Run G16 has much higher chlorine conversion than that of Run G15. Based on results given in Table 5-3, higher moisture level in the inlet gas results in higher outlet gas phase chloride and higher chloride conversion from solid sample to gas phase.

**Table 5-2. Effect of Input Gas Composition on
Outlet Gas Phase Chloride Level**

Run No.	Inlet Gas Composition dry basis	Outlet, Cl X10 ⁶ mole	Cl Conversion* x10 ⁴
G11	N ₂	6.2	7.33
G13	5% O ₂ 95 N ₂	6.3	7.33
G5	24.4% CO ₂ , 4.65% O ₂ 70.95% N ₂	20	24.67
G6	24.4% CO ₂ , 4.65% O ₂ 0.04% SO ₂ 70.91% N ₂	65	77.50

* moles of outlet gas Cl /moles of input solid Cl

**Table 5-3. Effect of Inlet Gas Moisture on Outlet
Gas Phase Chloride Level**

Run No.	Inlet Gas Composition (vol.%)	Moisture (wt%)	Outlet, Cl X10 ⁶ mole	Cl Conversion x10 ⁴
G11	N ₂	14%	6.2	7.33
G14	N ₂	30%	12	14.00
G15	24.4% CO ₂ , 4.65% O ₂ 0.04% SO ₂ , 70.91% N ₂	10%	49	58.50
G16	24.4% CO ₂ , 4.65% O ₂ 0.04% SO ₂ 70.91% N ₂	30%	365	431.50

5.3.2 Composition of Solid Samples

Two sets of experiments were carried out to study the effects of different KCl levels, and different K₂CO₃ levels in the solid samples on the chlorine conversion from solid to gas phase.

Constant test parameters used for the first set of experiments include 450 °F reaction temperature, 2000 ml/min gas flow rate, 2 hours sampling time, and 15.86% CO₂, 4.65% O₂, 0.04% SO₂, 30% H₂O, 4.45% N₂ gas composition. The gas composition used volume percentage. The test results are given in Table 5-4.

From Table 5-4, KCl concentrations in the solid samples are in a sequence of G18 < G19 < G20 < G16, while the outlet gas phase Cl mole numbers are also in a trend of G18 < G19 < G20 < G16. However, the chlorine conversion for each run remained similar. Figure 5-2 demonstrates graphically the effect of KCl(s) concentration on the outlet gas phase chlorine level and the chlorine conversion.

**Table 5-4. Effect of KCl(s) Levels in Solid Samples
on Outlet Gas Chloride Level**

Run No.	Solid Samples (wt%)	Outlet, Cl X10 ⁶ mole	Cl Conversion x10 ⁴
G18	99 % K ₂ SO ₄ 1% KCl	200	4.73
G19	98% K ₂ SO ₄ 2% KCl	241	2.85
G20	95 % K ₂ SO ₄ 5 % KCl	317	4.5
G16	80 % K ₂ SO ₄ 20 % KCl	365	4.32

Another set of experiments was carried out to test the influence of K₂CO₃ levels in the solid samples on the chlorine conversion from solid to gas phase. Besides temperature, other constant parameters used for this set of experiments include 2000 ml/min gas flow rate, and 2 hour sampling time. Temperature used for this set was 350 °F. 5000 ppm KCl was used in each solid sample. And weight percentage of K₂CO₃ in the solid samples are 0, 2.5, 5, 7.5, 10, 12.5, 15, and 20. Figure 5-3 shows different chlorine conversions at different K₂CO₃ levels in the solid samples.

From Figure 5-3, it is obvious that the higher the K₂CO₃ level in the solid samples, the lower the chlorine conversion from solid phase to gas phase.

5.3.3 Effect of Gas Temperature on Chlorine Conversion

The solid samples used in this set of experiments contained 5000 ppm KCl in K₂SO₄(s). Constant parameters used here include 2000 ml/min gas flow rate,

2 hours sampling time, and gas containing 20.98% CO₂, 4.65% O₂, 0.04% SO₂, 14% H₂O, 60.33% N₂ by volume. Temperatures were varied in these experiments from 250 °F to 600 °F. Figure 5-4 shows the effect of gas temperature on the resulting chlorine conversion from solid phase to gas phase.

From Figure 5-4, it can be seen that the higher the gas temperature, the higher will be the chlorine conversion from solid to gas phase.

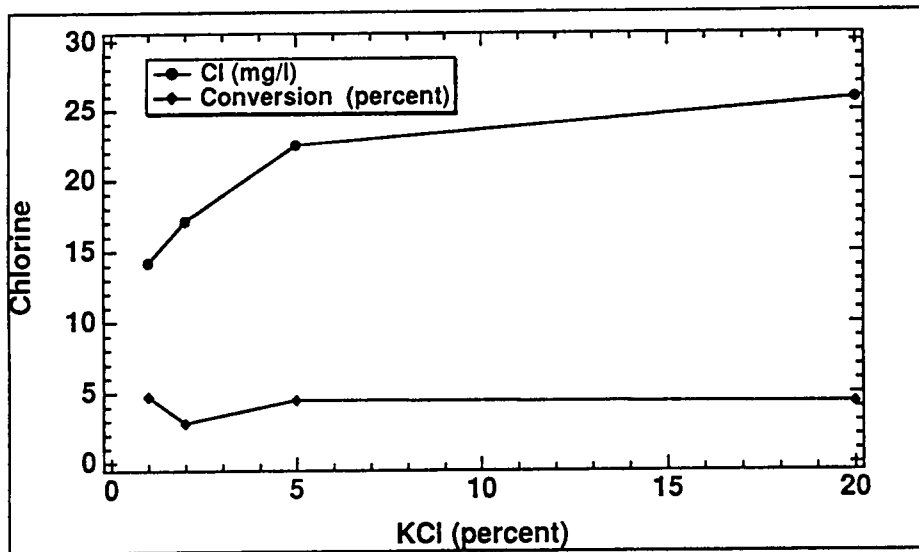


Figure 5-2. The Effect of KCl Concentration on Chloride Conversion

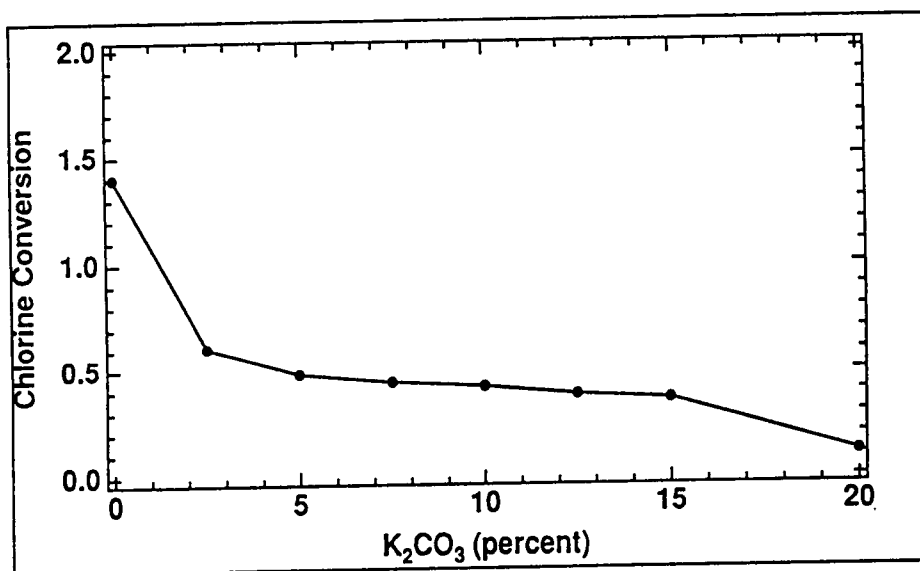


Figure 5-3. The Effect of K₂CO₃ Levels on Chlorine Conversion

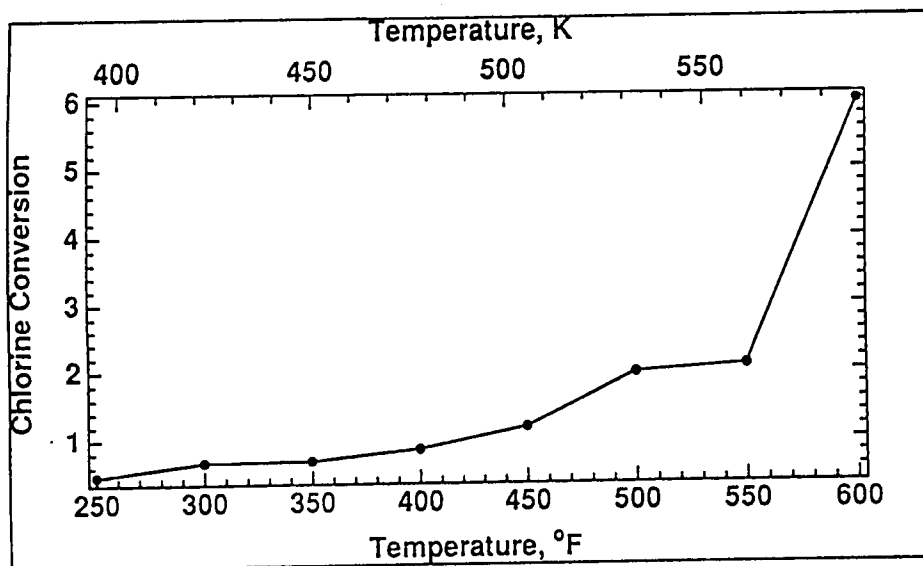


Figure 5-4. The Effect of Gas Temperature on Chloride Conversion

CHAPTER 6

COMPARISON AND DISCUSSION OF RESULTS

6.1 Comparison of Results

6.1.1 Effects of Temperature and K_2/S Ratio on HCl-Emission

From Figures 2-2 to 2-4, CFFF measurements show that at each gas sampling location, higher gas temperature results in higher gas phase HCl concentration. Whereas from Figures 2-5 to 2-7, CFFF measurements show that HCl concentration decreases sharply as K_2/S ratio increases above 1. Figure 6-1 shows the effect of temperature and K_2/S ratio on equilibrium gas phase concentration of HCl. Figure 6-1 shows that at temperature 300 - 500 K, the calculated HCl concentration goes up as temperature rises and decreases significantly as K_2/S ratio increases from 1.06. Based on the above comparison, the measured and calculated data agree well as far as the effects of temperature and K_2/S ratio on HCl concentration are concerned, providing that the measured data came from one sampling location.

Figure 5-4 shows that higher temperature favors the chloride conversion from solid to gas phase for the bench scale experiments. Meanwhile, Figure 5-3 shows that increasing K_2CO_3 level in the solid samples results in decreasing chloride conversion from solid phase to gas phase. As higher K_2/S ratio results in higher K_2CO_3 concentration in the condensed phase of combustion products, the results of bench scale experiments support the above conclusion. Figure 4-6 (a) shows that in the temperature range of 350 - 1000 K, the condensed phase chloride concentration increases as K_2/S ratio increases. This is the main reason why HCl concentration in gas phase decreases as K_2/S ratio increases.

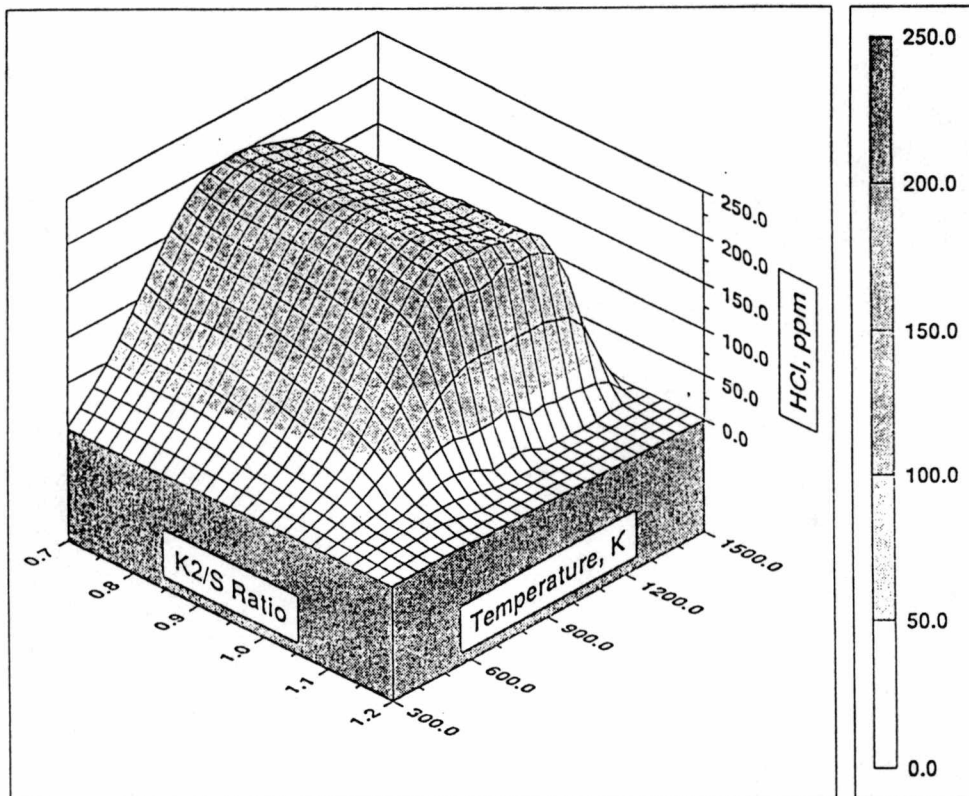


Figure 6-1. Effect of Temperature and K₂/S Ratio on
Equilibrium HCl Gas Temperature

6.1.2 Comparison of Measured and Calculated Results

Table 6-1. Comparison of Results

Sampling Location	Temperature (K)	Measured HCl Concentration (ppm)	Calculated HCl Concentration (ppm)	Condensed Phase Cl Concentration (ppm)
SHTM Outlet	460	50	150	2195
ESP Outlet	440	94	130	1646
BH Outlet	420	127	110	1418

In Table 6-1, temperature ranges and measured gas phase chloride concentrations come from Figure 3-1 to figure 3-3. The fifth column gives the average measured condensed phase chloride concentrations at each sampling location.

From Table 6-1, the temperature ranges of different sampling locations are in the order of SHTM outlet > ESP outlet > BH outlet, while the measured gas phase chloride concentration follows an order of SHTM outlet < ESP outlet < BH outlet. This disagrees with the calculated concentration results, showing a trend of SHTM outlet > ESP outlet > BH outlet.

There are two reasons for this discrepancy between the measured and the calculated gas phase HCl concentrations. First, the metal sampling probe used in the CFFF extracted gas sampling could adsorb considerable amount of HCl [24] on its inside walls. The higher the temperature is, the more adsorption will take place.

Table 6-2 gives comparison of metal probe sampling results and glass line sampling results (LMF 4-W test) under similar conditions.

**Table 6-2. Metal Probe vs. Glass Probe in
Gas Phase Chloride Measurements**

Sampling Location	Metal Probe		Glass Line		Difference *
	Cl, ppm	Cl, g/min	Cl, ppm	Cl, g/min	
SHTM Outlet	58.5	19	85.5	29	34.48 %
BH Outlet	41.3	6	52.5	8	25 %

* Difference percentage calculated as chlorine mass load difference between glass probe sampling and metal probe sampling divided by chlorine mass load from glass probe sampling and converting the fraction to percentage.

From Table 6-2, one can see that there is much more HCl adsorption on the metal probe at SHTM outlet than at BH outlet. This also explains why in Table 6-1, the measured gas phase chloride concentrations agree quite well with the calculated results at BH outlet.

From Table 6-1, one can also see that the measured condensed phase chloride concentration follows a trend of SHTM outlet > ESP outlet > BH outlet. This gives us a hint that certain chemical reactions may take place in the BH and ESP. Results from the bench scale experiments discussed in Chapter 5 confirmed that considerable amount of chloride could be converted from the condensed phase into gas phase. Since BH gas stream has a much better contact with the solid phase than the ESP gas stream, more chloride could be converted from solid into gas phase in BH than in ESP. Therefore, BH outlet would tend to have a higher gas phase chloride concentration than the ESP outlet.

6.2 Proposed Chlorine Reaction Pathways in CFFF

6.2.1 Distribution of Chlorine-Containing Species Before

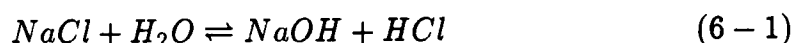
Secondary Combustion

From Figure 4-2 (a), KCl and HCl are the two major chlorine-containing species, with KCl comprising about 90 % or higher of the total chloride species present in this region.

6.2.2 Distribution of Chlorine-Containing Species After

Secondary Combustion

From Figure 4-2 (b), after secondary combustion and in the temperature range of 1000 - 1600 K, chlorides exist in gas phase, mainly as KCl, HCl, and NaCl. The KCl concentration drops quickly as temperature goes down, while HCl concentration increases at the same time. The model of Halstead and Raask [7] involves the gas phase sodium chloride reaction with water vapor to form NaOH and HCl:



Similarly, it can be assumed that transformation of KCl to HCl after secondary combustion is due to the gas phase potassium chloride reacting with the water vapor to form KOH and HCl:

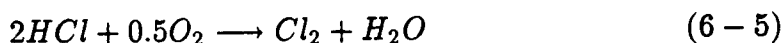


Both KCl and KOH undergo overall reaction with SO₂, SO₃, H₂O, and O₂ to form gaseous potassium sulfate, K₂SO₄. From Figures 4-2 (b) and 4-6 (a),

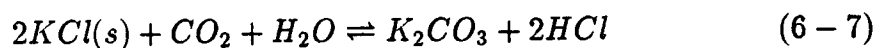
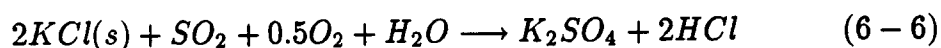
a major chloride redistribution or a phase transition reaction seems to be taking place around 800 - 1000 K. Gas phase KCl and NaCl undergo condensation to form KCl(s) and NaCl(s) respectively:



Figure 4-2 (b) shows that at K_2/S equals to 1.00, only NaCl(s) exists as condensed phase chloride, while Figure 4-6 (a) indicates that KCl(s) starts forming at K_2/S equals to 1.06. Figure 4-2 (b) also shows that between 500 - 600 K, equilibrium HCl concentration starts decreasing as temperature goes further down. Meanwhile, Cl_2 concentration increases as HCl concentration decreases. This can be explained as:



From bench scale experimental results shown in Table 5-2, both G5 and G6 gas mixtures when treated with the solid samples containing KCl(s), considerable amount of chloride concentration was detected in the outlet gas samples. Reactions (6-6) and (6-7) may explain this chloride conversion for solid to gas phase:



6.2.3 Proposed Reaction Pathways for Chlorine-Containing Species **In MHD System**

Based on the previous discussions, the proposed reaction pathways for chlorine-containing species in MHD system can be summarized as shown in Figure 6-2.

6.3 Factor Analysis on HCl-Emission

Table 6-3 gives selected calculated HCl concentrations between 550 - 350 K and at K_2/S ratio of 1.05 - 1.10.

Table 6-3. Calculated Gas Phase HCl Concentrations at Equilibrium

K ₂ /S	HCl Concentration (ppm)							
	550 K	500 K	475 K	450 K	425 K	400 K	375 K	350 K
1.05	180	170	160	140	110	80	50	30
1.06	160	150	140	120	100	70	50	30
1.07	120	120	110	100	80	60	40	20
1.08	90	80	80	70	60	50	30	20
1.09	50	50	40	40	40	30	20	10
1.10	10	10	10	10	10	10	10	0

From Table 6-3, there are a levels of factor A (K_2/S) and b levels of factor B (Temperature), and only one observation per cell. In this situation, there are exactly as many parameters in the variance analysis model as observations, and the error degree of freedom is zero. Thus a no-interaction assumption is made and the interaction mean square is used as an error mean square in our variance analysis. The factorial is also assumed to completely randomized design.

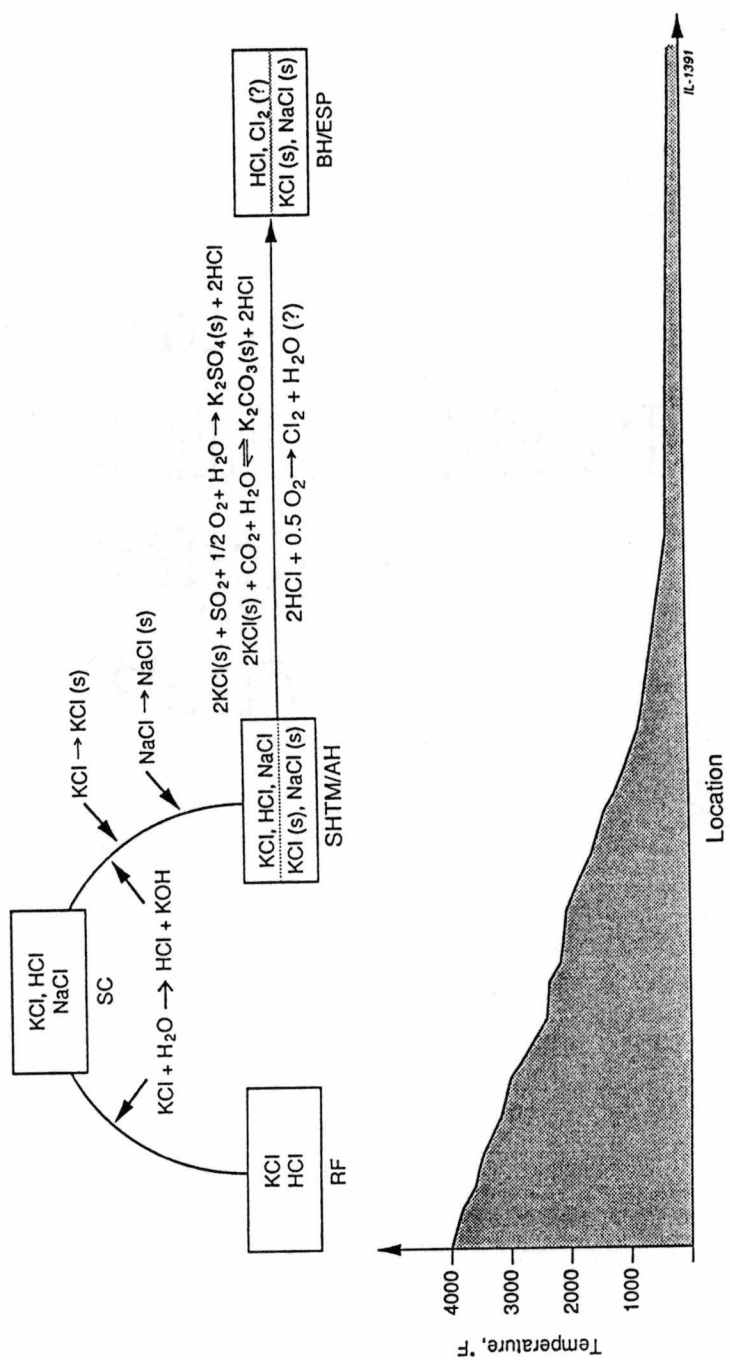


Figure 6-2. Proposed Reaction Pathways for Chlorine-Containing Species in MHD System

Therefore, a two-factor fixed-effects linear statistical model can be described by the following equation:

$$y_{ijk} = u + t_i + b_i + e_{ijk} \quad (6-8)$$

where

$$i = 1, 2, \dots, a$$

$$j = 1, 2, \dots, b$$

$$k = 1, 2, \dots, n$$

and e_{ijk} is actually $(tb)_{ijk}$

In order to test $H_0 : t_i = 0$ (no row factor effects), $H_0 : b_i = 0$ (no column factor effects), the analysis of variance is carried out as follows and the results are summarized in Table 6-4.

$$SS_T = \Sigma \Sigma Y_{ij}^2 - Y^2 / abn$$

$$SS_T = 18^2 + 17^2 + \dots + 1^2 - 322^2 / 48$$

$$= 3368 - 2160.0833$$

$$= 1207.9167$$

$$SS_{K2/S} = \Sigma Y_{i.}^2 / bn - Y^2 / abn$$

$$SS_{K2/S} = (92^2 + 82^2 + \dots + 7^2) / 8 - 2160.0833$$

$$= 658.6667$$

$$SS_{temp.} = \Sigma Y_{.j}^2 / an - Y^2 / abn$$

$$SS_{temp.} = (61^2 + 58^2 + \dots + 11^2) / 6 - 2160.0833$$

$$= 394.25$$

$$SS_{interac.} = \Sigma Y_{ij}^2 / n - Y_{..}^2 / abn - SS_{tr.} - SS_{temp.}$$

$$SS_{interac.} = 3368 - 2160.0833 - 658.6667 - 394.25$$

$$= 155.$$

$$SS_E = SS_T - SS_{subtotal}$$

$$SS_E = 1207.9167 - 1207.9167$$

$$= 0$$

Table 6-4. Variance Analysis for HCl Concentration

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	$F_{cal.}$	$F_{.05,5,35}$ $F_{.05,7,35}$	Decision
K ₂ /S	658.67	5	131.73	29.746	2.49	Rejected
Temperature	394.25	7	56.32	12.718	2.29	Rejected
Error	155	35	4.43			
Total	1207.92	47				

From Table 6-4, it is concluded that the Null hypothesis should be rejected. That is, both the row factor (K₂/S) and column factor (gas temperature) have effects on the objective function (HCl concentration). It should be noted that although we assume that the interaction effects between the row factor and the column factor are zero, the analysis does show that the mean square of interaction effect exists. Therefore, to find out a better relationship between the HCl concentration, temperature and K₂/S, one needs to include the interaction effect also.

Table 6-4 also shows that the calculated F cal. of K₂/S is 29.746, which is much bigger than the one for temperature (12.718). Magnitude of Fcal. for each factor indicates the sensitivity of its influence on the data. Therefore, statistical

analysis for HCl concentration shows that within the parameter ranges given in Table 6-3 (i.e. $K_2/S = 1.06 - 1.10$, Temperature = 350 - 550 K), K_2/S has more influence on HCl-emission than the temperature.

CHAPTER 7

CHLORINE MASS BALANCE IN THE CFFF

The chlorine mass balance has been calculated for the LMF4-V test. The calculations are based on different operation time periods during which relatively stable test conditions were achieved. Both BH/ESP material balance and overall chlorine mass balance across CFFF were attempted. The balance results are to be discussed in the following sections.

7.1 Chlorine Mass Balance for BH and ESP

Three time periods were chosen for the BH and ESP mass balance calculations. The chlorine input of BH was obtained by multiplying the BH input gas flow fraction and the total BH/ESP chlorine input. Similarly, ESP chlorine input could be obtained. For three selected time periods Table 7-1 gives the flow fraction of BH, flow fraction of ESP and total BH/ESP chlorine input. While Table 7-2 presented the calculated results for BH and ESP.

**Table 7-1. Flow Fractions and Total Chlorine Input
of BH/ESP for Test LMF4-V**

Period No.	BH Flow Fraction %	ESP Flow Fraction %	BH/ESP Fraction %	Total BH/ESP Cl Input, g/min
1	42	49	91	8.85
2	36	46	82	12.95
3	38	53	91	11.88
Average	38.67	49.33	88.00	11.23

Table 7-2. Chlorine Mass Balance in BH and ESP for Test LMF4-V

Period No.	BH Input (g/min)	BH Output (g/min)	ESP Input (g/min)	ESP Output (g/min)	BH Mass* Balance %	ESP Mass** Balance %
1	3.78	12.59	4.34	10.09	333.06	232.49
2	4.66	20.86	6.09	11.77	447.64	193.27
3	4.51	10.74	6.03	7.67	238.14	127.20
Average					339.61	184.32

* Defined as total BH output x 100/BH input

** Defined as total BH ESP output x 100/ESP output

From Table 7-1 the average of BH flow fraction is about 39%, and the average ESP flow fraction is about 49%. Table 7-1 also shows that only about 88% flow enters BH/ESP by average, while the other 12% flow enters cyclone/venturi. This information can be used to normalize the overall chlorine mass balance results to be discussed in the next section. From Table 7-2, it is interesting to see that both BH and ESP do not achieve reasonable balance closures for BH and ESP (339.61%, and 184.32%, respectively).

7.2 Overall Chlorine Mass Balance across CFFF

Four different time periods were chosen to calculate the chlorine mass balance across CFFF. The calculation results are presented in Table 7-3.

**Table 7-3. Overall Chlorine Mass Balance
in the CFFF for Test LMF4-V**

Period No.	Total Input (g/min)	Total Output (g/min)	Mass Balance Closure %*	Normalized Mass Balance Closure%
1	55.55	24.72	44.50	48.90
2	51.09	34.68	67.88	82.78
3	39.85	20.46	51.34	56.42
4**	7.89	5.21	66.03	75.03
Average			57.44	65.78

* Defined as total output x 100/total input.

** Test conducted while burning coal with much lower chlorine.

It should be pointed out that the total output data in the Table 7-3 are only the summation of the total chlorine output from BH and ESP. From Table 7-1 in the previous section, the average flow fraction which goes through BH and ESP in the selected time periods is about 88% of the total SHTM output flow. Therefore, to account for the flow fraction which goes through the venturi/cyclone section, normalization of the mass balance results is also considered and included in Table 7-3. Generally, about 45 - 70% chlorine mass balance across CFFF was achieved for the LMF4-V test, and approximately 50 - 85% was possible after normalization.

The main material flow scheme for chlorine in the CFFF together with one of the chlorine mass balance used is shown in Figure 7-1.

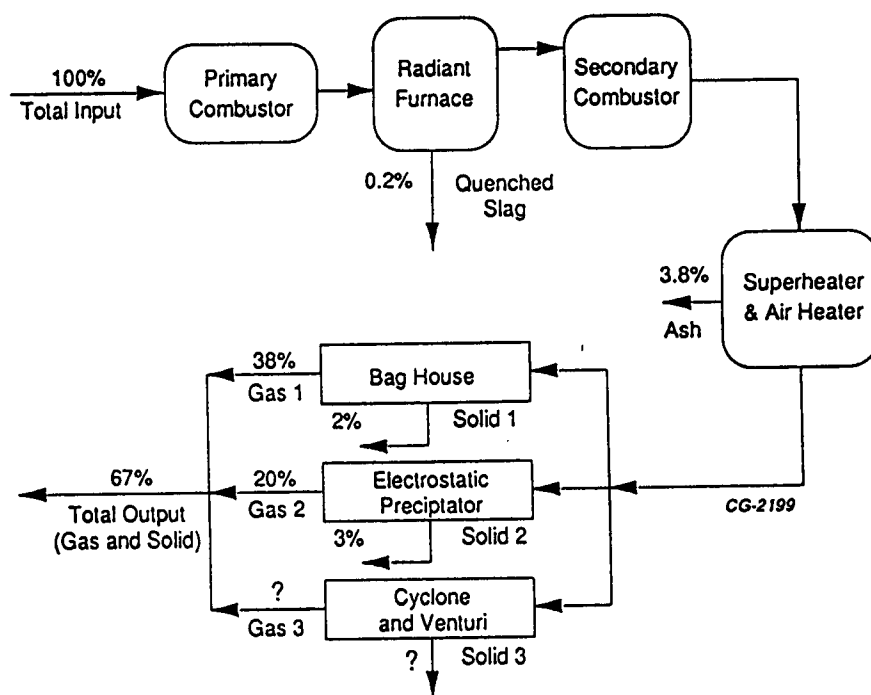


Figure 7-1. A Typical Chlorine Mass Balance in CFFF

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

From the CFFF measurements, equilibrium calculations, and bench scale experiments presented in previous chapters, the following conclusions can be drawn:

- Before secondary combustion, the chlorine-containing species exist mainly as gas phase KCl and HCl.
- After secondary combustion, chloride species exist both in gas phase and in condensed phase. Phase transition takes place at 800 - 1000 K. HCl dominates the gas phase components and KCl(s) dominates the condensed phase components.
- Calculated, measured, and experimental results agree well in relation to the strong dependence of HCl-emission on gas temperature and K_2/S ratio at BH/ESP outlet. Statistical analysis indicates that K_2/S ratio has more sensitive influence on the HCl-emission than the temperature.

8.2 Recommendations for Future Work

Some of the suggestions for future work are as follows:

- Determine the acceptable level of chlorine-containing species in an MHD seed loop and then develop a mathematical model to predict the HCl-emission from MHD stack using various coals of known chlorine content, and also allowing for necessary chloride removal in the seed recovery/regeneration

operations.

- Determine the optimum gas temperature and K_2/S ratio to achieve the acceptable HCl-emission level and chloride build-up in an MHD system.

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LIST OF REFERENCES

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