AN ABSTRACT OF THE THESIS OF

Victor Vinicius Reis for the degree of Master of Science in Chemical Engineering presented on July 29, 1994.

Title: Potassium and Chloride Release During Black Liquor Combustion

Abstract approved: Redacted for Privacy

Professor William James Frederick

Potassium and chloride are two important non-process elements in kraft pulping. Their presence in the recovery boiler is often a concern because they reduce the melting range of the predominantly sodium salt deposits and, as a consequence, may enhance corrosion, increase the tendency to form more deposits, and increase the rate of sintering and hardening of fume deposits. [1]

The release of potassium and chloride was measured during combustion of dried black liquor solids in a laminar entrained-flow reactor at 700-1100°C. Experiments were made with dry black liquor solids, 90-125 μm, in N_2, 4% O_2, and 21% O_2 environments. The particle heating rate was of the order of 10^4- 10^5 °C/second and the residence time 0.5 sec. The samples were quenched with nitrogen to stop the reactions, the solid products of combustion were collected as char (> 3 μm) and fine particles (fume, < 3 μm), and the gases analyzed. The black liquor solids originally contained 22.6% sodium, 0.62% potassium, and 0.67% chloride.

For potassium, the greatest enrichment was obtained at 700°C, in N_2, where enrichment factors of more than 10 were achieved. At higher temperatures and oxygen contents, the enrichment was less, decreasing to essentially no enrichment at 1100°C. There was neither any enrichment in air at any temperature.

For chloride, the trend was similar but even higher enrichment factors were found. Enrichment was modeled as the competing processes of volatilization of alkali metal chlorides, and sodium and potassium vaporization via reduction of Na_2CO_3. The decrease in enrichment with increasing temperature or oxygen content is attributed to the greater temperature dependence of Na_2CO_3 reduction.

The implications to recovery boiler operations are that higher operational temperatures in the lower furnace and increased air supplied there may reduce enrichment but increase fume generation. Conversely, lower temperatures and air, as sometimes is used to combat NO_x, may increase K and Cl enrichment while decreasing fume generation.

Potassium and Chloride Release During Black Liquor Combustion

by

Victor Vinicius Reis

A THESIS

submitted to

Oregon State University

in partial fulfillment of

the requirements for the

degree of

Master of Science

Completed July 29, 1994

Commencement June 1995

APPROVED:

Redacted for Privacy

Professor of Chemical Engineering in charge of major

Redacted for Privacy

Head of the Department of Chemical Engineering

Redacted for Privacy

Dean of the Graduate School

Date thesis is presented July 29, 1994

Typed by Karen Reis for Victor Vinicius Reis

ACKNOWLEDGMENTS

I would like to take this opportunity to thank all those that directly or indirectly helped me in accomplishing this major step of my life.

A special thanks to:

- my professors and fellow colleagues, particularly those of the combustion group.
- Dr. Frederick, for his advice, guidance, and financial support throughout my stay with this department. The opportunity to be his research assistant will not be forgotten.
- Dr. Iisa and Dr. Jovanovic, for their valuable advice.
- Dawn Belveal and Jordana Chambers, for always being there when needed.
- my parents, for all their support and care.
- my wife Karen, for being with me through all moments and to whom I owe everything.

This work has been supported by a research consortium of the following companies: ABB Combustion Engineering, Ahlstrom Recovery Inc., Babcock & Wilcox Company, Gotaverken Energy Systems, Mitsubishi Heavy Industries, Tampella Power Inc., Union Camp Corporation, and Weyerhaeuser Paper Company, and by the US Department of Energy's Office of Industrial Technologies. The support of all of these organizations is gratefully acknowledged.

TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

TABLE OF CONTENTS - Continued

LIST OF FIGURES

LIST OF FIGURES - Continued

LIST OF TABLES

LIST OF APPENDIX FIGURES

LIST OF APPENDIX TABLES

LIST OF APPENDIX TABLES - Continued

LIST OF APPENDIX TABLES - Continued

CHAPTER 1
INTRODUCTION

The main objectives of the chemical recovery process are to recover the chemicals used for pulping the wood, and to make good use of the energy in the organic fraction of the black liquor. A schematic of the kraft recovery cycle is shown in Figure 1.1.

The black liquor contains almost all of the inorganic cooking chemicals along with lignin and other organics separated from the wood during pulping. It is concentrated by evaporation from 15% dry solids content to about 70% in order to be able to be burnt in large units called recovery boilers. The inorganic residue of combustion is sodium and sulfur-containing salts that are then recycled and reprocessed to regenerate the pulping chemicals [2].

The kraft recovery boiler is a major piece of equipment in the chemical recovery process. A general schematic diagram of a kraft furnace is shown in Figure 1.2. The two main sections of a recovery boiler are the furnace section, where mixing and combustion of the fuel and air occur, and the convective heat transfer section, composed of the superheater, boiler bank, and economizer [3].

Black liquor burns in four stages: drying, devolatilization, char burning and smelt reactions [2]. These stages of the burning process are shown schematically in Figure 1.3. About 30% of the strong black liquor is water, and the water evaporates before and during devolatilization. During the devolatilization stage, the organic material in the black liquor solids (BLS) degrades thermally,

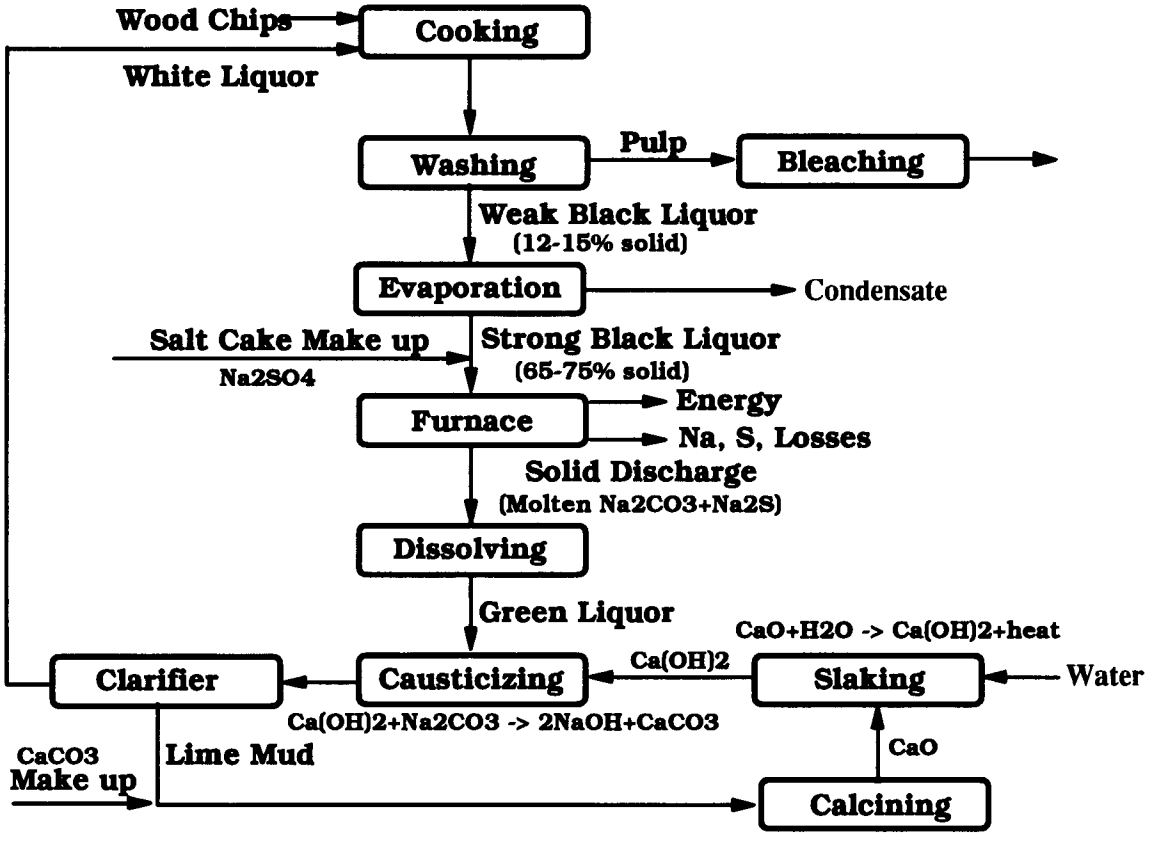


Figure 1.1: Schematic of recovery cycle of a kraft pulping process

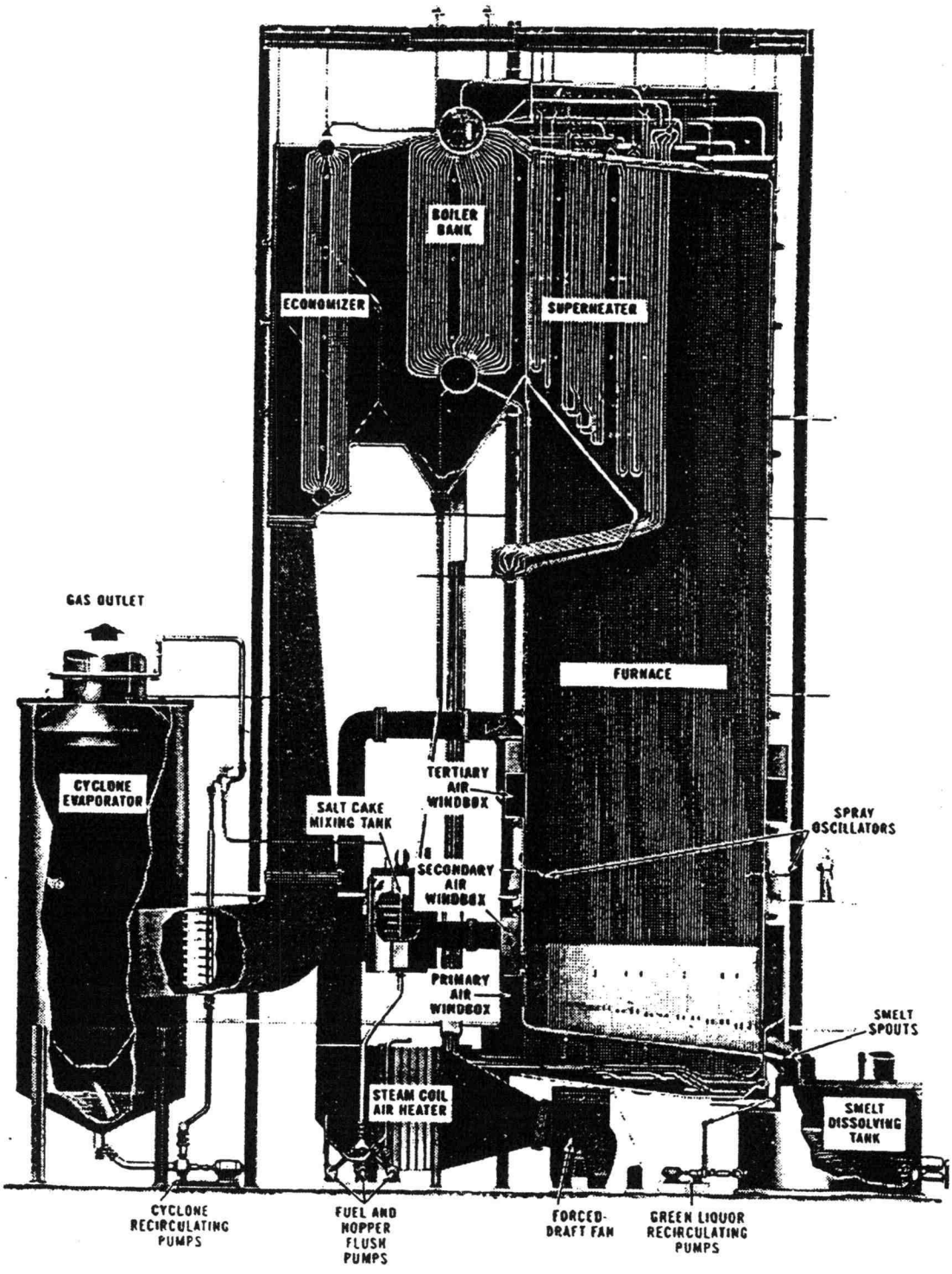


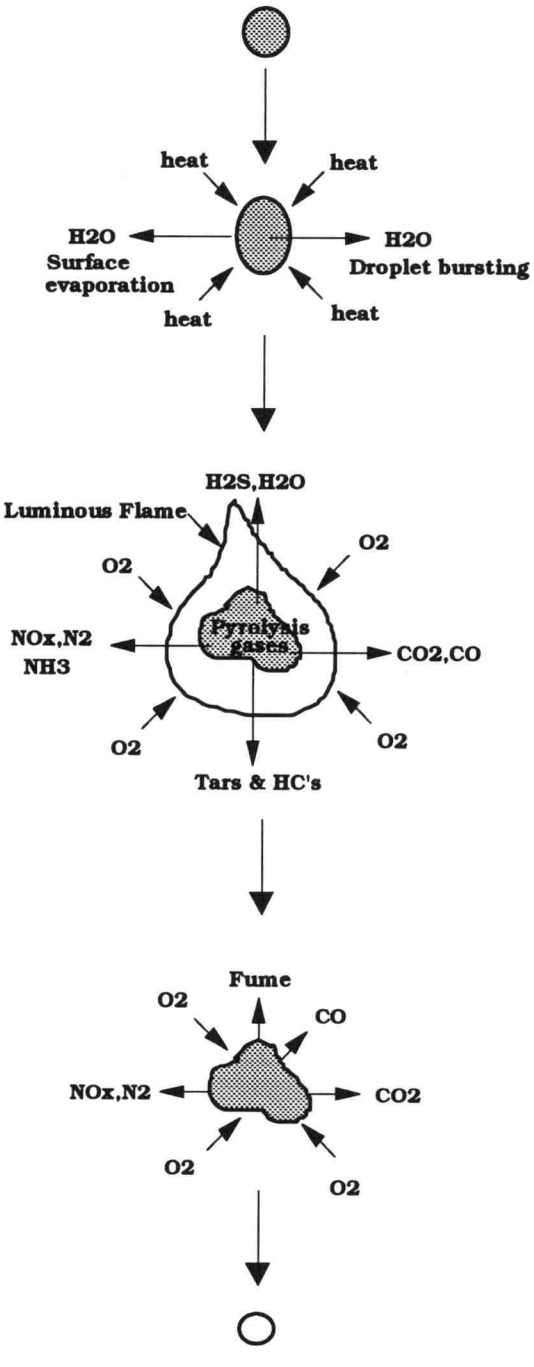
Figure 1.2: Kraft recovery furnace [4]

producing some gases and light hydrocarbons. Some sodium, potassium, and chloride salts are volatilized [5,6] and the droplet swells rapidly to several times its initial diameter [7]. At the end of this stage, the char consists of fixed carbon and inorganics from the pulping chemicals. During the next stage, char burning, the fixed carbon is consumed and more fume is produced by the vaporization of volatile salt species and decomposition of inorganic sodium and potassium compounds. What remains after char burning is the smelt that is the pulping chemicals which were converted to alkali carbonate and sulfide during combustion. During the final stage, smelt reactions, oxidation of sulfide, conversion of sulfide to H_2S, and volatilization of alkali metals and chloride can occur.

Fume is typically very small particles in the order of 1 μm in diameter. They are composed mainly of Na_2SO_4 and Na_2CO_3 with the presence of some other salts such as NaCl, KCl and K_2SO_4 [5]. The presence of fume particles in the recovery boiler has both positive and negative aspects. On the positive side, they react with sulfur and nitrogen oxides, reducing the amount of pollutants released. Since most of the fume is collected by an electrostatic precipitator and recycled, it also helps in reducing the loss of sulfur from the pulping cycle. The reduction of SO_2 and SO_3 levels from the gases also reduces corrosion problems. On the negative side, fume particles form deposits on the heat transfer surfaces. This reduces heat transfer rates and may plug the gas path, and require expensive dust handling systems.

Potassium and chloride are two important non-process elements in kraft pulping. The major source of potassium is the wood. Seawater transportation of logs, makeup chemicals and bleaching effluent (for the case of closed cycle mills) are the major sources of chloride. These elements have been shown to be important in deposition and hardening of deposits in recovery boilers [1,15,16].

The fume particles collected in recovery boilers are typically enriched by a factor of 2-3 in potassium and chloride [1].



Drying
Water is evaporated.
Slight swelling.
Low temperature.
Relatively slow process.

Devolatilization
Two processes :
pyrolysis and gaseous combustion.
Visibile yellow flame.
Rapid swelling.
Relatively fast process.

Char burning
Reaction at the partical surface.
No clear flame.
Slow process.

Smelt Reactions and Coalescence

Figure 1.3: Schematic of kraft black liquor burning process [2]

This thesis deals with the question of how enrichment of potassium and chloride occur in recovery boilers. First, the literature is reviewed (Chapter 2), then, based on this review, a mechanism of enrichment is hypothesized (Charter 3). This hypothesis is tested experimentally by pyrolysis and combustion experiments with black liquor solids (Chapter 5). It is further tested by theoretical modeling the potassium and chloride enrichment factors (Chapter 6). Finally, experimental and model results are compared and conclusions are drawn (Chapters 7 and 8).

CHAPTER 2
LITERATURE REVIEW

The mechanism of sodium, potassium and chloride release in the recovery boilers has been overlooked until recently. Although a number of studies have been made regarding the release and deposition of inorganic material during coal combustion [17], they cannot be applied directly to recovery boilers. The main reason for that is the far lower alkali metal content and the dominance of silicates in deposits in coal fired boilers as compared to those of recovery boilers. Figure 2.1 shows the ash deposit elemental composition in the region of the boiler nose of a coal utility boiler.

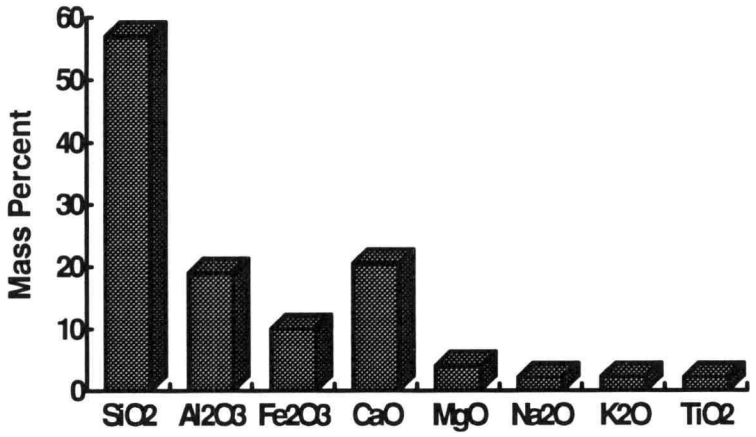


Figure 2.1: Typical elemental composition of a coal boiler and deposits [17]

Deposits in recovery boilers contain mainly sodium, sulfate, and carbonate but there is also some chloride and potassium present. The deposits are formed basically by these different mechanisms: impaction of entrained droplet residue particles (carry-over) in the combustion gases, thermophoretic deposition of sub-micron fume particles, and condensation of vapors [1,15,16]. Chemical analysis of fireside deposits in recovery boilers show that carry-over deposits

are predominantly sodium carbonate and sulfate with the presence of some sodium hydroxide. The condensation deposits are depleted in sodium carbonate, contain almost no sodium hydroxide, and are enriched in chloride and potassium. Deposits collected from higher temperature zones of the boiler were found to be stripped of volatile chloride and potassium. Sulfation has been shown to happen toward the inner surface of the deposits, increasing with the age of that deposit [1,15,16]. Figure 2.2 shows a typical elemental composition of a recovery boiler deposit.

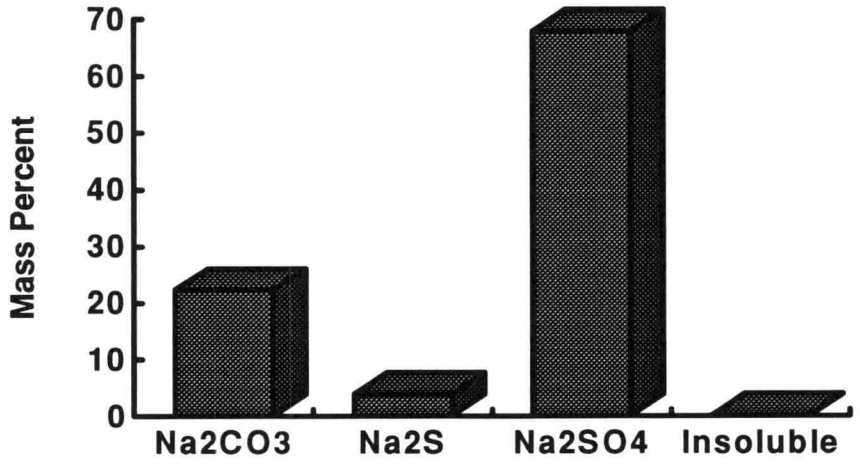


Figure 2.2: Typical elemental composition of a recovery boiler deposit

Deposits formed essentially by thermophoretic deposition of sub-micron fume particles and vaporization and condensation of vapor contain relatively high amounts of potassium and chloride. The mechanism of release of these two elements during black liquor combustion has not been thoroughly investigated. Two of the few relevant studies in this area were done by Cameron [8,10] and Li and Van Heiningen [9].

Cameron [8,10] has shown that a large amount of sodium carbonate fume is produced when sodium sulfide in a sodium sulfide/carbonate melt is oxidized using air. The rate of fume generation under oxidizing conditions was found to be greater than the rate under reducing conditions. This behavior was explained by sodium oxidation in the gas phase. The oxidation of sodium vapor just above the melt surface lowers the partial pressure of sodium in the gas phase and increase the sodium vapor gradient near the surface of the particle. This mechanism has been called oxidation-enhanced fuming and is schematically shown in Figure 2.3.

Cameron's experiments were performed using an induction heated reactor, mass flow meters and fume filter, as shown in Figure 2.4. The fume produced from alkali carbonate/sulfate/sulfide/chloride melts were monitored under several experimental conditions. The results presented in that study also indicate that sodium chloride vaporization is an equilibrium process and that its vaporization rate during oxidation enhanced fume generation can be determined assuming Raoult's law is applicable. Also, no potassium enrichment was observed during oxidation-enhanced fuming when chlorides were absent in the melt. When chlorides were present, the fume was enriched in potassium. Therefore, the potassium enrichment in fumes from inorganic melts is believed to be due to the presence of chloride.

Li and van Heiningen [9] studied the sodium emission during pyrolysis and gasification of black liquor solids by thermogravimetry at temperatures up to 800°C. Their system, shown schematically in Figure 2.5, was first purged with either helium or nitrogen to assure the elimination of oxygen. Then, the furnace temperature was raised to the gasification temperature at a rate of 20°C/min in an inert atmosphere. Gasification was started by adding CO_2 when a stable pre-set reaction temperature was reached. The composition of the exhaust gas was determined by gas chromatography, and the concentration of

the carbonate and sulfur species in the solid product was measured by ion chromatography. The concentration of sodium in the solids was determined by atomic absorption spectroscopy.

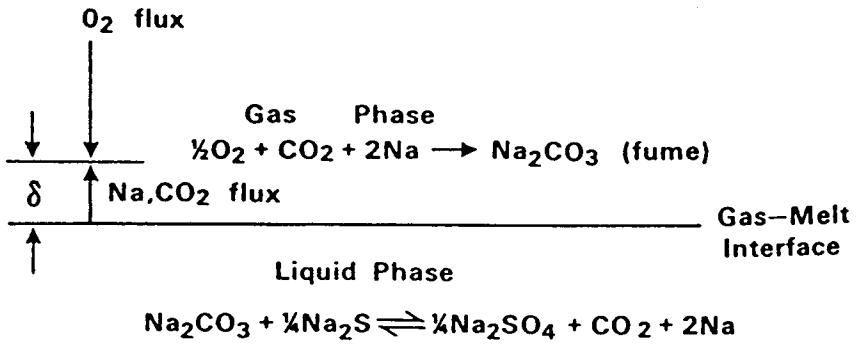


Figure 2.3: Cameron's model for fume generation under oxidizing conditions [8]

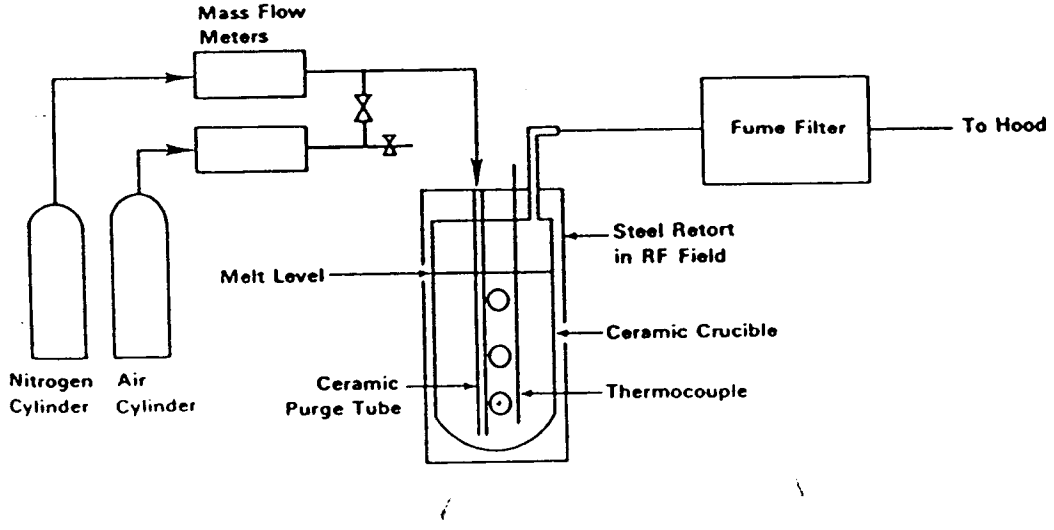


Figure 2.4: Cameron's experimental system [8]

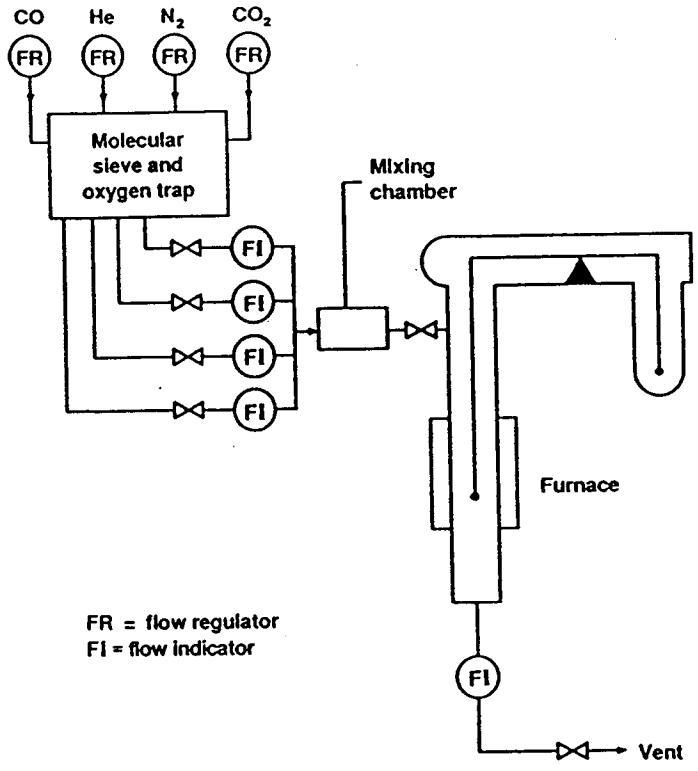


Figure 2.5: Li and van Heiningen's experimental system [9]

They concluded from their studies that, during pyrolysis of black liquor char in an inert atmosphere at temperatures above 675°C, sodium carbonate reacts with carbon to produce sodium vapor, carbon monoxide, and carbon dioxide according to the following reactions:

$$Na_2CO_3 + 2\ C \longrightarrow 2\ Na + 3\ CO \qquad (2.1)$$

$$Na_2CO_3 + C \longrightarrow 2\ Na + CO + CO_2 \qquad (2.2)$$

The metallic sodium released reacts with oxygen to form sodium oxide by the reaction:

$$4\ Na + O_2 \longrightarrow 2\ Na_2O \qquad (2.3)$$

Then the following reactions take place:

$$2\ Na_2O + 2\ SO_2 + O_2 \longrightarrow 2\ Na_2SO_4 \qquad (2.4)$$

$$Na_2O + CO_2 \longrightarrow Na_2CO_3 \qquad (2.5)$$

The solid products formed by these reactions are the two major compounds found in the upper part of the furnace and electrostatic precipitator. Li and van Heiningen [9] have shown also that the decomposition of sodium carbonate (Reactions 2.1 and 2.2) below 800°C can be suppressed by the addition of either carbon monoxide or carbon dioxide to the inert atmosphere. This mechanism of decomposition of sodium carbonate, as in reaction 2.1, is also known as the sodium carbonate reduction mechanism.

From the concepts and mechanisms reviewed above, two are particularly important for the understanding of the results presented in this thesis: the volatilization of sodium chloride and the sodium carbonate reduction mechanisms. The chemical characterization of deposits, the mechanisms involved in their formation, and the oxidation-enhanced fuming will also help in interpreting the experimental results of this work.

CHAPTER 3
HYPOTHESIS AND OBJECTIVES

The presence and enrichment of chloride and potassium in fume are important in recovery boiler operation. These elements reduce the melting range of the predominantly sodium salt deposits and, as a consequence, may enhance corrosion, increase the tendency to form more deposits, and increase the rate of sintering and hardening of fume deposits [1].

Although the impact of the presence of potassium and chloride in the recovery boiler operation has earlier been addressed, the mechanism of release of sodium, potassium, and chloride during black liquor combustion has yet to be thoroughly investigated.

The work reported by others (Cameron [8] and Li and van Heningen [9]) suggests that the mechanism of potassium and chloride enrichment in fume during black liquor combustion may be a result of evaporation of NaCl and KCl and of reduction of Na_2CO_3 and K_2CO_3 to metallic Na and K. With the relatively large size of black liquor particles, transport processes may also influence the overall rates of these processes and degree of potassium and chloride enrichment. The hypothesis on which this thesis is based is that potassium and chloride enrichment during black liquor pyrolysis and combustion can be predicted based on a mechanism involving evaporation of NaCl and KCl and reduction of Na_2CO_3 and K_2CO_3 to metallic Na and K and the effects of mass transfer and diffusion. The objective of this thesis is to test this hypothesis through a combination of experimental measurements and modeling.

The experimental portion of this work is based on the collection of fume from black liquor pyrolysis and combustion using the LEFR and on the determination of the sodium, potassium, and chloride content in the fume

under several experimental conditions. For the modeling portion, mass transfer and chemical reaction concepts are used to predict the release of sodium, potassium, and chloride as fume.

CHAPTER 4
EXPERIMENTAL METHODS

4.1 - LEFR

The pyrolysis and combustion experiments with black liquor were conducted in a laboratory scale laminar entrained-flow reactor (LEFR). A schematic of the apparatus used in the experiments is shown in Figure 4.1.

The laminar entrained-flow reactor is a vertical 3-zone high temperature electrical furnace with two mullite tubes inside. It operates with a downward flowing gas stream at high temperatures and laminar conditions. The primary flow, a low temperature gas stream, is injected at the center of the reactor. The secondary flow, a high temperature gas stream, is injected coaxially with the primary flow. The annular space between the tubes is used to preheat the secondary flow. When traveling upward through this space, the gas reaches the operation temperature and then turns and flows downward through a flow straightened and into the smaller of the tubes. The primary and secondary flows merge to form a single laminar flow with uniform temperature.

The particles are initially entrained in the low temperature gas stream to prevent changes from occurring before reaching the reaction zone of the reactor. The particles, injected near the top of the unit, travel downward along the centerline of the reactor in a narrow, laminar column. At the moment when the particles enter the reactor, they are simultaneously exposed to the high temperature secondary flow and the hot walls of the reactor. The small particle size results in a rapid heat transfer rate. It can be assumed that the laminar gas velocity and particle velocity are the same for small particles. When particles and gases reach the collector, they are quenched with nitrogen to stop reactions. Most of the quench gas is fed into the first inch of the

collector to ensure a rapid quench. The rest flows through the porous wall of the collector to avoid thermophoretic deposition of the aerosol particles. The residence time is set by moving the collector up or down or by changing the gas velocities. After the quench, the products of reaction are separated. The particles larger than 3 μm in diameter (char) are removed by a cyclone and the fine particles (fume) are collected on a nylon membrane filter with 0.5 μm pore size located before the exhaust duct. Filters with this pore size are effective in collecting particles as small as 0.1 μm. The cyclone/filter setup is shown in Figure 4.2.

The length of the heated zone is 80 cm and the inside diameter of the smaller tube is 70 mm. The electrical heater can operate at temperatures up to 1200°C. The temperature of the reactor wall and the secondary flow are expected to be about the same. The heating zones of the reactor are controlled with an Omega CN 76000 Microprocessor Based Temperature/Process Controller capable of ramping to its set point temperature at a maximum heating rate of 300°C/hour. All gas flows are controlled by Omega FMA 5600 Electronic Mass Flowmeters (MFM).

4.2 - SEM

The scanning electron microscope (SEM) is an instrument that can provide a high-magnification image of the surface of a material that is very similar to what should actually be seen if the surface could be viewed by the naked eye. In addition the topographical information, SEMs can provide details of chemical composition of near-surface regions of the specimen, when x-ray spectroscopy is also used.

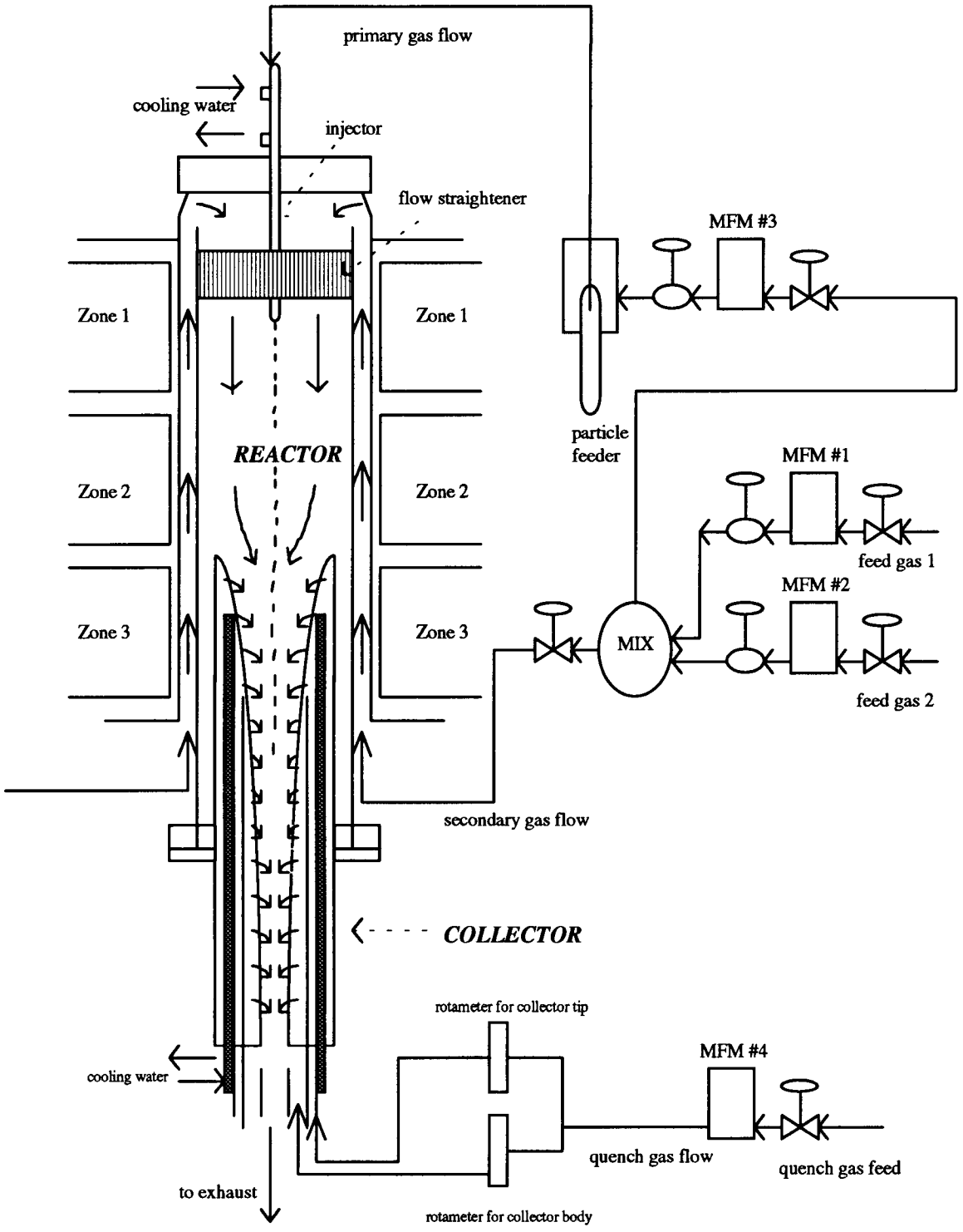


Figure 4.1: Schematic of the OSU laminar entrained-flow reactor

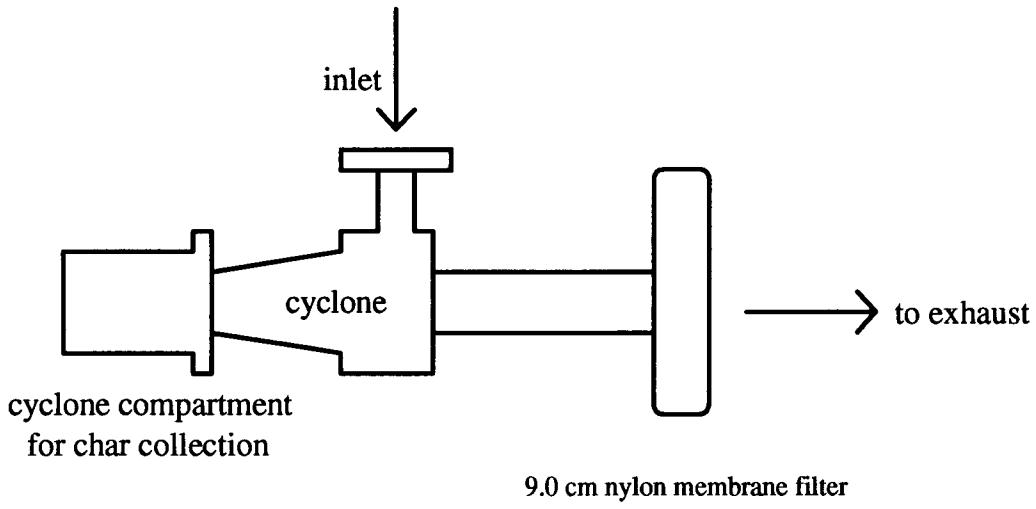


Figure 4.2: Schematic of cyclone/filter set-up for the OSU LEFR

the surface. The electrons emitted are collected by a detector that transform the signals, and produce an image of the specimen surface on a monitor. The contrast of the image is due to topographical variations and atomic number differences in the specimen. The SEM produces better micrographs than those originated by the light microscope and the transmission electron microscope, when dealing with irregular surfaces of relatively large specimens. Schematics describing the basics of SEM operations and optics are shown in Figures 4.3 and 4.4, respectively.

The EDAX or Energy-Dispersive X-ray Analyzer is a tool used with the electron microscope to determine the elemental composition of a small, chosen area of a specimen. The excited specimen atom produced by the collision of the primary electron will return to its original state by emitting a characteristic x-ray signal. The wavelength spectrum of the X-ray emitted is characteristic for the element bombarded. This allows the determination of the composition

of the specimen through weight and atomic percentage. The SEM can use the signals to produce images that show the spatial distribution of particular elements in the field of view.

The SEM was an important tool for the work presented in this thesis for either morphological or chemical characterization of the solids used or produced during the experiments

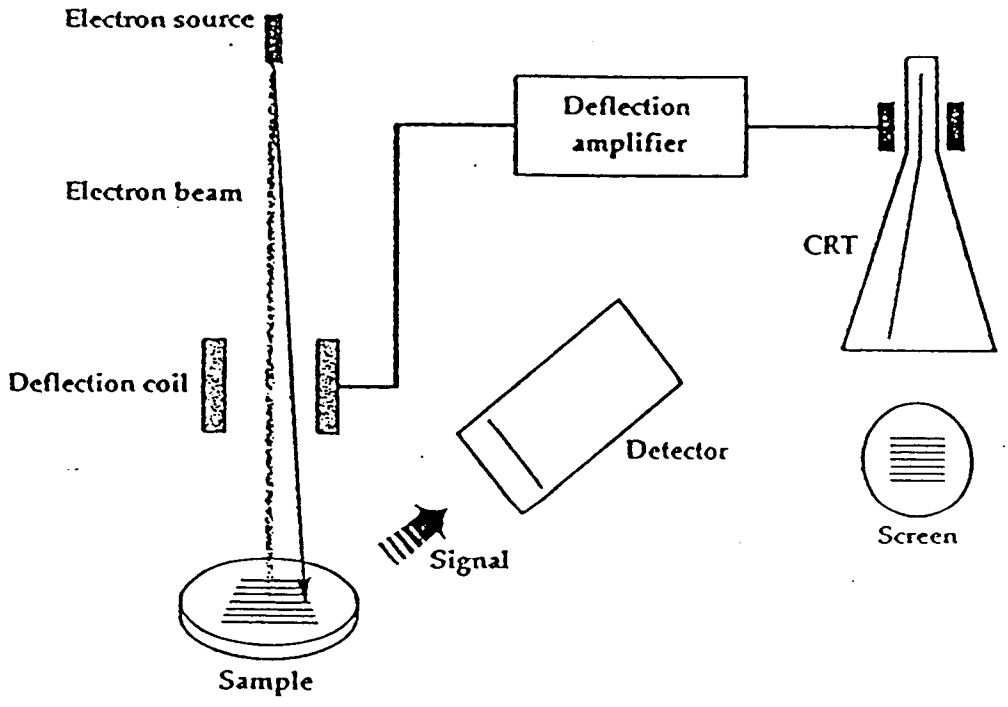


Figure 4.3: Schematic describing the basics of SEM operations [11]

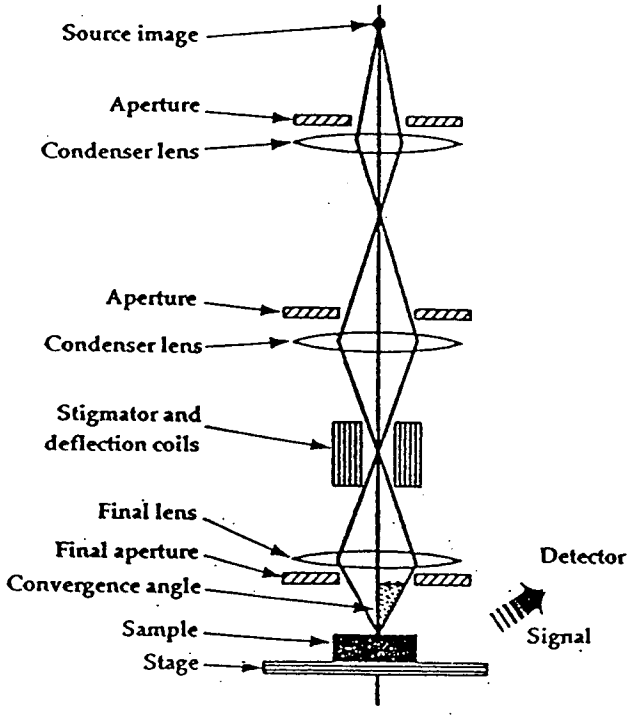


Figure 4.4: Schematic providing details of SEM optics [11]

4.3 - CES

The CES (Capillary Electrophoresis System) is an instrument used to determine ion concentration based on capillary electrophoresis. Capillary electrophoresis is a simple, high resolution technique which separates ions based on their relative velocity in an applied electric field. Ions with high charge-to-mass ratios have the greatest migrational velocity in an electric field, and these are detected first. Ions with lower charge-to-mass ratios have a lower migrational velocity and are detected later.

Sodium, potassium and chloride as well as most of the inorganic cations and anions have no optical absorbance. In order to detect them, indirect photometric detection is used. When using an indirect absorbance method with

capillary electrophoresis, an absorbing ion is incorporated in the electrolyte to provide a background signal. Ions present in the sample will displace an absorbing ion in the electrolyte and the result is a negative peak. The negative peaks are then inverted to positive signals on the screen for better visualization.

The signals generated by the samples are then compared with the signals of known concentrations of several ions for accurate determination of the composition of the sample.

A detailed description of the CES operation is included in Appendix C.

4.4 - ISE

Analysis using Ion-Selective Electrode (ISE) is a fairly quick, accurate and economic way to determine ion concentrations in aqueous solutions when systems like atomic absorption (AA) or ion chromatography (IC) are not available.

The electrical potential of an ion-selective electrode is a function of the logarithm of the activity of the ion to be measured. The relationship is given by the Nernst equation:

$$E = E^\circ - \frac{2303\ R\ T}{F} \log a_{ion}$$ where:

E° = constant characteristic of the electrode (volts)

R = universal gas constant = 8.314 J/K mol

T = absolute temperature (Kelvin)

F = Faraday constant = 96.489 Coulombs/mol

a_{ion} = activity of the ion

This equation can be simplified to:

$$E = \text{Constant} - S \log a_{ion}$$

where S is the slope of the calibration curve. The measured potential E can only be measured against a reference electrode placed in the same solution. A reference electrode is an ion-selective electrode whose potential is held constant by fixing the composition of the internal filling solution.

For potassium analysis, an Orion Model 93-19 potassium electrode was used. To determine chloride concentration, we used a Corning 476126 chloride electrode. For potassium and chloride analysis, the Corning double junction 476067 reference electrode was used. A sodium combination electrode, Corning 476138, was the electrode used for sodium ion analysis.

CHAPTER 5
LEFR EXPERIMENTS

5.1 - Experimental Conditions

5.1.1 - Black Liquor Solids

A southern pine kraft black liquor was used for all of the potassium and chloride enrichment experiments. The original liquor was dried in an oven at 110°C, ground in a jar mill, sieved, and the desired 90-125 µm diameter fraction was collected. The composition of the liquor solids are shown in Table 5.1. A 90-125 µm particle size was chosen to minimize temperature gradients across the particle, to eliminate external mass transfer effects, and to allow the particles to be fed at an uniform rate with the feeding system.

Table 5.1: Elemental composition of dried black liquor solids

Elemental Composition (Dry Basis)	
Element	%
Carbon	34.90
Hydrogen	3.05
Oxygen *	35.21
Sodium	22.65
Sulfur	2.90
Potassium	0.62
Chloride	0.67

* Calculated by difference

5.1.2 - Reactor Temperature

The temperatures of the reactor for the experiments were chosen to be 700°C, 900°C and 1100°C. This is approximately the temperature range found in the combustion zone of recovery boilers.

5.1.3 - Oxygen Content in Reaction Gas

A wide range of oxygen contents was used. Two extreme conditions that can be found in a recovery boiler furnace are the combustion of black liquor in air (21% O_2) or the pyrolysis in nitrogen (0% O_2). These two conditions and a N_2/O_2 mixture (4% O_2), which is about the average oxygen concentration in the combustion zone, were chosen to be used in the experiments.

5.1.4 - Residence Time

The residence time of the particles inside the reaction zone of the furnace depends on the reactor temperature, secondary flow, primary flow, and the distance between the injector and the collector. The secondary flow, primary flow and the path length of the particles inside the reactor were kept constant throughout the experiments at 15 liters/min, 0.1 liters/min, and 15 inches, respectively. The reactor temperature was changed, from 700°C to 1100°C, affecting the gas velocities inside the reactor, and therefore, the residence time.

The residence time was calculated for a primary flow velocity/secondary flow velocity ratio of one. The relationship between the gas flow rates (primary and secondary), path length and residence time has yet to be completely understood. The residence time equation used was:

$$\tau = \frac{V}{V_o} \qquad (5.1)$$

where:

V = volume of reactor = $\frac{\pi d^2 l}{4}$

l = path length = 15 in = 38.1 cm

d = diameter transversal to gas flow = 7 mm, based on secondary flow

V_o = volumetric flow of secondary gas at reactor temperature

= (secondary flow, l/min) x $\frac{\text{(reactor temperature, K)}}{\text{room temperature, K}}$ x $\frac{\text{(60 seconds)}}{\text{min}}$

5.1.5 - Feeding Rate

The gases and solids feeding rates were chosen based mainly on equipment limitations. Higher particle feeding rates increase the probability of plugging problems in the feeding system. A high gas flow rate reduces the concentration of the gaseous pyrolysis or combustion products to the point where they cannot be measured accurately by the analytical instruments.

5.1.6 - Heating Rate

The particle heating rate was calculated using the results from a droplet devolatilization model [12]. The heating rate can be estimated in °C/sec as $\frac{T_{i+1} - T_i}{dt}$, that is the slope of the curve in an average droplet temperature (°C) versus time (sec) graph.

For the range of conditions used in this work, it was estimated that the particle heating rate would be of the order of 10^4 - 10^5 °C/sec. Figures 5.1

gives an example of a particle heating rate calculation for an 1100°C furnace and in air (21% O_2).

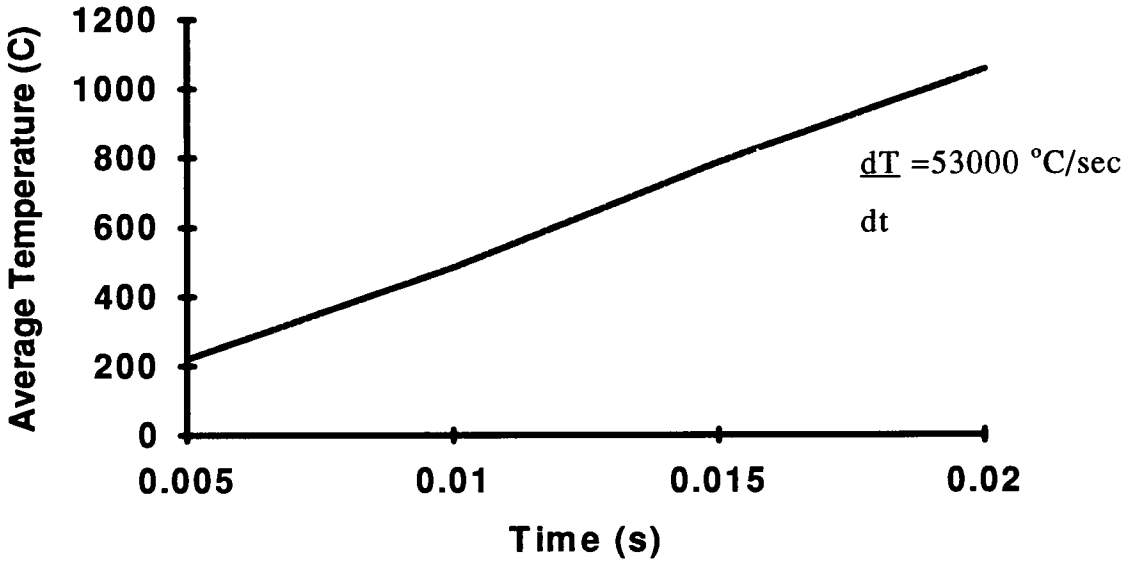


Figure 5.1: Calculated particle heating rate (1100°C and 21% O_2)[12]

5.2 - Experimental Results

All experimental data used in this chapter is shown in Appendix B.

5.2.1 - Particle Characteristics

Figures 5.2 and 5.3 are scanning electron micrographs of typical char and fume respectively. Char particles are usually large (>100 μm), spherical and porous. Fume particles, on the other hand, are very small (0.1 - 1 μm) and non-porous particles. The solid black liquor particles, when pyrolyzed, swelled to about 4

times their initial diameter. Studies on swelling characteristics of the original

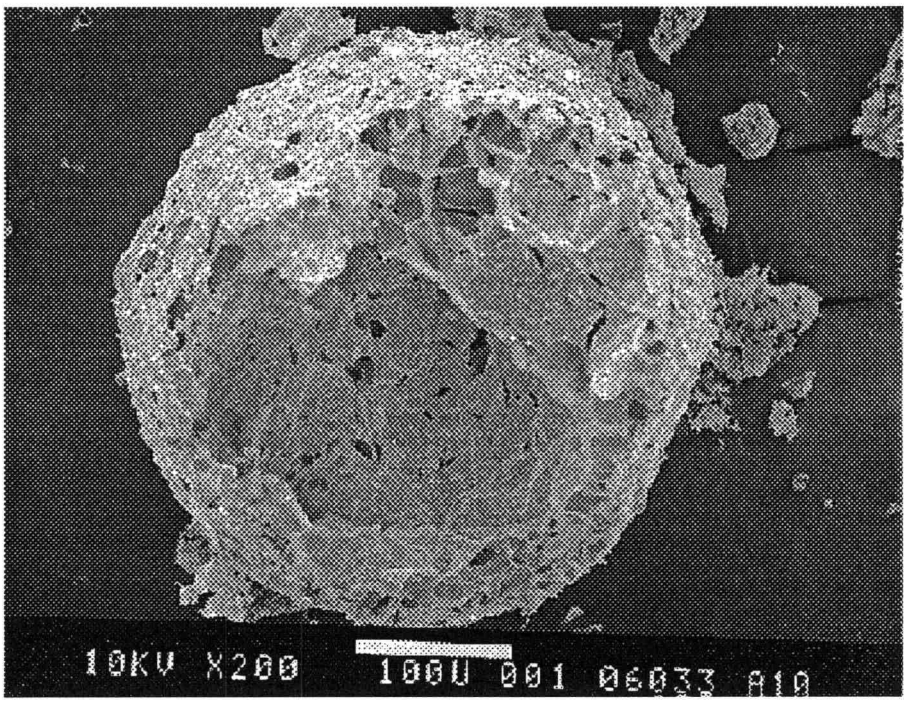


Figure 5.2: Typical SEM micrograph of black liquor char

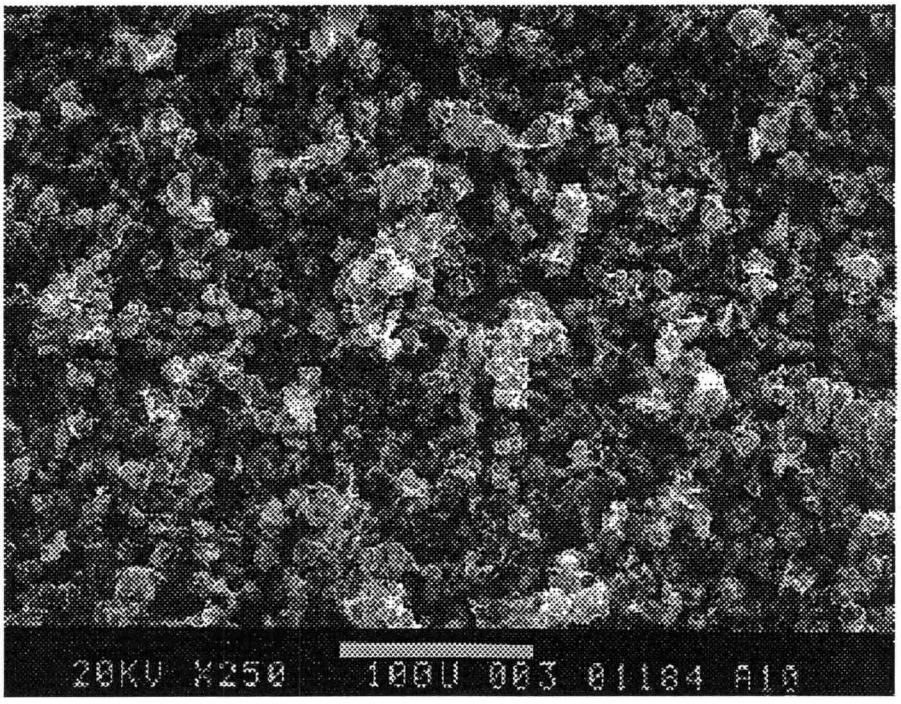


Figure 5.3: Typical SEM micrograph of black liquor fumes

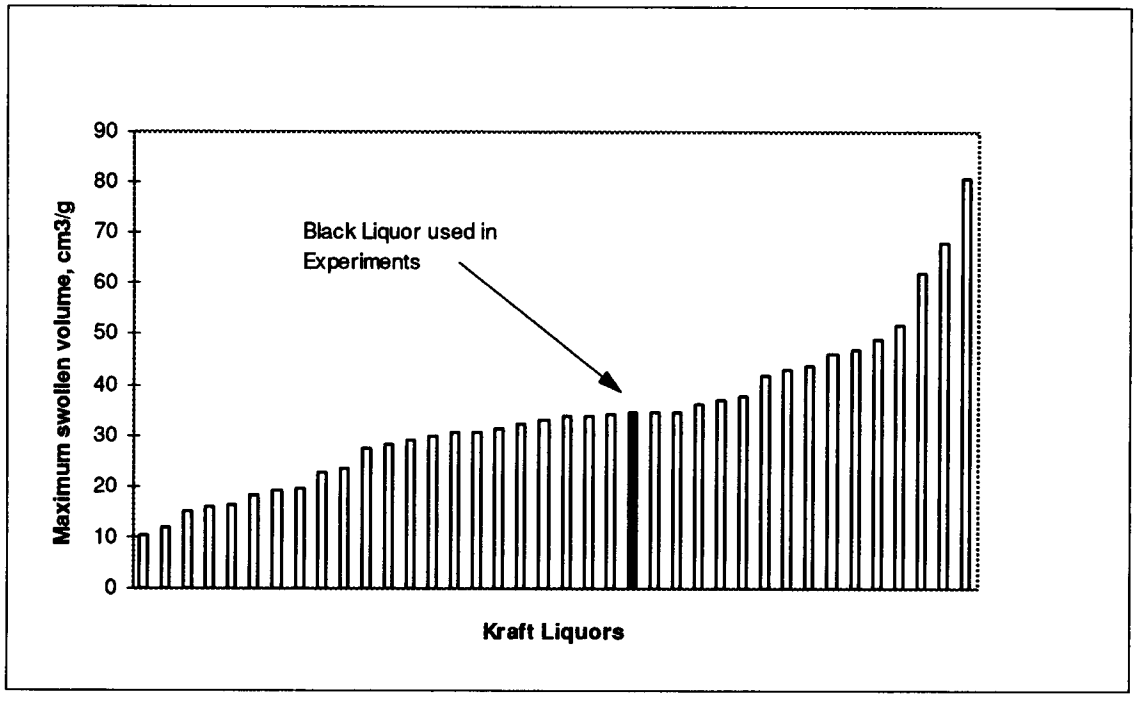


Figure 5.4: Specific swelling volume of black liquors [18]

black liquor were also performed. This liquor behaved as an average liquor, Figure 5.4, swelling about 3 times it's initial droplet diameter (specific swollen volume of 35 cm^3/g black liquor solids).

5.2.2 - Fume Generation

Based on the amount of solids collected on the fume filters and the analysis of sodium, potassium and chloride content of these solids (fume), the amount of chlorides released as fume was calculated. It was assumed that all the alkali metal (potassium and sodium) not in the form of chloride salt was in the form of either carbonate or sulfate. When the fume consists only of NaCl and Na_2CO_3, it is referred in Table 5.2 as the minimum (min) inorganic content that the fume could have, based on the molecular weight. When the fume

consists only of NaCl and Na_2SO_4, it is referred as maximum (max). Table 5.2 shows the results obtained.

The filter catch collected from pyrolysis and 4% O_2 experiments is not only sodium and potassium salts. A part of it consists of fixed carbon. The inorganic in the fume at 700°C, 0% O_2 was almost entirely NaCl. The NaCl content of the fume samples decreased with increasing furnace temperature and O_2 content although the total amount of NaCl in the fume per gram of black liquor solids increased.

Figure 5.5 shows the ratio of fume collected to the amount of black liquor solids fed at different temperature and oxygen contents in the gas. From the results shown, we can imply two things. First, the amount of fume at oxidizing conditions is considerably higher than that in reducing conditions. Second, the temperature has a great effect on fuming, especially at lower oxygen content where fuming is an order of magnitude higher at 1100°C than at 700°C.

Table 5.2: Inorganic content in fume, weight %

		700°C	900°C	1100°C
0% O_2	NaCl	48.1	12.9	12.5
	min (NaCl + Na_2CO_3)	48.6	62.7	73.2
	max (NaCl + Na_2SO_4)	48.8	79.5	93.7
4% O_2	NaCl	64.6	16.0	7.1
	min (NaCl + Na_2CO_3)	80.6	83.6	89.1
	max (NaCl + Na_2SO_4)	85.3	106.4	116.8
21% O_2	NaCl	6.0	3.2	5.4
	min (NaCl + Na_2CO_3)	101.4	100.6	87.6
	max (NaCl + Na_2SO_4)	133.7	133.5	115.3

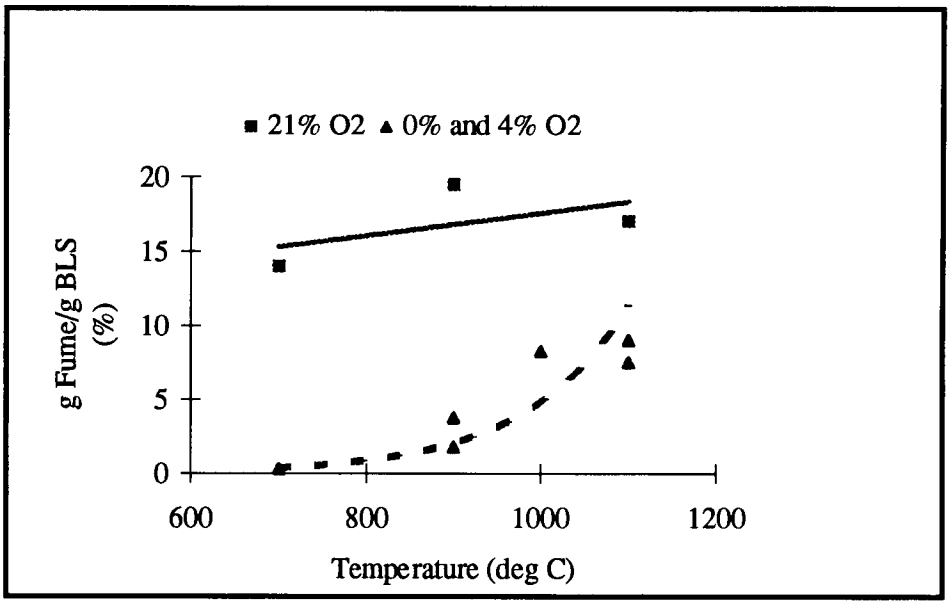


Figure 5.5: Fume generation versus reactor temperature from LEFR experiments

5.2.3 - Potassium and Chloride Enrichment

The potassium enrichment factor is defined as the ratio of the concentration of potassium to that of sodium in fume divided by the ratio of potassium to sodium in the black liquor (BLS), or

$$\text{Potassium Enrichment Factor} = \frac{\left[\frac{\text{K in Fume}}{\text{Na in Fume}}\right]}{\left[\frac{\text{K in BLS}}{\text{Na in BLS}}\right]} \qquad (5.2)$$

An analogous definition is valid for the chloride enrichment factor,

$$\text{Chloride Enrichment Factor} = \frac{\left[\frac{\text{Cl in Fume}}{\text{Na in Fume}}\right]}{\left[\frac{\text{Cl in BLS}}{\text{Na in BLS}}\right]} \qquad (5.3)$$

The potassium and chloride enrichment factors have also been defined by others as a ratio of the concentration of potassium or chloride to that of alkali metals (Na + K) in fume divided by the ratio of potassium or chloride to alkali metals in the black liquor. The first definition is more sensitive to potassium and chloride enrichment, which is the reason it was chosen to be used in this study.

Using equations 5.2 and 5.3, we calculated the potassium and chloride enrichment factors for several experimental conditions. For potassium, the greatest enrichment factor, over 15, was obtained at 700°C in nitrogen, as shown in Figure 5.6. At higher temperatures the enrichment factor was smaller. The general trend is that at a higher temperature, the enrichment decreases to the point that no potassium enrichment was obtained at 1100°C. Another interesting finding is that there was virtually no potassium enrichment in air at any temperature.

For chloride, Figure 5.7, a similar trend was found but even higher enrichment factors were obtained. An enrichment factor of about 80 in nitrogen at 700°C was achieved. Some enrichment was obtained in air, an enrichment factor of about 3, but it did not seem to be affected by the reactor temperature.

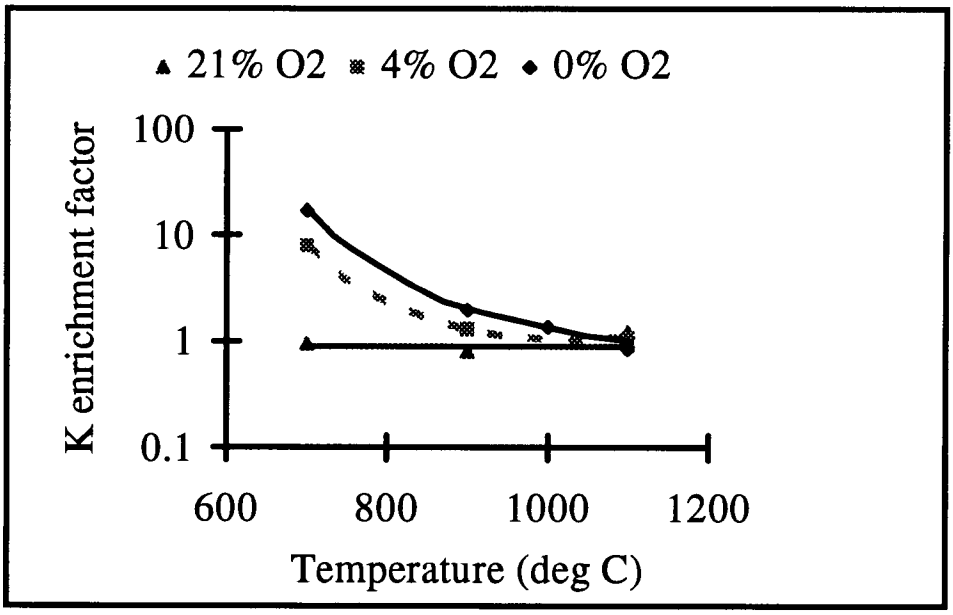


Figure 5.6: Potassium enrichment factor versus reactor temperature from LEFR experiments

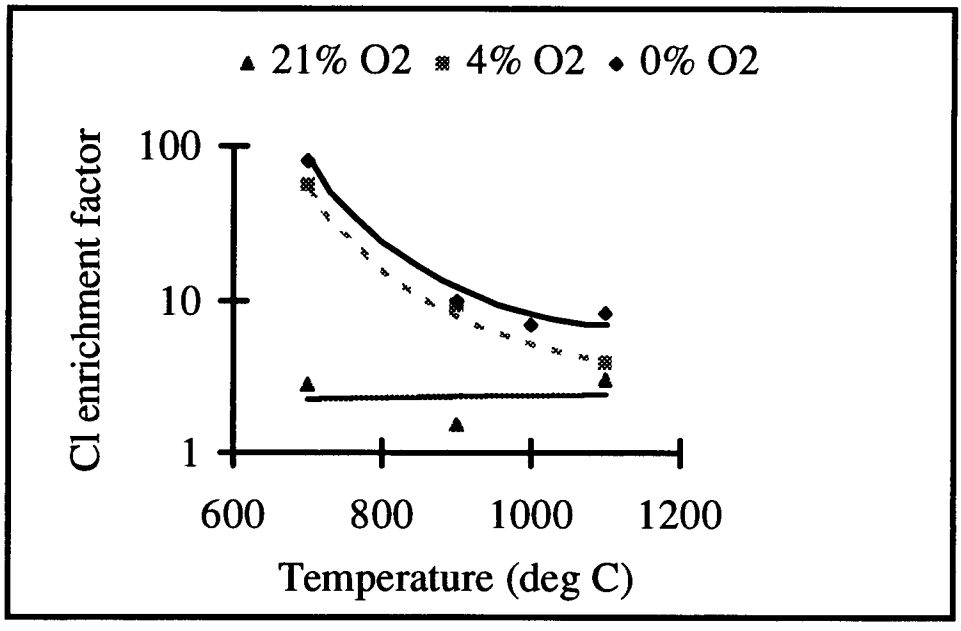


Figure 5.7: Chloride enrichment factor versus reactor temperature from LEFR experiments

CHAPTER 6
ENRICHMENT FACTOR MODEL

6.1 - Modeling

Cameron [8] suggested that fuming processes involve salt vaporization and that sodium and potassium chloride vaporization are responsible for potassium and chloride enrichment observed in the fume. Cameron demonstrated this by comparing measured sodium chloride vaporization rates from molten salt pools with calculated values. The calculated rates were based on Raoult's Law (Equation 6.1) after assuming that the vaporization of sodium chloride is an equilibrium process, the smelt is an ideal system, and the gas stream is saturated with sodium chloride.

$$P_{NaCl}(T) = P^{o}_{NaCl}(T) * X_{NaCl} \qquad (6.1)$$

where:

$P_{NaCl}(T)$ = equilibrium partial pressure of NaCl at temperature T

$P^{o}_{NaCl}(T)$ = vapor partial pressure of pure NaCl at temperature T

X_{NaCl} = mole fraction of NaCl in smelt

To explain the high enrichment factors found in our experiments we are assuming that vaporization of sodium and potassium salts is the dominant mechanism at lower particle temperatures and O_2 contents. At higher temperatures the sodium is also released by the sodium carbonate reduction mechanism proposed by Li and van Heiningen [9]. The reaction is:

$$Na_2CO_3 + 2C \longrightarrow 3CO + Na_{(v)} \qquad (6.2)$$

A model was developed based on the above assumptions to predict theoretical potassium and chloride enrichment during black liquor combustion.

A new theoretical chloride enrichment factor can be defined by the ratio of sodium chloride and potassium chloride vaporization rate and the rate of sodium released by the sodium carbonate reduction and NaCl volatilization.

$$\text{Chloride Enrichment Factor} = \frac{\int\left(\frac{dNaCl}{dt}\right)dt + \int\left(\frac{dKCl}{dt}\right)dt}{\int\left(\frac{dNa}{dt}\right)dt + \int\left(\frac{dNaCl}{dt}\right)dt} \quad \frac{[Na]_{BLS}}{[Cl]_{BLS}}$$

where:

$\int\left(\frac{dNaCl}{dt}\right)dt$ = chloride or sodium released by NaCl vaporization, mol

$\int\left(\frac{dKCl}{dt}\right)dt$ = chloride released by KCl vaporization, mol

$\int\left(\frac{dNa}{dt}\right)dt$ = sodium released by carbonate reduction mechanism, mol

$[Na]_{BLS}$ = concentration of sodium in black liquor solids, mol %

$[Cl]_{BLS}$ = concentration of chloride in black liquor solids, mol %

The integrations are performed over the time at which the particles were in the hot zone of the furnace by using the forward Simpson numerical integration method.

The theoretical potassium enrichment factor can be defined by the ratio of potassium released by potassium chloride volatilization and by potassium carbonate reduction to that of sodium released by sodium carbonate reduction and NaCl volatilization.

$$\text{Potassium Enrichment Factor} = \frac{\left[\int\left(\frac{dKCl}{dt}\right)dt + \int\left(\frac{dK}{dt}\right)dt\right]}{\left[\int\left(\frac{dNa}{dt}\right)dt + \int\left(\frac{dNaCl}{dt}\right)dt\right]} \frac{[Na]_{BLS}}{[K]_{BLS}}$$

where:

$\int\left(\frac{dKCl}{dt}\right)dt$ = potassium released by KCl vaporization, mol

$\int\left(\frac{dK}{dt}\right)dt$ = potassium released by carbonate reduction mechanism, mol

$\int\left(\frac{dNa}{dt}\right)dt$ = sodium released by carbonate reduction mechanism, mol

$\int\left(\frac{dNaCl}{dt}\right)dt$ = chloride or sodium released by NaCl vaporization, mol

$[Na]_{BLS}$ = concentration of sodium in black liquor solids, % mol

$[K]_{BLS}$ = concentration of potassium in black liquor solids, % mol

The model took into account the reaction kinetics as well as film mass transfer and diffusion out of the particles, but it does not account for the suppression of sodium carbonate reduction by CO and CO_2. These suppression effects were expected to be negligible in our experiments because of the dilution effect of the reaction gas. When the particles were pyrolyzed in N_2, the concentrations of CO an CO_2 resulting from the pyrolysis products were low, of the order of 1000 ppm or less.

The model was written using the Microsoft Excel 5.0a for Windows software where each set of temperature and oxygen content was treated in one spreadsheet. The results from the equilibrium calculations and salt volatilization were incorporated in the model and can be found in Appendix E.

As presented in Figure 6.1, the flow diagram for the enrichment factor model has six routines of calculations, which are:

- Surface temperature calculation (TEMP)
- Equilibrium partial pressure calculations (HSC)
- Calculation of the amount of salt volatilized (Volatilization)
- Calculation of the amount of alkali metal released by Na_2CO_3 reduction mechanism (Carbonate)
- Theoretical enrichment factor calculation
- Calculation of the initial char composition for the next time interval

Below is a list of all the variables used in this model. The terminology used in this chapter corresponds directly to the one used in the spreadsheet model.

η is effectiveness factor

CO3 is the alkali carbonate concentration (mol)

DeltaHr is the heat of reaction of CO = 110525 (J/mol)

Diff is the diffusivity of molecule in N2 at given temperature (m^2/sec)

Dp is the diameter of the particle (m)

Gr is the Grashf number

heff is effective heat transfer coefficient (J/sec.m^2.K)

k is thermal conductivity coefficient (J/sec.m.K)

MW is the molecular weight (g)

Nu is the Nusselt number

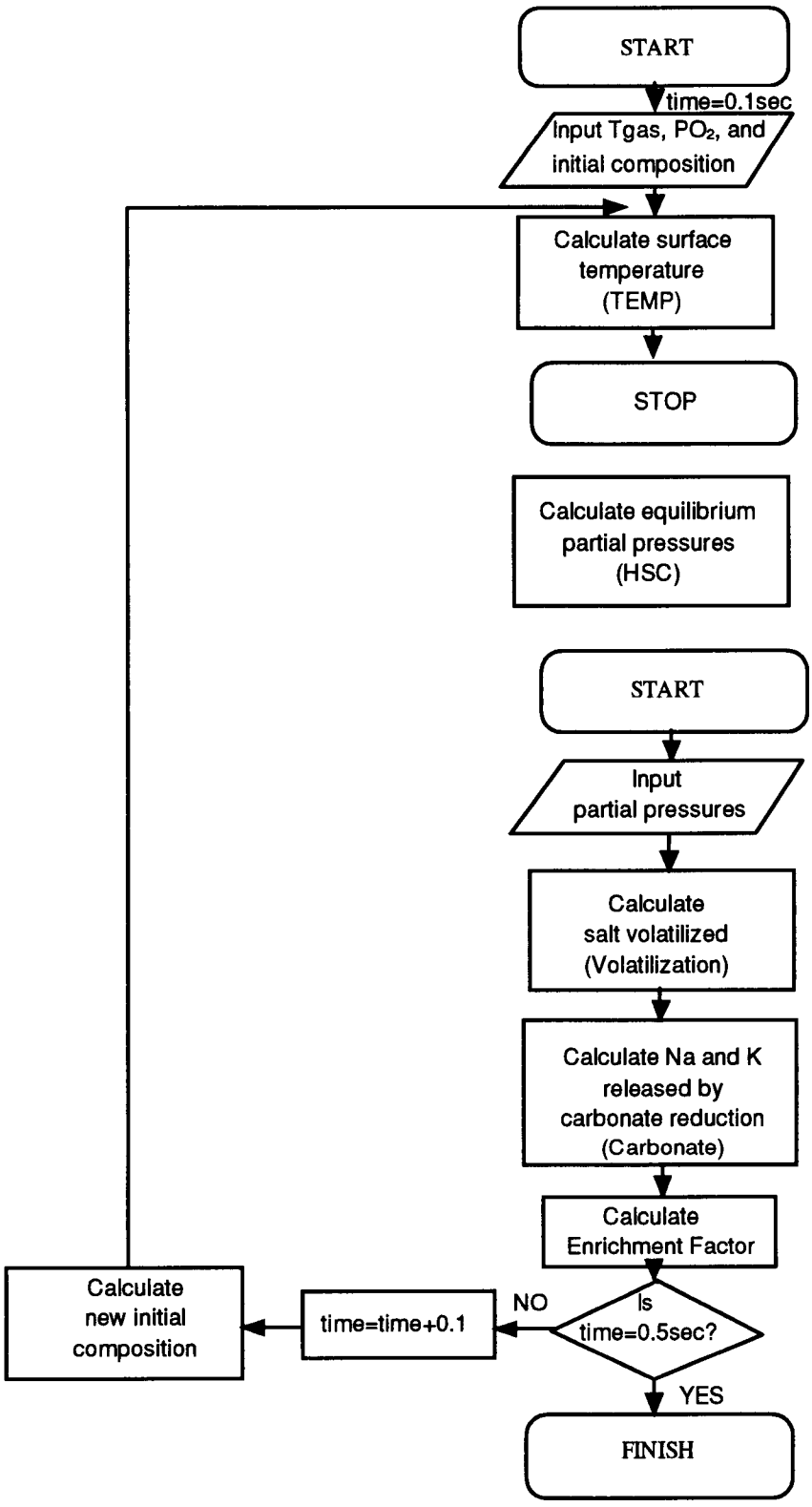


Figure 6.1 - Flow-diagram for the enrichment factor model

OverallRate is the overall rate of alkali release by carbonate reduction mechanism (mol/sec)

PO_2 is the O_2 content in the reaction gas (%)

Psalt is the partial pressure of the salt at equilibrium using HSC (bar)

Pvapor is the partial pressure of alkali metal at equilibrium using HSC (bar)

R is the constant of gases = 0.08314 (bar*liter/mol*K)

Rate is the rate of reaction of carbon with O_2 around the particle ($mol/m^2.sec$)

Re is the Reynolds number

Rkinetic is the chemical kinetic rate of the carbonate reduction mechanism (mol/sec)

Rmt is the rate of alkali metal mass transfer from the particle surface to the gas phase (mol/sec)

Salt is the initial amount of the salt in the stage (mol)

Sh is the Sherwood number

Sigma is the Stefan-Boltzmann constant = 0.0000000567 ($J/(sec.m^2.K^4)$)

Tf is the film temperature as an average between Tgas and Tparticle (°C)

Tg is reactor's temperature (°C)

Time is the time interval between iterations (sec)

Tp is the particle surface temperature (°C)

vgas is the gas velocity relative to the particle (m/sec)

Visc is the gas kinematic viscosity (m^2/sec)

6.1.1 - Surface Temperature Calculations

For the surface temperature calculations, the function TEMP was created, which estimates iteratively the difference between the particle surface temperature and furnace temperature during its combustion.

$$TEMP = Tp - Tg = \frac{(-DeltaHr)\,(-Rate)}{h_{eff}} \qquad (6.2)$$

where:

Tg = reactor's temperature (°C)

Tp = particle surface temperature (°C)

DeltaHr = heat of reaction of CO = 110525 (J/mol)

Rate is the rate of reaction of carbon with O_2 around the particle ($mol/m^2.sec$) and is calculated as:

$$Rate = \frac{kg\left(\frac{PO_2}{100}\right)}{\left(R(Tf + 273.15)\right)} \tag{6.3}$$

where:

PO_2 = O_2 content in the reaction gas (%)

Tf = film temperature as an average between Tgas and Tparticle (°C)

R = constant of gases = $8.314*10^{-5}$ ($bar.m^3/mol.K$)

'kg' is the mass transfer coefficient that is estimated for given film temperature (Tf), diameter of the particle (Dp), and the molecular weight (MW) of the molecule diffusing in the reaction gas. First, the diffusivity of the molecule in N_2 is estimated by using equation 6.4 that was obtained by fitting a curve on diffusivity data available in the literature [20] for various gas species of different molecular weights. The data used for fitting this curve can be found in Appendix F.

$$Diff = 1.0662 * 10^{-4} * (MW)^{-0.4834} * \left(\frac{Tf + 273.15}{273.15}\right)^{1.75} \tag{6.4}$$

Thus, kg is estimated as:

$$kg = \frac{Sh * Diff}{Dp} \tag{6.5}$$

where Sh is the Sherwood number assumed to be 2.

The effective coefficient of heat transfer for the particle surface (heff) is calculated as:

$$h_{eff} = \frac{k\,(2 + 0.39Gr^{0.25} + 0.37\,Re^{0.6})}{Dp} + \frac{Sigma\,(Tp^4 - Tg^4)}{(Tp - Tg)} \qquad (6.6)$$

where:

Sigma = Stefan-Boltzmann constant = $\sigma = 5.67*10^{-8}$ (J/sec.m^2.K^4)

k is thermal conductivity coefficient (J/sec.m.K)

$$k = 0.0238 + 0.0000685 * Tf - 0.00000001614 * (Tf)^2$$

Gr is the Grashf number

$$Gr = 9.8 * (Tp - Tg) * Dp^3 / (Tf * Visc^2)$$

Re is the Reynolds number

$$Re = vgas * Dp / Visc$$

vgas is the gas velocity relative to the particle (m/sec)

Visc is the gas kinematic viscosity (m^2/sec)

6.1.2 - Equilibrium Partial Pressure Calculation

The salt vapor partial pressure was estimated for each set of conditions by using the Gibbs energy routine from the HSC Chemistry for Windows software. The HSC is a chemical reaction and equilibrium software with extensive thermochemical database developed by Outokumpu Research - Finland. The objective of this software is to make conventional thermodynamic calculations faster and easier to carry out. The software requires the input of the composition of the phases of your system, total pressure, and temperature range. All species of interest or relevant for your system should be selected, even if their initial concentration are zero. The amount of reaction gas in the

input should be in the same order of magnitude of the system you are studying. Figure 6.2 and Figure 6.3 show examples of output files from the Gibbs calculations using HSC.

C:\THESIS\MODEL\THESIS.OGI									
Temperature	Na(g)	K(g)	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	K2S(g)	Na2SO4(g)	K2SO4(g)
C	mol-%	mol-%	mol-%	mol-%	mol-%	mol-%	mol-%	mol-%	mol-%
700	2.30E-02	3.02E-03	1.12E-05	1.30E-05	8.60E-06	1.10E-05	5.45E-14	3.67E-29	2.75E-29
900	4.40E-01	7.19E-03	1.50E-03	1.60E-04	7.30E-05	8.28E-06	2.86E-12	7.99E-27	5.71E-29
1100	4.45E-01	7.16E-03	6.56E-03	5.51E-04	6.35E-06	5.58E-07	4.80E-10	2.21E-28	1.09E-30

Figure 6.2 - Output table containing the molar fraction of some species in the gas phase (HSC software)

6.1.3 - Calculation of the Amount of Salt Volatilized (Volatilization)

The user-defined function 'Volatilization' calculates the amount of salt released by volatilization mechanisms during a given period of time from a single particle. The release of volatiles is equal to the product of the rate of release ($mol/m^2.sec$), the residence time (sec), and the external surface area (m^2). The unit for the 'Volatilization' function is mol.

The molecules allowed to volatilize by this mechanism are NaCl, KCl, and KOH. The maximum amount of salt volatilized during a specific period of time is limited to the its input amount. The salt partial pressure used in the rate of reaction calculation was determined from the HSC software. The equations to calculate the amount of salt volatilized are shown below:

$$\text{Volatilization} = \text{Rate} \cdot \text{Time} \cdot \pi \cdot Dp^2$$

GIBBS 2.0 WINDOWS	FOR MULTIPHASE E	QUILIBRIUM CA	LCULATIONS
Copyright (C) Outo	kumpu Research O	y, Pori Finla	nd 1974-94
T.Talonen, J.Eskel	inen, T.Syvajarv	i and A.Roine	
Temperature	973.15 K		
Pressure	1 b	ar	
Volume	4.486E-08 m	3 (NPT)	
Reaction enthalpy	4.231E-05 kJ		
Reaction entropy	7.294E-05 J	/K	
Iterations	101	(Limit = 10	0)
	INPUT AMOUNT	EQUIL AMOUNT	MOLE FRACT
PHASE 1:	mol	mol	
CH4(g)	0.00E+00	9.68E-12	4.84E-06
CO(g)	0.00E+00	1.04E-09	5.21E-04
CO2(g)	0.00E+00	6.58E-13	3.29E-07
Cl2(g)	0.00E+00	2.93E-40	1.46E-34
HCl(g)	0.00E+00	4.90E-19	2.45E-13
H2O(g)	1.00E-10	5.03E-12	2.51E-06
H2S(g)	0.00E+00	2.13E-19	1.07E-13
K(g)	0.00E+00	6.05E-11	3.02E-05
KCl(g)	0.00E+00	2.60E-13	1.30E-07
KOH(g)	0.00E+00	2.21E-13	1.10E-07
K2S(g)	0.00E+00	1.09E-21	5.45E-16
K2SO4(g)	0.00E+00	5.50E-37	2.75E-31
N2(g)	2.00E-06	2.00E-06	9.99E-01
NO(g)	0.00E+00	1.90E-24	9.48E-19
NO2(g)	0.00E+00	3.85E-39	1.92E-33
NO3(g)	0.00E+00	1.15E-59	0.00E+00
Na(g)	0.00E+00	4.61E-10	2.30E-04
NaCl(g)	0.00E+00	2.23E-13	1.12E-07
NaOH(g)	0.00E+00	1.72E-13	8.60E-08
Na2SO4(g)	0.00E+00	7.34E-37	3.67E-31
O2(g)	0.00E+00	4.38E-34	2.19E-28
S(g)	0.00E+00	4.12E-28	2.06E-22
SO2(g)	0.00E+00	1.49E-31	7.46E-26
SO3(g)	0.00E+00	5.45E-45	2.72E-39
Total :	2.00E-06	2.00E-06	1.00E+00
PHASE 2 :			INIT GUESS
C	2.91E-08	2.84E-08	8.52E-01
K	0.00E+00	1.90E-12	5.70E-05
K2CO3	7.77E-11	1.23E-11	3.70E-04
KCl	3.05E-12	6.49E-11	1.95E-03
KOH	0.00E+00	5.37E-12	1.61E-04
K2S	0.00E+00	2.97E-13	8.90E-06
K2SO4	0.00E+00	2.01E-29	6.04E-22
Na	0.00E+00	5.91E-11	1.77E-03
Na2CO3	4.50E-09	4.20E-09	1.26E-01
NaCl	1.87E-10	1.24E-10	3.72E-03
NaOH	0.00E+00	1.45E-10	4.36E-03
Na2S	3.31E-10	3.31E-10	9.93E-03
Na2SO4	0.00E+00	1.25E-28	3.74E-21
S	0.00E+00	1.22E-21	3.65E-14
Total :	3.42E-08	3.33E-08	1.00E+00

Figure 6.3 - Example of an input and output data file from HSC software

where:

Volatilization = amount of salt volatilized (mol)

Rate = Rate of reaction (mol/m^2.sec)

$$\text{Rate} = \frac{\text{kg}\left(\frac{\text{Psalt}}{100}\right)}{\left(\text{R}(\text{Tf} + 273.15)\right)} \qquad (6.7)$$

Psalt = Partial pressure of the salt at equilibrium (bar)

Time = Time interval (sec)

6.1.4 - Calculation of the Amount of Alkali Metal Released by Carbonate Reduction mechanism (Carbonate)

This routine calculates the amount of salt released by carbonate reduction mechanisms. The release of alkali metals (sodium or potassium) is equal to the product of the rate of release of these elements by the carbonate reduction mechanism (mol/sec) and the residence time (sec). The units of Carbonate are mol.

$$\text{Carbonate} = \text{OverallRate} * \text{Time} \qquad (6.8)$$

where:

Carbonate = Amount of alkali metal released by the carbonate reduction mechanism (mol)

OverallRate = Overall rate of alkali metal release by carbonate reduction mechanism (mol/sec)

$$\text{OverallRate} = \frac{1}{\left(\left(\frac{1}{\text{Rmt}}\right)+\left(\frac{1}{\eta \,.\, \text{Rkinetic}}\right)\right)} \qquad (6.9)$$

The effectiveness factor (η) for this size of particle at the conditions used in the experiments is approximately equal to 1.

Rmt = rate of alkali metal mass transfer from the particle surface to the gas phase (mol/sec)

$$\text{Rmt} = \frac{\text{kg}\left(\frac{\text{Pvapor}}{100}\right)}{\left(\text{R}(\text{Tf} + 273.15)\right)} * \pi * \text{Dp}^2 \qquad (6.10)$$

Pvapor = partial pressure of alkali metal at equilibrium using HSC (bar)

kg = mass transfer coefficient (m/sec)

Rkinetic = chemical kinetic rate of the carbonate reduction mechanism[19] (mol/sec)

$$\text{Rkinetic} = 2 * 10^9 * [CO_3] * e^{\left(\frac{-244000}{8.314*(\text{Tp}+273.15)}\right)} \qquad (6.11)$$

CO_3 = alkali carbonate concentration (mol)

6.2 - Results

The results for chloride and potassium theoretical enrichment factors for reactor temperatures of 700, 900 and 1100°C are shown in Tables 6.1, 6.2 and 6.3, respectively. The spreadsheet developed to predict the theoretical enrichment factor with formulas and results can be found in Appendix E.

Table 6.1: Calculated chloride and potassium enrichment factors at 700°C

Temperature: 700°C			
Chloride Enrichment Factor			
	O_2 Content (%)		
Residence Time (sec)	0	4	21
0.1	35.3	63.6	1.9
0.2	35.3	57.2	1.7
0.3	35.3	49.9	1.6
0.4	35.3	46.3	1.6
0.5	35.3	44.0	1.5
Potassium Enrichment Factor			
	O_2 Content (%)		
Residence Time (sec)	0	4	21
0.1	40.1	34.2	1.2
0.2	40.2	26.4	1.1
0.3	40.2	17.9	1.0
0.4	40.2	13.6	1.0
0.5	40.2	11.0	1.0

Table 6.2: Calculated chloride and potassium enrichment factors at 900°C

Temperature: 900°C			
Chloride Enrichment Factor			
	O_2 Content (%)		
Residence Time (sec)	0	4	21
0.1	17.8	12.4	1.9
0.2	17.6	11.0	1.7
0.3	17.4	10.3	1.6
0.4	17.2	9.8	1.6
0.5	17.1	9.4	1.5
Potassium Enrichment Factor			
	O_2 Content (%)		
Residence Time (sec)	0	4	21
0.1	2.7	3.1	0.9
0.2	2.6	2.0	0.9
0.3	2.6	1.6	0.9
0.4	2.6	15	0.9
0.5	2.6	1.4	0.9

Table 6.3: Calculated chloride and potassium enrichment factors at 1100°C

Temperature: 1100 °C			
Chloride Enrichment Factor			
	O_2 Content (%)		
Residence Time (sec)	0	4	21
0.1	3.5	1.6	0.7
0.2	3.3	1.5	0.7
0.3	3.1	1.4	0.7
0.4	2.9	1.4	0.7
0.5	2.7	1.3	0.8
Potassium Enrichment Factor			
	O_2 Content (%)		
Residence Time (sec)	0	4	21
0.1	1.2	1.1	0.8
0.2	1.2	1.0	0.8
0.3	1.1	1.0	0.9
0.4	1.1	1.0	0.9
0.5	1.1	1.0	1.0

CHAPTER 7
DISCUSSION

Table 7.1 compares the theoretical and experimental enrichment factors for chloride. At higher temperatures, the combustion of black liquor is controlled by fume mass transfer, so the rate of reaction increases slowly with the increase in temperature. The heat transfer coefficient is controlled by radiation and increases rapidly with temperature. Therefore, knowing that the difference between the particle temperature (T_p) and the reactor temperature (T_g) is a function of the ratio between the rate of reaction and the heat transfer coefficient, (T_p - T_g) will decrease with the increase of reactor temperature. So, the temperature of the particle will not be as high at higher reactor temperatures. The enrichment factor model predicts this behavior during the particle surface temperature, as shown in Figure 7.1.

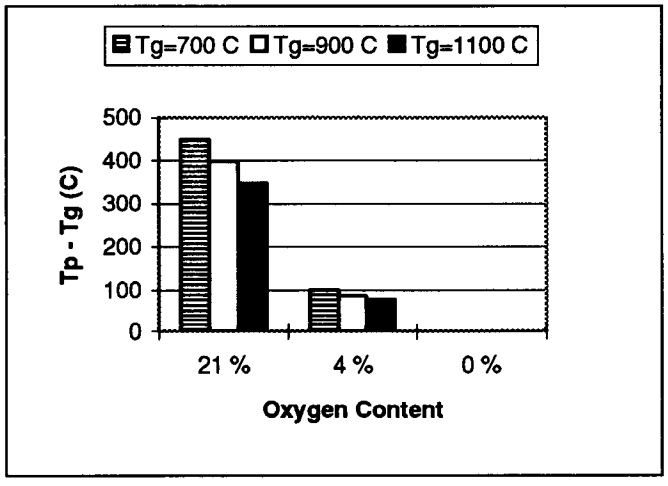


Figure 7.1: Relationship between oxygen content in gas and particle surface temperature

Table 7.2 shows a comparison between the theoretical and experimental enrichment factors for potassium.

The main reason for the high enrichment factors at lower temperatures and reducing conditions is the low sodium release rate via Na_2CO_3 reduction. In Figure 7.2, we plot the molar ratio of sodium in fume and in BLS versus temperature at several oxygen contents. As temperature increases, the rate of sodium released increases, by as much as 18 times from 700°C to 1100°C in N_2. The release of chloride, Figure 7.3, is increased only by a factor of about 3.5 at the same conditions (of those of the sodium release). Again, in Figure 7.2, it can be observed that the release of sodium fume in air is high even at lower temperatures. There are two principles that could be simultaneously helping to increase the amount of sodium being released by carbonate reduction: the oxygen-enhanced fuming mechanism and the particle burning temperature.

Table 7.1: Comparison of chloride experimental and theoretical enrichment factors

		Experimental	Theoretical
700°C	0% O_2	80.7	35.3
	4% O_2	56.8	44.0
	21% O_2	2.8	1.5
900°C	0% O_2	10.0	17.1
	4% O2	9.4	9.4
	21% O_2	1.5	0.8
1100°C	0% O_2	8.4	2.7
	4% O_2	3.9	1.3
	21% O_2	3.0	0.8

Conditions: 100 μm BLS particle, 0.5 sec

Table 7.2: Comparison of potassium experimental and theoretical enrichment factors

		Experimental	Theoretical
700°C	0% O_2	16.7	40.2
	4% O_2	7.9	11.0
	21% O_2	0.9	1.0
900°C	0% O_2	2.0	2.6
	4% O_2	1.3	1.4
	21% O_2	0.8	0.9
1100°C	0% O_2	0.8	1.1
	4% O_2	1.1	1.0
	21% O_2	1.2	1.0

Conditions: 100 μm BLS particle, 0.5 sec

Cameron [8] suggested that the high sodium release in air is due to oxidation-enhanced fuming mechanism. In this mechanism, the sodium vapor is oxidized just above the melt's surface lowering the partial pressure of sodium in the gas phase and increasing the rate of sodium vaporization. The data obtained in this work suggests that the increase in sodium release is much more significant with the increase of temperature than with the increase of oxygen content. Also, there is a hidden temperature effect on the sodium release with the increase of oxygen content. It can be said, therefore, that for this case, the carbonate reduction mechanism is limited by reaction kinetics instead of equilibrium in which the oxidation-enhanced fuming mechanism is based. If the resistance to mass transfer diffusion from the particle were higher, the oxygen-enhance mechanism could play a more important role on the release of sodium under oxidizing conditions.

The hidden temperature effect on the sodium release with the increase of oxygen content can be explained by the higher surface temperature that a small particle achieves when burning in air compared with those at 0% and 4% O_2. Frederick et al.[13] measured, for larger particles (3-10 mm), the surface temperature during char burning at several O_2/N_2 mixtures in an 800°C furnace. They concluded that surface temperature for droplets burned in air increases by 300-400°C above the furnace temperature during char burning, but only by about 40°C at 4% O_2 content, according to equation 7.1.

$$\Delta T = 883\ P_{ox} + 2966\ P_{ox}^2 \qquad (7.1)$$

where:

P_{ox} = oxygen partial pressure (bar)

ΔT = temperature difference (°C)

Hurt and Mitchell [14] reported that coal particles with 106-125 μm initial diameter have a surface temperature of about 200°C higher than the gas temperature when burning in 12% O_2. Black liquor solids may burn even hotter because of the presence of sodium and sulfur compounds that act as catalysts. For the same oxygen content, 12%, and a larger particle size, Frederick et al. found a difference of about 150°C. The particle surface temperature estimation from the enrichment factor model also predicted the same results, as seen in Figure 7.1. Therefore, we can conclude that black liquor particles of about 100 μm in diameter may achieve surface temperatures higher than 400°C above the furnace temperature when burned in air.

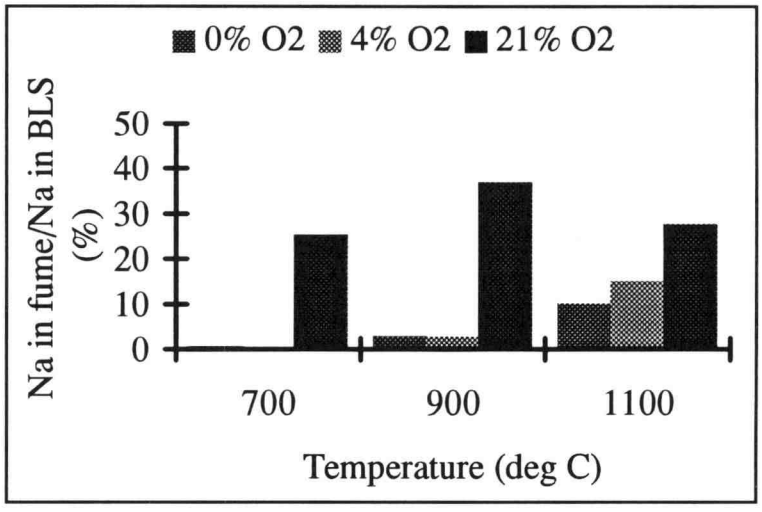


Figure 7.2: Molar ratio of sodium in fume and in BLS versus temperature

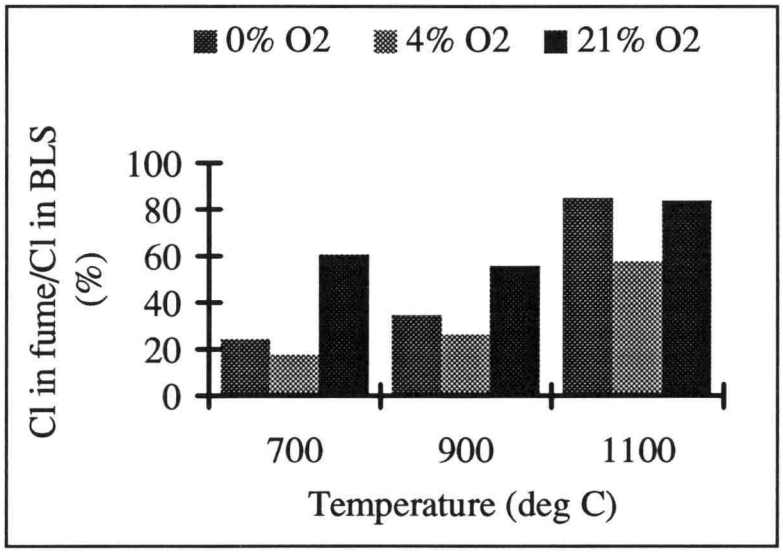


Figure 7.3: Molar ratio of chloride in fume and in BLS versus temperature

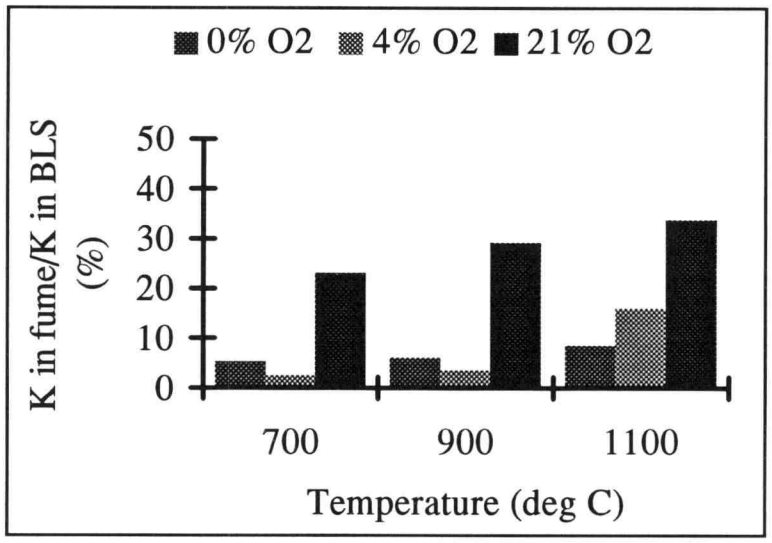


Figure 7.4: Molar ratio of potassium in fume and in BLS versus temperature

At the much higher particle temperatures achieved in air, Na_2CO_3 reduction proceeds rapidly and sodium release is high compared with that of particles burned in 4% O_2 or pyrolyzed in N_2. The enrichment factor is highly dependent on sodium carbonate reduction which increases sharply with temperature. This resulted in a large fraction (25-35%) of the sodium in the black liquor solids being volatilized at the higher furnace temperature and O_2 content conditions, and it explains why there was almost no enrichment in air at any temperature. Figure 7.5 shows the effect of particle surface temperature on the potassium and chloride enrichment factors. The data for potassium and chloride fall in a smooth curve, independent of the oxygen content of the reaction gas.

The behavior of potassium, Figure 7.4, is a mix of the behavior of both chloride and sodium. It is released as potassium chloride by volatilization and also as potassium vapor by the carbonate reduction mechanism.

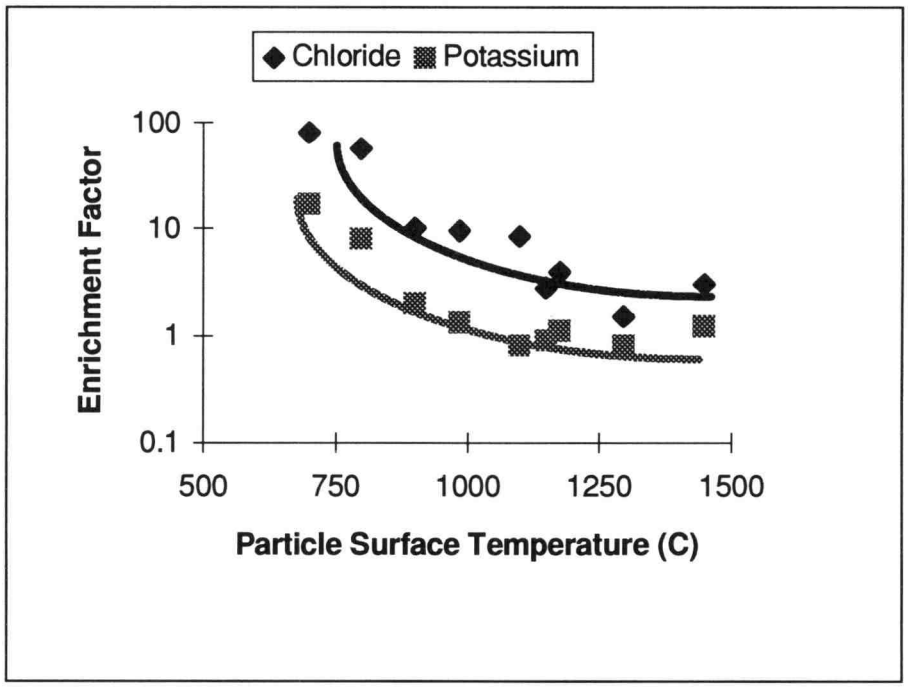


Figure 7.5: Effect of particle surface temperature on enrichment factors

CHAPTER 8
CONCLUSIONS AND RECOMMENDATIONS

8.1 - Conclusions

From the results presented in this work, it was shown that it is possible to predict potassium and chloride enrichment during black liquor pyrolysis and combustion based on a mechanism involving volatilization of NaCl and KCl and reduction of Na_2CO_3 and K_2CO_3 to metallic Na and K and the effects of mass transfer and diffusion. The results from this work has also led to the following additional conclusions:

- Particles Characteristics and Fume Generation

1- The dry black liquor particles, when pyrolyzed, swelled considerably to about 4 times their initial diameter.
2- Fumes collected from pyrolysis and 4% O_2 experiments consisted not only of sodium and potassium salts but also fixed carbon.
3- At lower temperatures and oxygen content, the inorganic in the fume was almost entirely NaCl. The NaCl content decreased with increasing temperature and O_2 content although the total amount of NaCl per gram of black liquor solids increased.
4- The amount of fume at oxidizing conditions is considerably higher than at reducing conditions.
5- The temperature has a great effect on fuming.

- Potassium and Chloride Enrichment

1- For potassium, the greatest enrichment factor, over 15, was obtained at 700°C in nitrogen.

2- At higher temperatures, the potassium enrichment factor decreases to the point that no enrichment was obtained at 1100°C.

3- Virtually there was no potassium enrichment in air at any temperature.
4- Chloride enrichment behaved similar to that of potassium.
5- A chloride enrichment factor of around 50 in nitrogen at 700°C was achieved.
6- In air, the chloride enrichment factor was around 3, at any temperature.

- Mechanisms

1- Prediction of the potassium and chloride enrichment factors are possible assuming KCl and NaCl volatilization and carbonate reduction mechanism.
2- The main reason for the high enrichment factors at lower temperatures and reducing conditions is the low sodium release rate via Na_2CO_3 reduction.
3- The increase in sodium release is much more significant with the increase of temperature than with the secondary effect of the increase of oxygen content.
4- The oxygen-enhanced mechanism apparently does not play an important role in the release of sodium by carbonate reduction.
5- The higher surface temperature that a small particle achieves when burning in air compared with those at 0% and 4% O_2 can explain why there was almost no enrichment in air at any temperature.

8.2 - Recommendations

The following are recommendations for future studies to better understand the release of potassium and chloride during black liquor combustion:

- Study black liquors with different compositions.
- Use of a wider range of residence time.
- Perform experiments under different environments with the presence of CO_2 and CO.
- Incorporate more accurate data into the model such as porosity, particle surface temperature and salts release rate.

CHAPTER 9

BIBLIOGRAPHY

1. Tran, H., Reeve, D. and Barham, D., *Formation of Kraft Recovery Boiler Superheater Fireside Deposits,* Pulp Paper Canada 84(1):36-41 (1983)

2. Adams, T. N. and Frederick, W. J., *Kraft Recovery Boiler Physical and Chemical Processes,* American Paper Institute, 1988

3. Nouch, G. W., *Chemical Recovery in the Alkaline Pulping Process,* Tappi Press, 1985

4. Boonsongsup, L., *SO_2 Capture and HCl Release at Kraft Recovery Boiler Conditions,* M.S. Thesis, Oregon State University, September 1993

5. Kauppinen, E., Jokiniemi, J., Mikkanen, P., Iisa, K., Frederick, J., Boonsongsup, L. and Sinquefield, S., *Fume Particle Characteristics and Their Reactions with SO_2 at Kraft Recovery Boiler Conditions,* Proceedings, 1993 Tappi Engineering Conference, Tappi Press, Atlanta, 1993

6. Frederick, W. J. and Hupa, M., *Evidence of Sodium Fuming During Pyrolysis of Black Liquor,* Tappi Jl., 11:192-194 (1991)

7. Hupa, M., Solin, P. and Hyoty, P., Pulp Paper Sci. 13(2):67-72 (1987)

8. Cameron, J. H., *Vaporization from Alkali Carbonate Melts with Reference to the Kraft Recovery Furnace,* Pulp and Paper Sci. 14(4):76-81 (1988)

9. Li, J. and van Heiningen, A. R. P., *Sodium Emission During Pyrolysis and Gasification of Black Liquor Char,* Tappi Jl. 12:213-219 (1990)

10. Cameron, J. H., *Reaction Enhanced Vaporization of Molten Salt,* Chem. Eng. Comm. 59:243-257 (1987)

11. Bindell, J. B., *Elements of Scanning Electron Microscopy,* Advanced Materials & Processes, 3:20-27 (1993)

12. Frederick, W. J., *Combustion processes in black liquor recovery: analysis and interpretation of combustion rate data and an engineering design model,* US DOE Report DOE/CE/40637-T8 (DE90012712), March, 1990.

13. Frederick, W. J., Hupa, M., Stenberg, J., and Hernberg, R., *Optical Pyrometric Measurements of Surface Temperatures During Black Liquor Char Burning and Gasification,* In press

14. Hurt, R. and Mitchell, R., *On the Combustion Kinetics of Heterogeneous Char Particle Populations,* Twenty-Fourth Symposium (International) on Combustion, The Combustion Institute, 1992 pp. 1233-1241

15. Reeve, D. W., Tran, H. N. and Barham, D., *The Effluent Free Bleached Kraft Pulp Mill - Part XI: Chemical and Thermal Properties of Recovery Boiler Superheater Fireside Deposits,* Pulp and Paper Canada 82(9):T315 (1981)

16. Reeve, D. W., Tran, H. N. and Barham, D., *Superheater Fireside Deposits and Corrosion in Kraft Recovery Boiler,* Tappi 64(5):109 (1981)

17. Baxter, L. L. and Desollar, R. W., *Ash Deposition as a Function of Coal Type, Location in a Boiler, and Boiler Operating Conditions: Predictions Compared to Observations,* AFRC/IFRC International Conference on Environmental Control of Combustion Processes (Honolulu, HI, October, 7-10, 1991)

18. Hupa, M. and Frederick, W.J., *Combustion of black liquor droplets,* Proc.1993 TAPPI Kraft Recovery Operations Seminar, Tappi Press, Atlanta, p.191-200, (1993)

19. Wag, K. J. and Frederick, W. J., *Sodium and Sulfur Release During Black Liquor Char Gasification: Assessment of the Mechanism and Rate,* Oregon State University, in progress

20. Perry, R. H. and Green, D., *Perry's Chemical Engineers' Handbook,* Sixth Edition, McGraw-Hill International Editions

Appendices

Appendix A

ANALYSIS OF DEPOSITS IN RECOVERY BOILERS

A.1 Introduction

The appearance and composition of a deposit changes according to the mechanism by which it was formed. The three mechanisms of deposit formation are the impaction of carry-over particles, deposition of sub-micron fume particles by thermophoresis, and the condensation of vapors. The relative degree of deposition by carry-over and by condensation is shown schematically in Figure A.1 [1]. A deposit formed by impaction of carry-over particles has more sodium carbonate and sodium hydroxide and less sodium sulfate, sodium chloride and potassium salts if compared to that formed by the thermophoretic deposition or condensation mechanisms. The carry-over mechanism cause the formation of a hard and thick outside layer, while the other two mechanisms cause the formation of an inside white powder layer which is enriched in chloride and potassium salts.

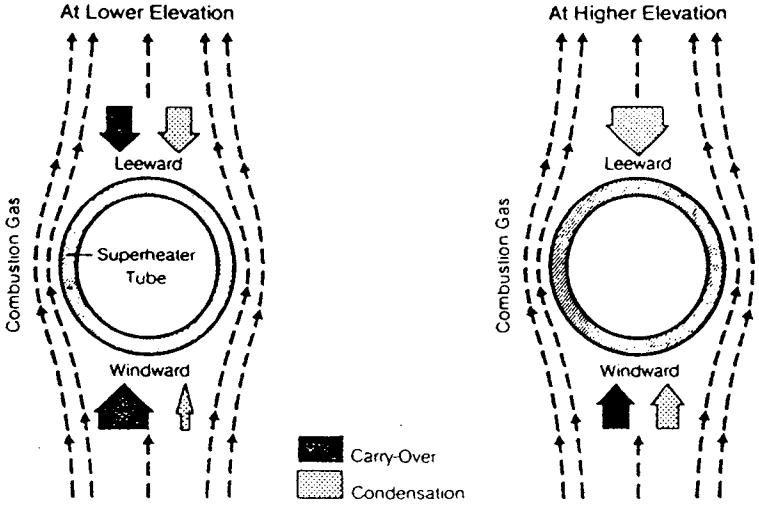


Figure A.1: Schematic of deposit formation [1]

A.2 Objectives

A preliminary evaluation of the elemental distribution in recovery boiler fireside deposits was conducted. My objective was to understand the characteristics of fume deposits in recovery boilers. To accomplish this, I obtained deposits from recovery boilers and examined them using microscopic techniques.

Some of the steps taken to achieve the objectives were:

- Obtain fume deposits of recovery boilers;
- Section the deposits so that the physical and chemical characteristics can be measured radially in the deposit;
- Analyze the deposits using scanning electron microscopy (SEM) and energy dispersive X-ray analyzer (EDAX) to determine the morphological characteristics (particle size, degree of sintering) and the distribution of chemical species (Na, S, K, Cl) radially in the deposits.

A.3 Experimental

The fireside deposits of recovery boilers used for this work were collected from different regions of boilers of several major pulp companies. By visual means, the several layers of the deposit were identified. Samples of the layers were removed by using a sharp knife. They were labeled and sent to a SEM lab for sample preparation (to be attached to a sample holder and coated with carbon) and analysis.

A.4 Findings

Scanning electron microscope (SEM) provides three-dimensional images of an object based on its surface topography and elemental composition. EDAX or

Energy-Dispersive X-ray Analyzer is used with SEM to determine the elemental composition of a small, chosen area of a specimen through weight and atomic percentage. Both are important tools for examination of surfaces.

A deposit was obtained from the back side of the tubes in front of the generator bank of a recovery boiler (Weyerhaeuser Company, Plymouth, NC - May 1992). This deposit contained 4 different layers that were analyzed by SEM. Figure A.2 shows, schematically, how the different layers were designated.

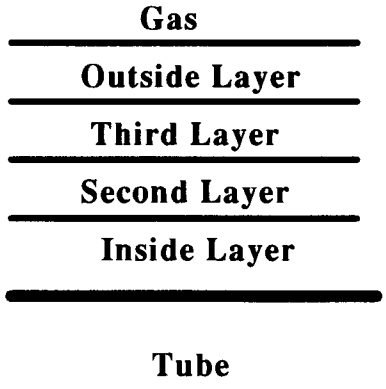


Figure A.2: Schematic of the different layers of deposit

The inside layer, shown in Figure A.3 with a 16X magnification, and in Figure A.4 with a 2000X magnification, resembles an agglomerate of particles beginning to fuse. This layer has a very porous surface. Macroscopically, the inside layer looks like a fine white powder.

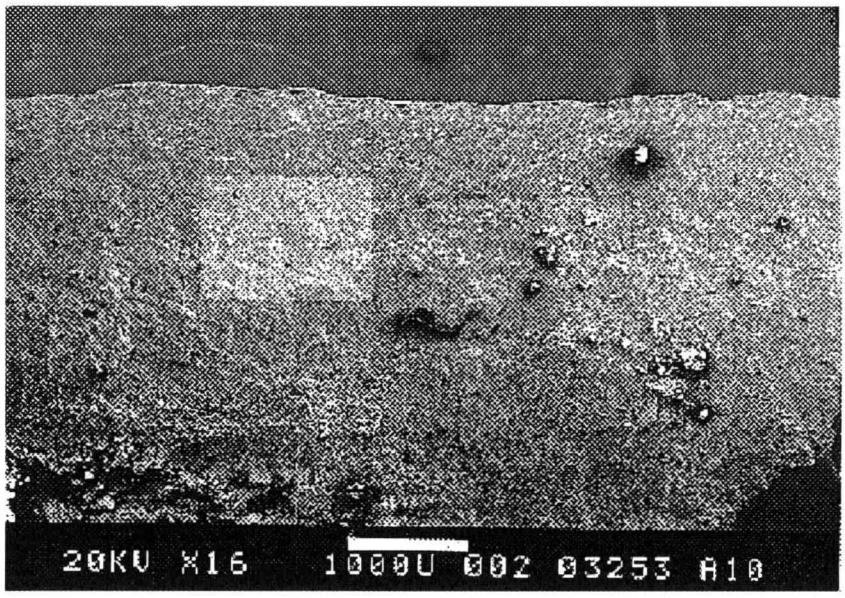


Figure A.3: SEM micrograph showing a typical surface of the inside layer of the deposit (16X magnification)

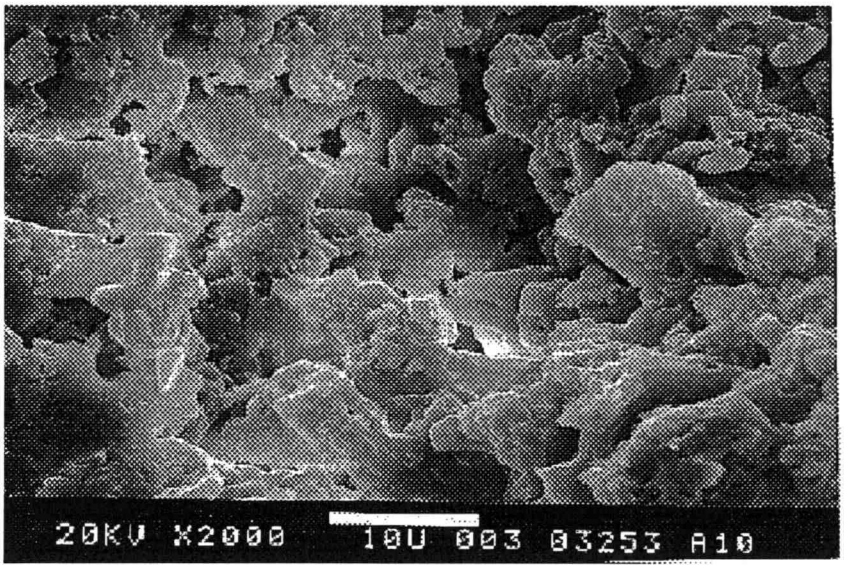


Figure A.4: SEM micrograph showing a typical surface of the inside layer of the deposit (2000X magnification)

The second layer is a hard material and very porous as in Figure A.5. From the SEM picture of that region, shown in Figure A.6, it was obvious that not many pores existed.

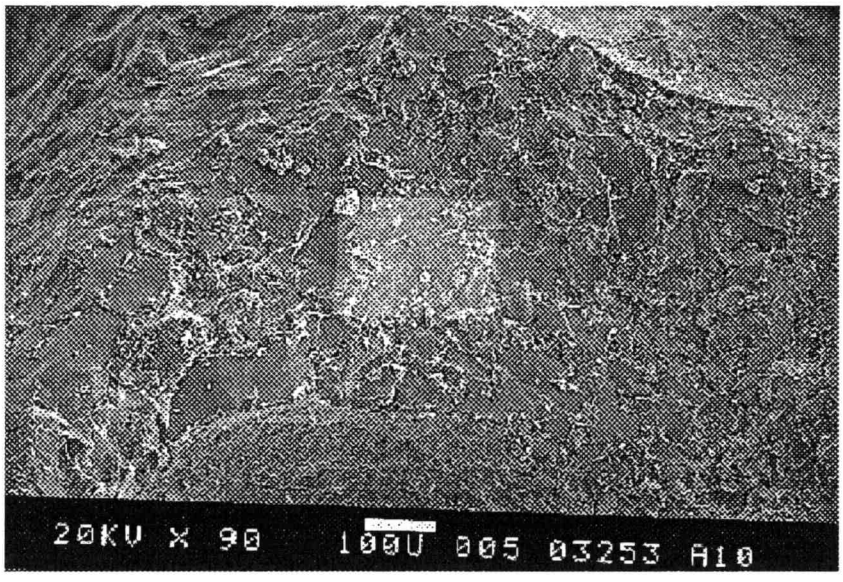


Figure A.5: SEM micrograph showing a typical surface of the second layer of the deposit (90X magnification)

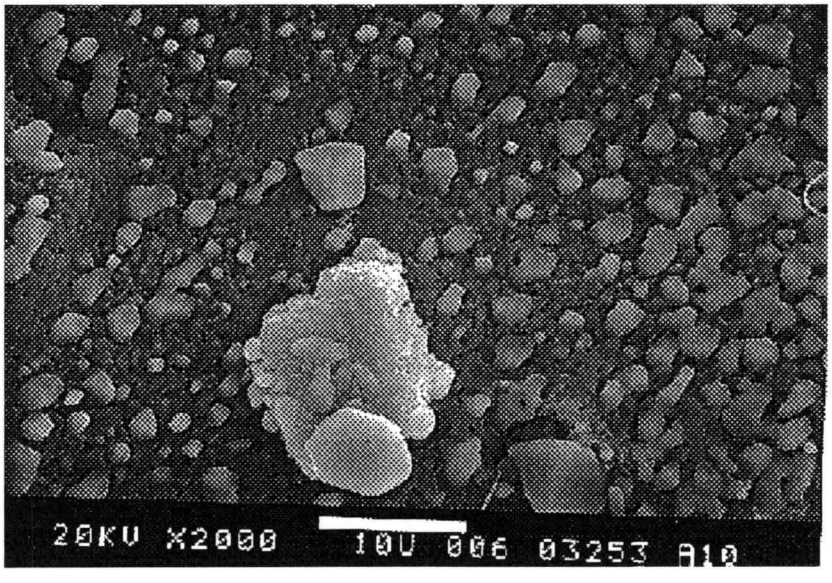


Figure A.6: SEM micrograph showing a typical surface of the second layer of the deposit (2000X magnification)

The third layer seemed to be the hardest to cut or break, with only some pores, Figure A.7. From Figure A.8, a higher magnification (2000X) of the surface, we could see that this layer was uniform and it seemed that it was formed originally by spherical particles that fused.

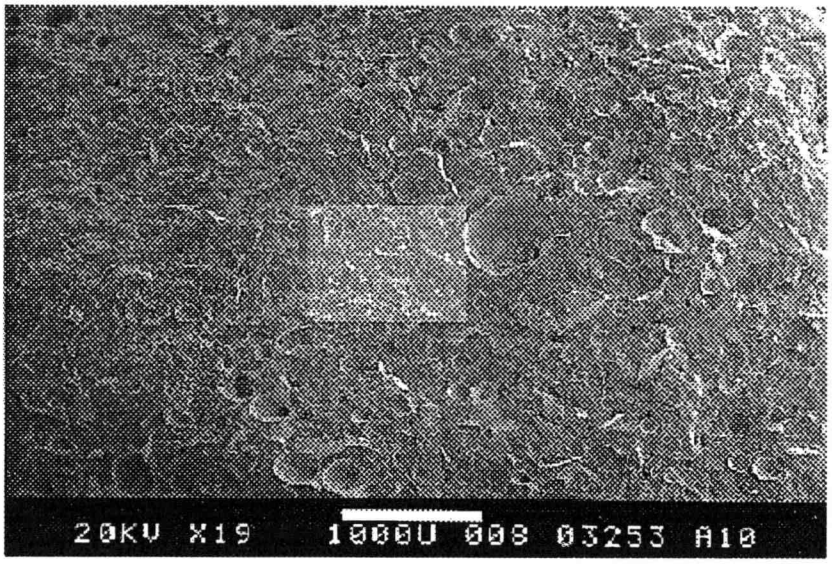


Figure A.7: SEM micrograph showing a typical surface of the third layer of the deposit (19X magnification)

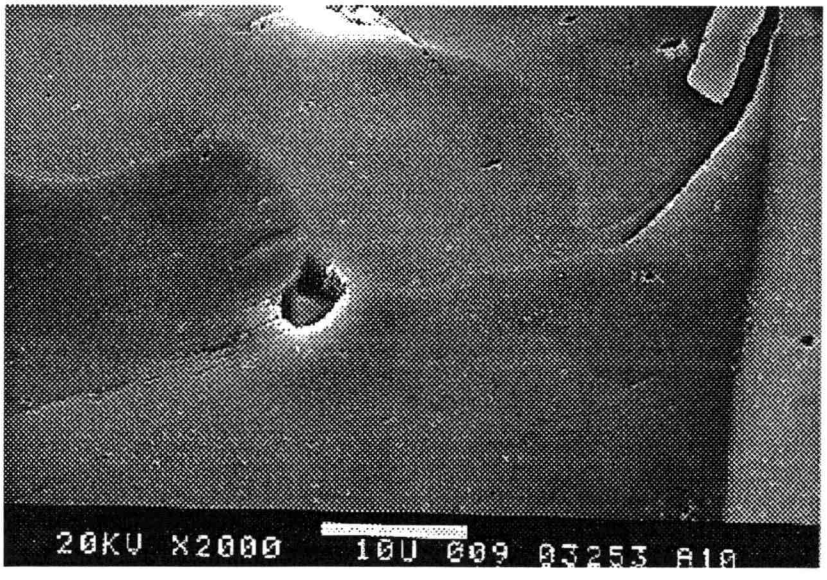


Figure A.8: SEM micrograph showing a typical surface of the third layer of the deposit (2000X magnification)

The outside layer, Figures A.9 and A.10, a non-porous white surface, showed similar morphological characteristics as those of the inside layer.

Figure A.9: SEM micrograph showing a typical surface of the outside layer of the deposit (20X magnification)

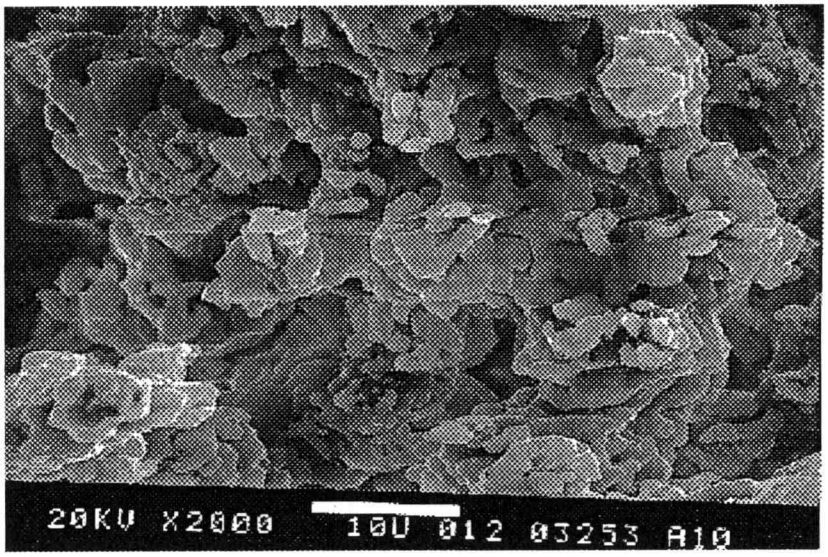


Figure A.10: SEM micrograph showing a typical surface of the outside layer of the deposit (2000X magnification)

Table A.1 shows the summary of data collected from each layer of this deposit. The following denominations were given to the different spectrums:

VR11A - Inside Layer of the Deposit

VR12A - Second Layer of the Deposit

VR13A - Third Layer of the Deposit

VR14A - Outside Layer of the Deposit

The full EDAX analysis of the layers can be found in Appendix A.

The sodium salts concentration should be interpreted as alkali (sodium + potassium) salts concentration. The carbonate concentration was calculated by difference. Figure A.11 is a plot of the mass fraction data presented in Table A.1.

Table A.1: Chemical composition of the layers in the deposit

SEM ANALYSIS : SAMPLE 1 — March 93

File : SEMDAT03

SAMPLE 1 - Plymouth 5/92 _ #4
Back side of tubes in front of generator bank
Ooring between tubes into sootblowing cavity

	Spectrum	Mass Fraction (%)			Mole Ratio (%)	
		Na2SO4	NaCl	Na2CO3	K/(Na+K)	Cl/(Na+K)
Inside	VR11A	69.9	6.3	23.9	10.0	7.0
Second	VR12A	80.1	4.0	15.9	16.7	4.5
Third	VR13A	66.5	0.3	33.2	5.3	0.3
Outside	VR14A	74.2	10.3	15.5	18.1	11.7

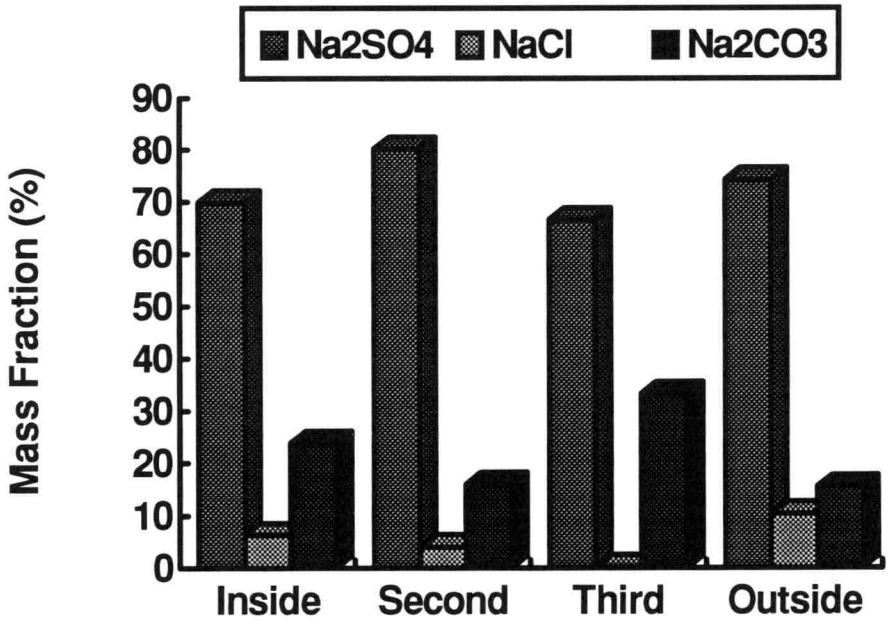


Figure A.11: Chemical composition of the layers in the deposit

The results presented in Table A.1 and Figure A.11 show that:

1- Sodium sulfate is behaving uniformly from the inside layer to the outside layer. Its concentration changes from 70 to 80% of mass fraction in the deposit.

2- Sodium chloride changed in concentration radially along the deposit, from less than 1% in the third layer to more than 10% in the outside layer.

3- Carbonate, calculated by difference, varies from 15 to 33% in mass fraction.

4- Alkali metal concentration in the deposit is relatively constant (Figure A.12).

5- Mole ratio of potassium in the alkali is quite variable (Figure A.13).

6- Mole ratio of chloride to Na + K has the same behavior as the sodium chloride, higher concentrations in the extremes and lower inside.

7- Different samples from same layers of deposit were analyzed and similar results were obtained, indicating that the analysis using EDAX were reproducible.

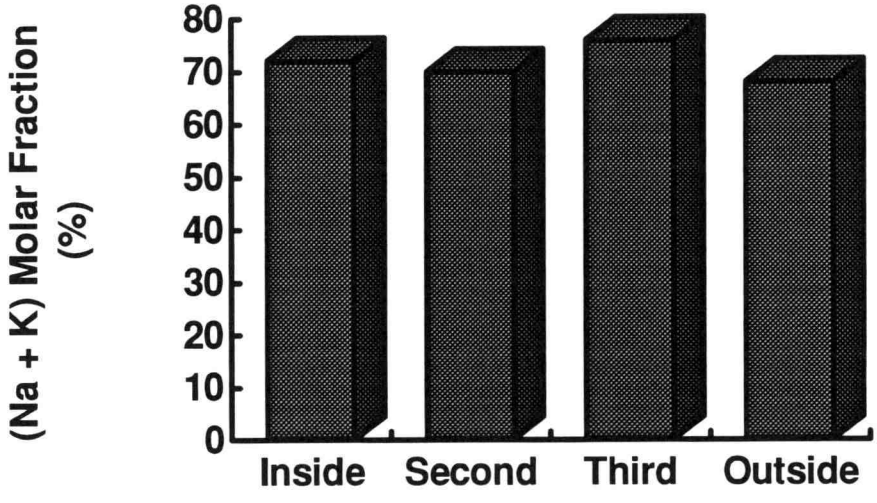


Figure A.12: Alkali metals concentration in the layers of the deposit

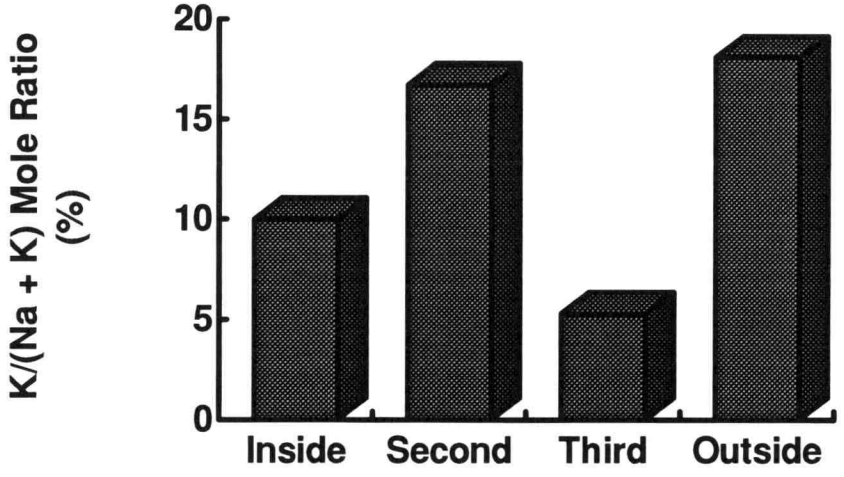


Figure A.13: Mole ratio of potassium to alkali metals in the layers of the deposit

Most of the results obtained from this work agree well with the literature [1,15,16]. Table A.2 compares some of the data from this work with the data available in the literature.

The inside and the outside layers of the deposit used in this thesis are similar and have an appearance of a white fine powder. This is one of the characteristics of a deposit formed by condensation mechanism, and therefore enriched in chloride and potassium salts. This is also in agreement with the data presented in Figure A.11, where the sodium chloride has its highest mass fraction with the inside and outside layer.

Table A.2: Data comparison of fireside deposits from recovery boilers

	Literature	Present work
Na_2SO_4 composition (%)	50 - 85	70 - 80
NaCl composition (%)	0.1 - 15	1 - 10
Na_2CO_3 composition (%)	10 - 40	15 - 33
K/K + Na	2 - 6	5 - 18

A.5 Conclusions

The conclusions of this study were:

- The SEM and EDAX are useful tools for characterization and study of deposits.
- Sulfate concentration does not vary significantly across the deposit.
- Chloride concentration is lower in the middle and higher on the extremities of the deposit.
- The alkali concentration does not change much within the deposit.
- The outside and inside layers of the deposit may have been formed by the condensation mechanism and the second and third layers by carry-over impaction.
- The results are in agreement with the published literature.

Table A-3: EDAX data from analysis of deposit

SEM ANALYSIS : SAMPLE 1 March 93

SAMPLE 1 - Plymouth 5/92 _ #4
Back side of tubes in front of generator bank
Ooring between tubes into sootblowing cavity

STANDARLESS EDS ANALYSIS

ELEMENT & SAMPLE	WEIGHT PERCENT	ATOMIC PERCENT	PRECISION	CTS/SEC	ITER	NORMALIZATION FACTOR
Spectrum VR11A		(Sample 1 - inside layer of the deposit)				
Na	55.20	64.48	1.48	19.07	15	0.634
Al	0.55	0.55	0.11	1.68		
S	27.30	22.86	0.48	50.09		
Cl	6.57	4.98	0.28	11.00		
K	10.39	7.13	0.34	15.91		
Spectrum VR12A		(Sample 1 - second layer from inside)				
Na	48.33	58.19	1.32	18.71	10	0.629
Al	0.53	0.54	0.10	2.21		
Si	0.11	0.11	0.03	2.38		
S	30.50	26.33	0.45	69.66		
Cl	4.05	3.17	0.20	9.57		
K	16.47	11.66	0.39	30.11		

Table A-4: EDAX results from analysis of deposit

SEM ANALYSIS : SAMPLE 1 March 93

SAMPLE 1 - Plymouth 5/92 _ #4
Back side of tubes in front of generator bank
Ooring between tubes into sootblowing cavity

ELEMENT & SAMPLE	WEIGHT PERCENT	ATOMIC PERCENT	PRECISION	CTS/SEC	ITER	NORMALIZATION FACTOR
Spectrum VR13A		(Sample 1 - third layer from inside)				
Na	64.62	72.41	1.58	21.78	20	0.674
Al	0.32	0.31	0.09	1.38		
Si	0.22	0.20	0.06	1.73		
S	28.42	22.83	0.53	44.41		
Cl	0.30	0.22	0.06	2.46		
K	6.12	4.03	0.27	8.86		
Spectrum VR14A		(Sample 1 - outside layer)				
Na	45.57	55.74	1.48	13.29	10	0.62
Al	0.32	0.34	0.08	1.48		
Si	0.19	0.19	0.05	1.71		
S	26.80	23.50	0.48	48.72		
Cl	10.00	7.93	0.35	14.78		
K	17.12	12.31	0.45	23.71		

Appendix B

EXPERIMENTAL DATA

Table B-1:Data from experiments #1 thru #5

EXPERIMENT	AIR	AIR	4% O2	4% O2	0% O2
LIQUOR TYPE	#1	#1	#1	#1	#1
TEMPERATURE (C)	900	900	900	900	900
ROOM TEMPERATURE (C)	23.5	23.5	23.5	23.5	23.5
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125
DATA ACQUISITION FILE	**1**	**2**	**3**	**4**	**5**
PRIMARY FLOW (l/min)	0.10	0.10	0.10	0.10	0.10
SECONDARY FLOW (total)	14.99	14.98	14.96	14.97	14.96
air (l/min)	14.99	14.98	2.78	2.78	
N2 (l/min)			12.18	12.19	14.96
QUENCH (l/min)	22.57	22.47	22.57	22.45	22.49
FILTER (l/min)	3.48	2.73	2.73	2.73	2.73
TOTAL RUNNING TIME (sec)	640	298	361	357	232
time at plug	564	284	351		167
filter flow time	640	298	361	357	232
RESIDENCE TIME					
effective reactor volume (l)	0.0033	0.0033	0.0033	0.0033	0.0033
primary flow rate (l/min)	0.40	0.40	0.40	0.39	0.40
injector velocity (cm/sec)	19.08	19.07	19.11	18.89	19.04
residence time (sec)	0.50	0.51	0.50	0.51	0.51
WEIGHT DATA					
TOTAL INPUT WEIGHT (g)	4.6055	2.3955	2.6129	2.8036	1.4717
MASS FLOW RATE (g/min)	0.4318	0.4828	0.4348	0.4710	0.3799
FUME WEIGHT	0.0893	0.0314	0.0037	0.0034	0.0032
% input weight in fume	20.95	18.00	1.95	1.66	2.98
RESIDUAL WEIGHT	1.2576	0.5882	1.3147	0.9247	0.4295
% input weight in cyclone	27.31	24.55	50.32	32.98	29.18
CHEMICAL ANALYSIS					
FUME					
weight analyzed (g)					
Na reading (mV)	-165	-192	-251	-254	-258
concentration (%)	43.19	42.42	35.27	34.11	30.96
Cl reading (mV)	166	182	196	199	196
concentration (%)	1.64	2.23	9.95	9.43	11.51
K reading (mV)	-203	-232	-272	-275	-268
concentration (%)	1.02	0.82	1.24	1.18	1.70
CHAR					
weight analyzed (g)	0.6517	0.6680	0.5371	0.5444	0.5043
Na reading (mV)	-116	-129	-138	-133	-143
concentration (%)	40.74	23.82	20.79	24.97	18.18
Cl reading (mV)	132	132	129	121	137
concentration (%)	1.08	1.05	1.50	2.14	1.11
K reading (mV)	-170	-171	-178	-173	-186
concentration (%)	0.94	0.89	0.85	1.01	0.67
MATERIAL BALANCE					
Na Fume/B.L. (%)	39.94	33.71	3.03	2.51	4.08
Char/B.L. (%)	49.12	25.83	46.18	36.37	23.43
Total (%)	89.06	59.54	49.21	38.87	27.51
Cl Fume/B.L. (%)	51.18	59.86	28.84	23.37	51.08
Char/B.L. (%)	43.76	38.39	112.33	105.00	48.00
Total (%)	94.94	98.25	141.16	128.37	99.09
K Fume/B.L. (%)	34.41	23.97	3.90	3.18	8.20
Char/B.L. (%)	41.63	35.19	69.12	53.84	31.71
Total (%)	76.04	59.16	73.02	57.02	39.91
ENRICHMENT FACTOR					
Cl	1.28	1.78	9.51	9.32	12.53
K	0.86	0.71	1.28	1.27	2.01

Table B-2: Data from experiments #6 thru #10

	EXPERIMENT			0% O2	AIR	AIR	4% O2	4% O2	
	LIQUOR TYPE			#1	#1	#1	#1	#1	
	TEMPERATURE (C)			900	1100	1100	1100	1100	
	ROOM TEMPERATURE (C)			23.5	29	29	26.9	26.9	
	PARTICLE SIZE (um)			90-125	90-125	90-125	90-125	90-125	
	DATA ACQUISITION FILE			**6**	**7**	**8**	**9**	**10**	
	PRIMARY FLOW (l/min)			0.10	0.10	0.10	0.10	0.10	
	SECONDARY FLOW (total)			14.89	14.98	14.97	14.98	14.91	
		air (l/min)			14.98	14.97	2.81	2.78	
		N2 (l/min)		14.89			12.17	12.14	
	QUENCH (l/min)			22.50	22.51	22.52	22.51	22.51	
	FILTER (l/min)			1.74	2.73	2.73	2.73	2.73	
	TOTAL RUNNING TIME (sec)			412	375	373	387	388	
		time at plug							
		filter flow time		412	375	373	387	388	
	RESIDENCE TIME								
		effective reactor volume (l)		0.0033	0.0033	0.0033	0.0033	0.0033	
		primary flow rate (l/min)		0.40	0.45	0.44	0.45	0.46	
		injector velocity (cm/sec)		19.07	18.96	18.55	18.69	19.23	
		residence time (sec)		0.51	0.44	0.45	0.45	0.43	
	WEIGHT DATA								
	TOTAL INPUT WEIGHT (g)			3.9488	2.6088	3.1539	3.5222	2.902	
	MASS FLOW RATE (g/min)			0.5755	0.4175	0.5068	0.5458	0.4488	
	FUME WEIGHT			0.0123	0.0358	0.0351	0.0234	0.0188	
		% input weight in fume		6.68	18.82	15.27	9.13	8.88	
	RESIDUAL WEIGHT			0.5609	0.2485	0.0969	0.1063	0.0219	
		% input weight in cyclone		14.20	9.53	3.07	3.02	0.75	
	CHEMICAL ANALYSIS								
	FUME								
		weight analyzed (g)							
		Na	reading (mV)	-232	-193	-192	-200	-211	
			concentration (%)	22.42	35.77	37.95	41.54	33.53	
		Cl	reading (mV)	189	170	172	174	179	
			concentration (%)	4.13	3.41	3.17	4.33	4.29	
		K	reading (mV)	-252	-218	-223	-230	-240	
			concentration (%)	0.89	1.33	1.09	1.21	0.97	
	CHAR								
		weight analyzed (g)		0.3263	0.2402	0.0544			
		Na	reading (mV)	-151	-150	-186			
			concentration (%)	20.51	28.98	31.01	#VALUE!	#VALUE!	
		Cl	reading (mV)	143	139	192			
			concentration (%)	1.30	2.12	0.81	#VALUE!	#VALUE!	
		K	reading (mV)	-195	-191	-231			
			concentration (%)	0.74	1.17	1.17	#VALUE!	#VALUE!	
	MATERIAL BALANCE								
		Na	Fume/B.L. (%)	6.61	29.73	25.59	16.74	13.15	
			Char/B.L. (%)	12.86	12.19	4.21	#VALUE!	#VALUE!	
			Total (%)	19.47	41.92	29.80	#VALUE!	#VALUE!	
		Cl	Fume/B.L. (%)	41.07	95.42	72.03	58.86	56.65	
			Char/B.L. (%)	27.39	30.00	3.72	#VALUE!	#VALUE!	
			Total (%)	68.46	125.42	75.75	#VALUE!	#VALUE!	
		K	Fume/B.L. (%)	9.55	40.30	26.86	17.78	13.97	
			Char/B.L. (%)	17.07	18.04	5.80	#VALUE!	#VALUE!	
			Total (%)	26.62	58.34	32.66	#VALUE!	#VALUE!	
	ENRICHMENT FACTOR								
		Cl		6.21	3.21	2.81	3.52	4.31	
		K		1.45	1.36	1.05	1.06	1.06	

Table B-3: Data from experiments #11 thru #15

	EXPERIMENT		AIR	AIR	AIR	AIR	AIR
	LIQUOR TYPE		#1	#1	#1	#1	#1
	TEMPERATURE (C)		700	700	700	700	700
	ROOM TEMPERATURE (C)		29	29	22.7	22.7	29
	PARTICLE SIZE (um)		90-125	90-125	90-125	90-125	90-125
	DATA ACQUISITION FILE		**11**	**12**	**13**	**14**	**15**
	PRIMARY FLOW (l/min)		0.10	0.10	0.10	0.10	0.10
	SECONDARY FLOW (total)		15.01	14.99	14.94	15.01	15.01
	air (l/min)		15.01	14.99	14.94	15.01	15.01
	N2 (l/min)						
	QUENCH (l/min)		22.56	22.53	22.40	22.58	22.54
	FILTER (l/min)		2.73	3.48	2.75	2.75	2.73
	TOTAL RUNNING TIME (sec)		388	416	362	309	207
	time at plug					299	199
	filter flow time		388	416	362	309	207
	RESIDENCE TIME						
	effective reactor volume (l)		0.0033	0.0033	0.0033	0.0033	0.0033
	primary flow rate (l/min)		0.32	0.32	0.33	0.33	0.32
	injector velocity (cm/sec)		18.66	18.74	19.22	19.14	18.67
	residence time (sec)		0.63	0.63	0.60	0.61	0.62
	WEIGHT DATA						
	TOTAL INPUT WEIGHT (g)		3.0699	3.5759	3.726	3.031	2.0587
	MASS FLOW RATE (g/min)		0.4744	0.5164	0.6176	0.5879	0.5970
	FUME WEIGHT		0.0199	0.0129	0.0553	0.0508	0.0309
	% input weight in fume		8.91	3.89	20.15	22.91	20.64
	RESIDUAL WEIGHT		0.0102	0.0017	0.6924	0.4702	0.3014
	% input weight in cyclone		0.33	0.05	18.58	15.51	14.64
	CHEMICAL ANALYSIS						
	FUME						
	weight analyzed (g)						
	Na	reading (mV)	-205	-210	-178	-182	
		concentration (%)	40.12	50.83	41.80	38.87	15.00
	Cl	reading (mV)	182	180	167	169	
		concentration (%)	3.53	5.96	2.53	2.51	#VALUE!
	K	reading (mV)	-240	-238	-214	-217	
		concentration (%)	0.92	1.55	1.02	0.98	0.50
	CHAR						
	weight analyzed (g)				0.7562	0.4735	0.0974
	Na	reading (mV)			-123	-130	-173
		concentration (%)	#VALUE!	#VALUE!	26.65	32.31	30.46
	Cl	reading (mV)			123	141	193
		concentration (%)	#VALUE!	#VALUE!	1.40	0.98	0.46
	K	reading (mV)			-170	-180	-221
		concentration (%)	#VALUE!	#VALUE!	0.81	0.90	1.00
	MATERIAL BALANCE						
	Na	Fume/B.L. (%)	15.78	8.72	37.19	39.31	13.67
		Char/B.L. (%)	#VALUE!	#VALUE!	21.87	22.13	19.69
		Total (%)	#VALUE!	#VALUE!	59.05	61.44	33.35
	Cl	Fume/B.L. (%)	46.75	34.50	75.92	85.68	#VALUE!
		Char/B.L. (%)	#VALUE!	#VALUE!	38.84	22.61	9.97
		Total (%)	#VALUE!	#VALUE!	114.77	108.29	#VALUE!
	K	Fume/B.L. (%)	13.24	9.72	33.20	36.08	16.67
		Char/B.L. (%)	#VALUE!	#VALUE!	24.42	22.44	23.61
		Total (%)	#VALUE!	#VALUE!	57.62	58.52	40.28
	ENRICHMENT FACTOR						
	Cl		2.96	3.96	2.04	2.18	#VALUE!
	K		0.84	1.11	0.89	0.92	1.22

(The shaded column corresponds to an unsuccessfull run.)

Table B-4: Data from experiments #16 thru #20

	EXPERIMENT			4% O2	4% O2	0% O2	0% O2	0% O2	
	LIQUOR TYPE			#1	#1	#1	#1	#1	
	TEMPERATURE (C)			700	700	700	700	1100	
	ROOM TEMPERATURE (C)			29	29	30.8	29.3	23.1	
	PARTICLE SIZE (um)			90-125	90-125	90-125	90-125	90-125	
	DATA ACQUISITION FILE			**16**	**17**	**18**	**19**	**20**	
	PRIMARY FLOW (l/min)			0.10	0.10	0.10	0.10	0.10	
	SECONDARY FLOW (total)			14.97	15.01	14.95	14.96	15.00	
		air (l/min)		2.80	2.80				
		N2 (l/min)		12.16	12.21	14.95	14.96	15.00	
	QUENCH (l/min)			22.57	22.53	22.49	22.56	22.50	
	FILTER (l/min)			2.25	2.25	1.98	1.99	2.50	
	TOTAL RUNNING TIME (sec)			387	387	330	327	330	
		time at plug				320			
		filter flow time			127	100	134	330	
	RESIDENCE TIME								
		effective reactor volume (l)		0.0033	0.0033	0.0033	0.0033	0.0033	
		primary flow rate (l/min)		0.33	0.32	0.32	0.33	0.46	
		injector velocity (cm/sec)		19.32	19.17	19.11	19.25	19.02	
		residence time (sec)		0.61	0.62	0.62	0.62	0.43	
	WEIGHT DATA								
	TOTAL INPUT WEIGHT (g)			4.3683	4.5713	2.9764	3.5264	2.5865	
	MASS FLOW RATE (g/min)			0.6769	0.7086	0.5409	0.6474	0.4703	
	FUME WEIGHT			0.0008	0.0008	0.0005	0.0006	0.0132	
		% input weight in fume		0.31	0.29	0.32	0.32	7.66	
	RESIDUAL WEIGHT			2.331	2.0534	1.0994	0.2305	1.1232	
		% input weight in cyclone		53.36	44.92	36.94	6.54	43.43	
	CHEMICAL ANALYSIS								
	FUME								
		weight analyzed (g)							
		Na	reading (mV)	-286	-310	-324	-322	-227	
			concentration (%)	41.12	15.98	14.73	13.28	25.43	
		Cl	reading (mV)	199	200	207	208	175	
			concentration (%)	40.10	38.29	44.38	35.32	7.34	
		K	reading (mV)	-276	-275	-275	-278	-258	
			concentration (%)	4.82	5.03	8.05	5.89	0.64	
	CHAR								
		weight analyzed (g)		0.4129	0.8852	0.6251	0.2490	0.5071	
		Na	reading (mV)	-141	-124	-127	-153	-138	
			concentration (%)	24.03	21.89	27.55	24.84	22.02	
		Cl	reading (mV)	151	125	113	141	112	
			concentration (%)	0.71	1.09	2.69	1.86	3.48	
		K	reading (mV)	-185	-168	-164	-181	-179	
			concentration (%)	0.85	0.75	1.23	1.64	0.87	
	MATERIAL BALANCE								
		Na	Fume/B.L. (%)	0.55	0.21	0.21	0.19	8.60	
			Char/B.L. (%)	56.61	43.41	44.92	7.17	42.22	
			Total (%)	57.17	43.62	45.13	7.36	50.81	
		Cl	Fume/B.L. (%)	18.24	16.65	20.95	16.89	83.60	
			Char/B.L. (%)	56.26	73.15	148.03	18.11	224.64	
			Total (%)	74.50	89.80	168.97	35.00	308.24	
		K	Fume/B.L. (%)	2.38	2.37	4.12	3.06	7.87	
			Char/B.L. (%)	73.50	54.31	73.39	17.32	60.88	
			Total (%)	75.87	56.69	77.52	20.38	68.75	
	ENRICHMENT FACTOR								
		Cl		32.87	80.76	101.53	89.62	9.73	
		K		4.29	11.52	19.99	16.23	0.92	

Table B-5: Data from experiments #21 thru #22A

	EXPERIMENT		0% O2	0% O2	0% O2	0% O2	0% O2
	LIQUOR TYPE		#1	#1	#1	#1	#1
	TEMPERATURE (C)		700	700	700	700	800
	ROOM TEMPERATURE (C)		24.7	25.5	26	22.2	25
	PARTICLE SIZE (um)		90-125	90-125	90-125	90-125	90-125
	DATA ACQUISITION FILE		**21A**	**21B**	**21C**	**21D**	**22A**
	PRIMARY FLOW (l/min)		0.10	0.10	0.10	0.10	0.10
	SECONDARY FLOW (total)		14.89	14.87	14.88	14.86	10.18
		air (l/min)					
		N2 (l/min)	14.89	14.87	14.88	14.86	10.18
	QUENCH (l/min)		24.95	27.91	24.96	19.90	19.92
	FILTER (l/min)		2.49	3.98	2.47	3.02	1.98
	TOTAL RUNNING TIME (sec)		450	238	802	234	273
		time at plug					
		filter flow time	450	230	96	280	281
	RESIDENCE TIME						
		effective reactor volume (l)	0.0033	0.0033	0.0033	0.0033	0.0033
		primary flow rate (l/min)	0.33	0.32	0.33	0.32	0.35
		injector velocity (cm/sec)	19.50	18.55	19.29	18.76	18.60
		residence time (sec)	0.60	0.63	0.61	0.62	0.57
	WEIGHT DATA						
	TOTAL INPUT WEIGHT (g)		3.1187	1.3928	6.4907	1.5125	2.2911
	MASS FLOW RATE (g/min)		0.4162	0.3515	0.4856	0.3875	0.5010
	FUME WEIGHT		0.0028	0.0023	0.0012	0.0101	0.0122
		% input weight in fume	1.43	1.77	0.30	7.69	4.04
	RESIDUAL WEIGHT		1.5240	0.7054	4.5307	0.6975	1.1305
		% input weight in cyclone	48.87	50.65	69.80	46.12	49.56
	CHEMICAL ANALYSIS						
	FUME						
		weight analyzed (g)					
		Na reading (mV)	-265	-269	-290	-235	-228
		concentration (%)	18.41	19.09	15.74	17.04	18.67
		Cl reading (mV)	179	179	180	175	174
		concentration (%)	10.72	13.05	23.87	3.59	3.11
		K reading (mV)	-265	-274	-274	-231	-268
		concentration (%)	3.86	3.10	5.93	5.21	0.77
	CHAR						
		weight analyzed (g)	0.2032	0.2032	0.2032	0.2032	0.2495
		Na reading (mV)	-154	-154	-154	-154	-147
		concentration (%)	24.46	24.46	24.46	24.46	23.67
		Cl reading (mV)	129	129	129	129	125
		concentration (%)	1.20	1.20	1.20	1.20	1.51
		K reading (mV)	-202	-202	-202	-202	-203
		concentration (%)	0.64	0.64	0.64	0.64	0.78
	MATERIAL BALANCE						
		Na Fume/B.L. (%)	1.17	1.40	0.21	5.78	3.35
		Char/B.L. (%)	52.77	54.69	75.38	49.80	51.68
		Total (%)	53.94	56.19	75.59	55.58	55.01
		Cl Fume/B.L. (%)	22.89	34.44	10.61	41.02	19.70
		Char/B.L. (%)	87.41	90.59	124.86	82.49	111.65
		Total (%)	110.30	125.03	135.46	123.51	130.35
		K Fume/B.L. (%)	8.96	8.87	2.86	64.71	5.04
		Char/B.L. (%)	50.86	52.71	72.65	48.00	62.11
		Total (%)	59.82	61.58	75.51	112.71	67.15
	ENRICHMENT FACTOR						
		Cl	19.62	23.04	51.10	7.10	5.61
		K	7.58	5.93	13.79	11.30	1.51

(The shaded columns correspond to unsuccessfull runs.)

Table B-6: Data from experiments #23A thru #25A

	EXPERIMENT		0% O2	0% O2	0% O2	0% O2		
	LIQUOR TYPE		#1	#1	#1	#1		
	TEMPERATURE (C)		1100	1100	900	1000		
	ROOM TEMPERATURE (C)		22.7	26.2	29	24		
	PARTICLE SIZE (um)		90-125	90-125	90-125	90-125		
	DATA ACQUISITION FILE		**23A**	**23B**	**24A**	**25A**		
	PRIMARY FLOW (l/min)		0.1010	0.1011	0.1018	0.1001		
	SECONDARY FLOW (total)		14.8891	14.9371	14.9381	14.8928		
	air (l/min)							
	N2 (l/min)		14.89	14.94	14.94	14.89		
	QUENCH (l/min)		22.46	22.42	22.56	24.93		
	FILTER (l/min)		3.98	3.98	3.98	3.98		
	TOTAL RUNNING TIME (sec)		356	545	371	432		
	time at plug		339		331	425		
	filter flow time		350	540	354	408		
	RESIDENCE TIME							
	effective reactor volume(l)		0.0033	0.0033	0.0033	0.0033		
	primary flow rate (l/min)		0.47	0.46	0.40	0.43		
	injector velocity (cm/sec)		19.21	19.22	19.37	19.04		
	residence time (sec)		0.43	0.43	0.51	0.47		
	WEIGHT DATA							
	TOTAL INPUT WEIGHT (g)		2.5884	4.2025	2.4786	3.2828		
	MASS FLOW RATE (g/min)		0.4368	0.4628	0.4004	0.4560		
	FUME WEIGHT		0.0199	0.0346	0.004	0.0271		
	% input weight in fume		7.21	7.72	1.52	8.26		
	RESIDUAL WEIGHT		1.3358	2.3358	1.4860	1.5278		
	% input weight in cyclone		51.61	55.58	59.95	46.54		
	CHEMICAL ANALYSIS							
	FUME							
	weight analyzed (g)							
	Na	reading (mV)	-200	-189	-250	-202		
		concentration (%)	35.24	31.53	23.54	23.88		
	Cl	reading (mV)	137	143	178	147		
		concentration (%)	10.81	4.69	7.86	4.97		
	K	reading (mV)	-255	-251	-277	-248		
		concentration (%)	0.87	0.60	1.55	0.88		
	CHAR							
	weight analyzed (g)		0.2722	0.2237	0.2278	0.2423		
	Na	reading (mV)	-143	-147	-147	-143		
		concentration (%)	25.42	26.34	25.87	28.56		
	Cl	reading (mV)	106	122	135	124		
		concentration (%)	3.38	1.94	1.04	1.63		
	K	reading (mV)	-198	-202	-206	-197		
		concentration (%)	0.90	0.91	0.74	1.06		
	MATERIAL BALANCE							
	Na	Fume/B.L. (%)	11.22	10.75	1.58	8.71		
		Char/B.L. (%)	57.92	64.64	68.47	58.68		
		Total (%)	69.14	75.39	70.05	67.39		
	Cl	Fume/B.L. (%)	116.03	53.92	17.80	61.09		
		Char/B.L. (%)	259.77	160.75	92.55	113.14		
		Total (%)	375.79	214.68	110.36	174.23		
	K	Fume/B.L. (%)	10.09	7.48	3.80	11.76		
		Char/B.L. (%)	74.81	81.40	71.58	79.40		
		Total (%)	84.90	88.88	75.38	91.16		
	ENRICHMENT FACTOR							
	Cl		10.34	5.02	11.26	7.01		
	K		0.90	0.70	2.41	1.35		

Appendix C
CES OPERATION MANUAL

Section 1 - CES Major Components

The major components of the CES (Figure C-1) are:

Autosampler - The two main parts of the autosampler are the sample vial carousel and the sampler head. The carousel holds a maximum of 40 500 µL microcentrifuge sample vials. The carousel rotates counterclockwise to bring the selected vial position under the sampler head. The sampler head contains the source end of the capillary and the source electrode. Nitrogen is used for actuation of the jaws that hold the vial during sampling operations.

Capillary - The capillary is the place where the separations occur. Generally, a conventional coated fused-silica capillary (50 cm x 50 µm I.D.) is used.

Detector - All of our applications require UV detection, but the CES also comes with a fluorescent detection option.

Controller - The controller has direct control of the other main components, except the detector, which is independently controlled.

High-Voltage Power Supplies - Voltage is applied across the ends of the capillary to move sample through the capillary. For cations detection, connect the high-voltage cable to the positive power supply. For anions' detection, connect the cable to the negative power supply.

Buffer and Waste Reservoirs - At the rear of the deck there are five glass bottles. The 1000 ml and the 500 ml are waste reservoirs and the three 250 ml are buffer reservoirs. The buffer reservoirs are pressurized with helium.

Source Buffer Vial - The source buffer vial is usually the fixed source buffer vial located to the right of the carousel, but any sample vial in the carousel may be used as the source vial.

Cell - The cell is enclosed in a light-tight cover and holds the destination end of the capillary and the detectors. Just below the cell is the destination vial but cannot be seen without removing the cell. The destination vial is rinsed and recharged with fresh buffer at the beginning of each run.

Screen - Operation of CES is controlled by menu-driven method programming via the CRT (Cathode-Ray Tube) screen.

Deck Cover - A safety interlock prevents the cover over the deck from being raised while the CES power is on. Never try to force open the safety cover. After pressing System Halt, wait about one second for the safety interlock to be released. You can hear a click sound as the safety interlock is released.

Section 2 - Functional Description

Operating Environment - The ambient temperature and relative humidity of the laboratory are important parameters on the CES performance. The ideal situation is when calibration and analysis are performed in a draft-free location, and under the same temperature (between 10 and 40°C) and relative humidity conditions (10-75%, non-condensing).

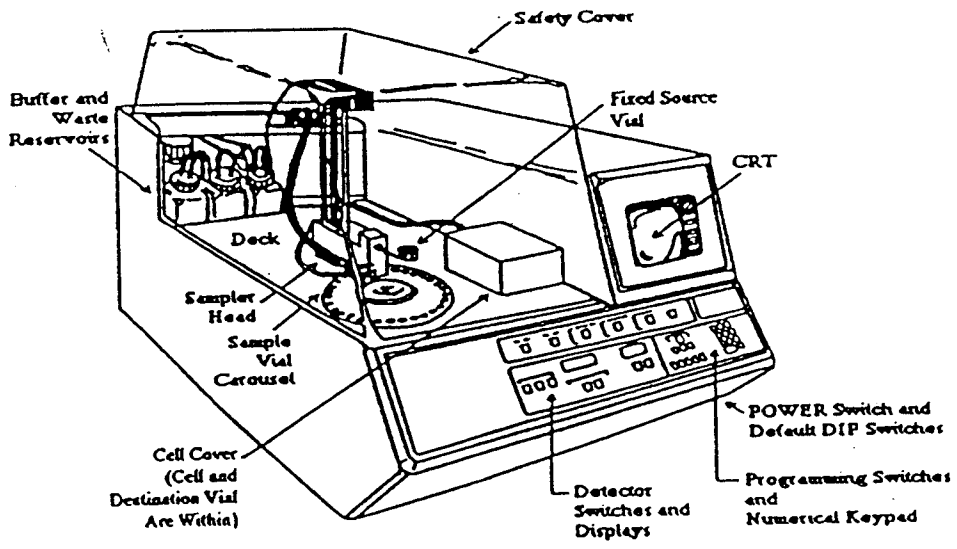


Figure C.1: Major components of the CES

Pneumatic Pressure - The air-operated valves require an air supply regulated to 100 ± 20 psi. Only instrument grade air or nitrogen should be used. The buffer reservoirs and sample injection require a helium supply regulated to 20-30 psi.

UV lamp - The UV lamp controls the deuterium lamp used for ultraviolet detection (190-350 nm). When the CES is turned on, the deuterium lamp is always off and the UV lamp off indicator is lit. When the UV lamp switch is pressed, the detector starts the lamp and the Start indicator lights. The deuterium lamp requires 20 seconds to warm-up. As the heater reaches operating temperature, the filament ignites and the UV lamp on indicator lights. The deuterium lamp has a limited life of about 2000 hours. If you do not intend to use it for an extended period, press UV lamp again to turn off the lamp. The lamp takes 10 -20 minutes to fully stabilize.

Injection Techniques - The CES can operate in three sample injection modes: gravity, electromigration, and pressure. Selection of an injection mode depends on factors such as the separation mode, the quantity to be injected, and the sample being analyzed.

Gravity is generally regarded as the ideal method because of the several advantages it offers:

- No sample discrimination; identical samples quantities for anionic, neutral, and cationic samples can be used.

- The sample head height can be adjusted from 0 to 150 mm in 1 mm increments for better precision.

- Simplicity; no need for calibrated sensors.

In gravity injection, the height difference between the two ends of the capillary creates a siphoning effect, which allow introducing the sample into the capillary. The sample volume depends on the height and time. In the electromigration injection method, the sample is introduced by electrophoresis/electrosmosis. In the pressure method, the sample is introduced by pressurization of the sample vial.

Sequence of events - The operation of the CES is composed by a sequence of 8 events:

1- Drain destination vial (Fixed - 10 seconds) - Helium forces liquid from the destination vial and overflow portion of the destination vial to the 1000 ml waste container.

2- Close waste valve (Fixed - 15 seconds) - Helium forces any remaining liquid in the overflow portion of the destination vial to be flushed to the 1000 ml waste container.

3- Fill destination vial with some overflow (Variable: 9 seconds at 5 psi) - Helium pressurized to about 5 psi (set by user) delivers buffer to the destination vial.

4- Rinse capillary (Variable - 120 seconds) - Helium pressurizes the destination vial and forces destination vial buffer to flow backwards through the capillary.

5- Drain source vial (Vacuum on, Fixed - 30 seconds) - The vacuum pump is turned on, producing negative pressure in the 500 ml source waste container, emptying the source vial.

6- Fill injection loop (Fixed - 5 seconds at 5 psi) - Helium at 5 psi will fill the injection system with buffer.

7- Inject buffer into source vial, then sample (Variable - 6 seconds) - Pressurized helium will transfer the buffer from the injection system to the source vial. At this point, the sample head will search for the sample vial to introduce the desired amount of sample into the capillary by one of the injection methods.

8- Run high voltage (Variable 0-999 minutes) - The detection starts.

Section 3 - Instructions

How to prepare a capillary: (Figure C-2)

1- On scale, cut a 50 cm long piece of the capillary with the small ceramic wafer. In order to cut it, just "mark" the capillary with the ceramic tool and bend it.

2- Lay the capillary on top of the burn fixture, a metal slide with a window. Set the end of the capillary with one end of the metal plate. Press a piece of tape onto the capillary on the other end of the metal plate.

3- With the capillary lying on the burn fixture and with the tape or "flag" on the end closest to the window, hold a cigarette lighter under the window on the fixture for about 10 seconds, or until the section of capillary lying across the window glows orange.

4- Burn also the coating on the ends of the capillary (1 or 2 mm).

5- Using propanol and paper tissue, gently clean the exposed section of the capillary. Be sure to remove all traces of burned coating. If necessary, repeat steps 3 and 4 to ensure that all the coating is removed.

How to install the capillary: (Figure C-3)

1- Open the latches on the top and side of the cell compartment cover and remove the front half of the cover.

2- Open the cell clamp by swinging the lever to the right (fully open position). Loosen the white thumbscrew on the platform of the cell.

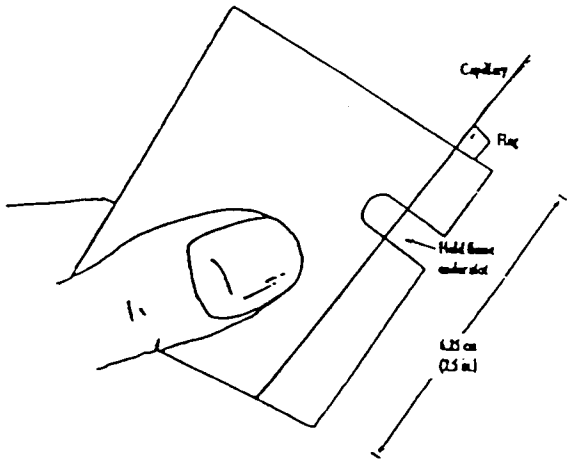


Figure C-2: Capillary burn fixture

3- Carefully, insert the capillary into the seal adjustment screw until the bottom of the flag touches the top of the cell body. Do not touch the window on the capillary.

4- Close the cell lever observing if the capillary sits correctly in the V-groove. Finger tighten the white thumbscrew on the platform.

5- Put the front half of the cell compartment cover in place. Note that where the capillary enters the cell compartment, there is a double thickness foam.

6- Insert the other end of the capillary into the sampler head (Figure C-4). It is normal to encounter some resistance. Continue inserting the capillary until the bottom of the capillary is almost even with the end of the electrode (2 mm above).

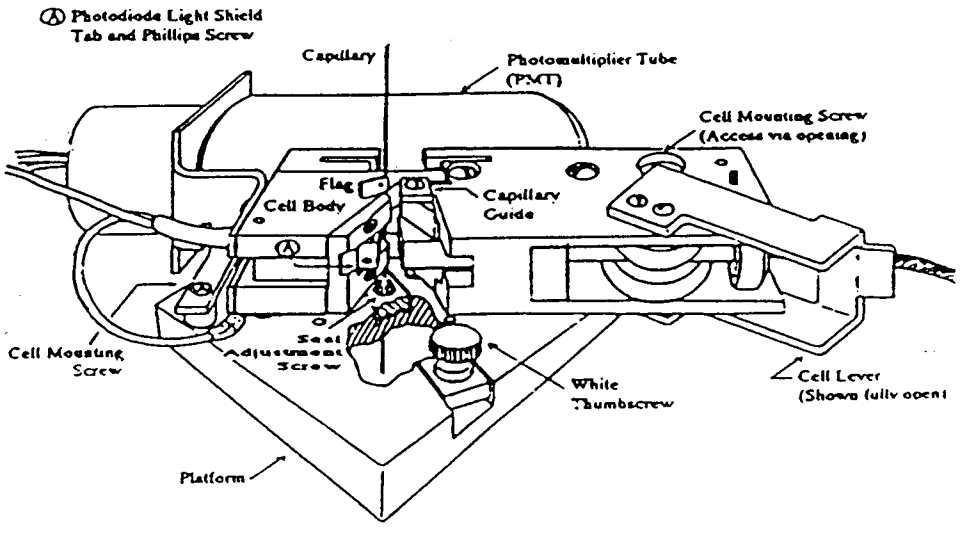


Figure C-3: Installation of the capillary in the cell

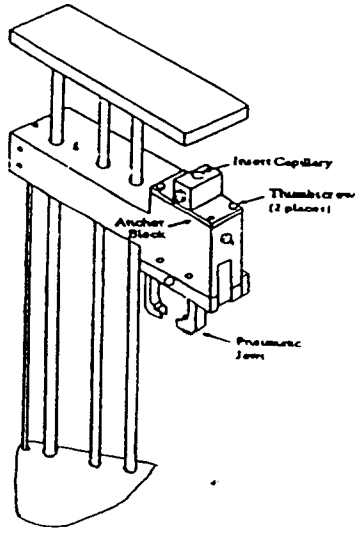


Figure C-4: Sampler head

How to write a program on CES:

Usually, the only parameters that one might want to change in a program are polarity and running time. To edit a program, go to the main menu, choose 1, and press ENTER. Now, select the program number, and press ENTER. Always press ENTER after making changes, otherwise the changes will no be saved. The parameters you can select are:

Polarity - The polarity of the high-voltage supply may be positive or negative depending on the application. It must reflect the polarity used for the high-voltage cable. Use positive if analyzing cations and negative for anions.

Air Cooling - This is an option for cooling the capillary in cases where high currents are used. For our case this function is always off.

Rinse -

Destination - You select a destination vial fill time of 0 to 9 seconds and which buffer reservoir should be used (A, B, or C). Usually we use reservoir A for the anion buffer, B for water or rinsing solution, and C for cation buffers. A rinsing time of 8 seconds is usually appropriate.

Capillary - For the purpose of backflow rinsing of the capillary, the vial can be pressurized for 0 to 999 seconds. Use 120 seconds.

Fixed Source - The fixed source rinse fills time can be from 0 to 9 seconds. Select the same fill times and buffer used for the destination vial.

Injection Mode - Select electro, gravity or pressure. Typically gravity with the sampler head height during injection set to 100 mm for 30 seconds is selected.

If using electro, set the voltage from 10 V to 30.000 V. If using pressure, set the injection period from 0 to 999 seconds.

Control Mode - This selects the parameters for operation. Usually, the settings in this mode do not need to be changed.

On the next screen, the steps of the program are set.

Step 1- Occurs at 0.0 minutes. Select the voltage (20.000 V for cations and 30.000 V for anions). Select fixed source vial. Select relay 1 ON. Relay 1 is used here to control the detector AUTO OFFSET.

Step 2- Occurs at 0.1 minutes. All relays are OFF. You do not need to set voltage or fixed vial, since the CES continues to use the last condition selected.

Step 3- The CES always displays a minimum of three steps. Keep it empty.

Step 4- End of program. Set the running time.

Step 5- Save the new program.

How to write a schedule on CES:

A schedule indicates the order in which programs run and which vials are involved. The CES cannot run a program automatically without a schedule. The schedule must contain at least one step and a maximum of 20 steps. In each step, it is necessary to define the number of interactions per program (1-9), the sample vials accessed (1-40), and programs used (1-20).

From the main menu select option 3 and press ENTER. Choose a schedule number on the next screen and again press ENTER.

As an example, assume that you plan to run programs 1 and 5, twice on vials 1, 2, 3, 4, 5, 6, 31 and 35.

Step 1- Enter "2" at the ITERATIONS PER PROG option of step 1 and press ENTER.

Step 2- At the VIAL option, enter "1", a decimal point, and then "6". (This command means that the CES will analyze the sequence of vials from vial 1 to vial 6). Enter "31" and "35". Remember to press ENTER after each element of the sequence.

Step 3- At the PROG option, insert "1" and "5". Press ENTER after each entry.

Step 4- After entering the schedule, press ESCAPE.

Step 5- Save the schedule.

How to prepare the vials:

For each sample:

Step 1- Homogenize the solution to be analyzed.

Step 2- Pour around 3 ml of the solution into a polystyrene weighing dish.

Step 3- Rinse the syringe (1 ml) 5 times with distilled water.

Step 4- Rinse the syringe twice with the solution present in the weighing dish.

Step 5- Fill the syringe once again and attach a 0.45 μm filter to the tip. (Two kinds of filters were used, 4 mm or 13 mm, depending on the concentration of particles present in the solution).

Step 6- Fill the vial with around 2 ml of the filtered solution.

Step 7- Eliminate all bubbles; specially if any are located at the bottom by gently tapping the vial with your finger. Empty the vial.

Step 8- Fill the vial once again with 0.5 ml of the filtered solution and eliminate all bubbles as described before.

Step 9- Place the filled vial in the holding board in appropriate numbered hole as designated by the schedule. Cover samples until transferring the vials to the carousel.

How to use the Dionex AI-450 Chromatography Software

The Dionex data acquisition software works in a window environment and therefore is user-friendly. It is necessary for any acquisition or interpretation of data generated by the CES. Its use has three phases: preparation for analysis, analysis, and post-analysis data processing.

The preparation for analysis includes:

METHOD Editor program - It is used to create and edit methods for an analysis or experiment. A method contains all of the instrument control and data handling instructions needed to run a single analysis. Double-click on the

method icon and choose new or open an old method to edit it. The main window shows the current setting for the method:

• System - Once it is being used only one system and one interface with the software, select ACI 1, SYS 1.

• Detectors used in these methods - The cations and anions analysis use only UV detection. For Number of Detector, select 1. Click on Detector 1 and select UV detection under Other Detector. Select the plot range (-100 to 1,000 is adequate).

• Run time - Enter the total time during which data will be collected. Typically, it is the time necessary for all peaks in the sample to show up.

• Sampling Rate - The sampling rate determines the number of data points per second. A rate of 5 or 10 samples/second is adequate.

• Instrument Control - Timed events needs to be created and saved before running the method. On step time, highlight Init and mark Autosmp in ACI. Highlight step 1, delete Autosmp and mark Begin Sampling. Save the file before exiting (usually under the same name of the method).

• Data Processing Parameters

- Integration - These parameters specify how the data is processed by the computer for peak detection and integration. In cases where the baseline is noisy, the ion concentration is very low, or there are too many peaks, a change of these parameters will be necessary to obtain results that reflect your need.

1 - Peak width - 2 or 3 seconds is adequate.

2 - Peak threshold - It is a measure of how sharp the peak must be before it is recognized as a peak. 50 is a good initial value. Increase it if undesired peaks or noise are detected.

3 - Area Reject - Specifies the minimum area a peak must have before it is included in the final report. An area of 2000 is adequate, as an initial value.

4 - Reference Reject - Specifies the minimum area a peck must have before it is recognized as a reference peak. 1000 is a good start.

- Data Events - It is useful when you get used with the shape of the chromatogram. The most useful event probably is the stop and start peak detection. If used at 0.0 and 2.0 min, respectively, they can stop the detection of the "water noise" in the beginning of the chromatogram.

- Calibration - Determines how detected peaks are identified and quantified.

1 - Levels (1 to 10) - Specifies the total number of different concentration calibration standards are going to be used. The best is if, at least, 3 standards are used. A good calibration standard combination for black liquor products analysis is: standards (0.2 ppm of Cl^-, 0.2 ppm of K^+, and 2 ppm of Na^+), standard 2 (1 ppm of Cl^-, 1 ppm of K^+, and 10 ppm of Na+) and standard 3 (5 ppm of Cl^-, 5 ppm of K^+ and 50 ppm of Na^+). The standard concentrations should bracket the expected sample concentration.

2 - Fit Type (Linear, Point to point, Quadratic or Cubic) - Selects the type of fit for the calibration curve. The point to point type has been a good option, unless one or more of the points are "off" of a linearity. In this case you should repeat the calibration or, as a last resource, eliminate that point. The linear fit works well at higher concentrations but may not be adequate for the lower 10% of the concentration range.

3 - Force Zero - It should be used whenever possible.

4 - Calibration Update - Use Replace

5 - Standardization = Use External calibration

6 - Resp. for Unknowns - An Area quantification is more reproducible.

7 - Amount Units - Specifies the unit of measure in the calibration standards.

- Components - The component table must be created if you want sample components to be identified and quantified automatically.

1 - Component Name

2 - Retention Time - Enter the expected retention time for the component (in minutes).

3 - Retention Window - Determines how much the specified peak can vary and still be identified (0.1 to 0.3 minutes is typically used).

4 - Calibrate By - Use area

5 - For each component in the component table, you should type the component amount at the corresponding calibration level. The concentration must increase as the level number increases.

- Report

1 - Do no select the printout text output as it prints a report after each analysis.

2 - Select All for components and Unknown for peaks in the test sections.

3 - The default.prf report format is adequate.

4 - In the graphics Options select only the Peak label and Fill Peaks. All other options are not necessary.

Once a method is crated or edited and saved, the only modification that one might need to do is a change on retention times and calibration parameters (levels, concentrations, etc.).

SCHEDULE Editor program - It is used to create, store, and edit a schedule of analysis. Each line in a schedule specifies the sample name and the method to be used for the analysis. It also incorporates automatic calibrations. A schedule can contain instructions for up to 99 separate injections. Enter sample name, method, and data file name in which all information will be stored. For the injection of the calibration standards use the special sample name AUTOCAL X, where X is the calibration level. The heights, areas and retention times for each peak are updated. Use AUTOCAL X A to have the method updated by averaging the new values with the previous ones.

The analysis includes:

Run program - It loads the ACI interface with a method or schedule. When an analysis is complete, RUN directs the computer to retrieve the raw data from the interface. It then detects and integrates peaks and calculates component concentrations, based on data from calibration standards. The RUN program will run a method, for a single analysis, or a schedule, for a series of analysis.

1 - For single analysis, load method to be used. For a series of analysis, load the schedule previously written. Before the schedule is loaded, it is necessary to set some conditions. Always use the option for starting successive runs upon receiving signal at interface. Also use data paths from the schedule.

2 - Start - This signals the interface to begin executing the events of the currently loaded method or schedule.

3 - Abort - Used if something goes wrong with the analysis.

The post-analysis data processing includes:

OPTIMIZE Program - It allows you to retrieve raw data from the disk drive for additional processing. The data file is first shown exactly as it was

processed at the time it was generated. By using the menu commands you can test several treatments of the raw data and update method, report files or data files after making modifications After selecting the option and opening a data file, you can:

1 - Scale the plot
2 - Export report, chromatogram, or data
3 - Print report or chromatogram
4 - View report
5 - Edit the method (integration, calibration, components, or data events)
6 - Set baselines manually
7 - Name or label peaks

Chances are that you are going to use the item 5 very often until you find the best set of conditions for your matrix. Please refer to the AI-450 CHROMATOGRAPHY SOFTWARE USER'S GUIDE for detailed information on how to edit a method from the OPTIMIZE PROGRAM. An example of a situation is when you have potassium and sodium peaks in your chromatogram but it is reported a higher than expected concentration for potassium and no presence of sodium. What happened in this case was a shift in retention time. This can be caused by a change of capillary, buffer matrix of your sample, or even room temperature. To correct the problem, read the retention times of the peaks and adjust the ones in the method. Another example of a situation where you have to make some changes, also very common, is when the ion in which you are interested has very low concentration and has not been detected as a peak. In this case, it is necessary to change the integration parameters.

Appendix D

ION SELECTIVE ELECTRODE MANUAL

Section 1 - Sodium Combination Electrode

Maintenance

Check if fill solution is not more than 2.5 cm below the fill hole. If necessary, add saturated KCl solution.

Place the electrode in a 1:1 dilution of 0.5 M Triethanolamine (TEA) and 100 ppm Na standard until next use.

Reference electrode: Internal reservoir - KCl
External reservoir - KNO_3

Calibration and measurement

Step 1- Prepare standards solutions to provide calibration points. These solutions should bracket the concentration expected for samples.

Step 2- Dilute the standards and samples 1:1 with 0.5 M triethanolamine (TEA). (20 ml of sample + 20 ml of TEA).

Step 3- Immerse the electrode, wait to achieve equilibrium.

Step 4- Read the potential of the standards and of the samples.

Section 2 - Chloride

Calibration and measurement

Prepare a 10.000 ppm stock standard (1.65g NaCl diluted to 100 ml). Make a serial dilution of 1000, 100, 10 and 1 ppm. Dilute all standard and sample 1/1 by volume with 1.0M KNO_3, the ionic strength adjustment buffer (ISAB).

Immerse the electrodes in the lower buffered standard (1 ppm) with gentle stirring. Turn the standardize knob until the display reads zero.

Remove the electrode, dry it out and immerse the electrode sequentially in the next higher buffered standards (10, 100, 1000 ppm) and record these potentials.

Construct a standardizing curve.

Immerse the electrode in the buffered sample and read the mV.

Section 3 - Potassium

Calibration and measurement

Soak the potassium electrode for at least one (1) hour in 100 ppm potassium standard solution.

Fill the inner chamber of the reference electrode with KCl solution. Fill the outer chamber with diluted ISA.

Prepared two (2) standards which bracket the expected sample concentration and differ in concentration by a factor of ten (10). Standards and samples should be at the same temperature.

Measure 50 ml of the more dilute standard into a 100 ml beaker. Stir thoroughly. Pipet 1 ml ISA into the beakers.

Rinse electrodes with distilled water, blot dry and place into beaker. Read mV value when a stable reading is displayed.

Repeat the last two steps for the most concentrated standard.

Section 4 - Sulfate

Calibration and measurement

Prepare 0.01 M $Pb(ClO_4)_2$ titrant by pipeting 100 ml of lead standard into a 1 liter volumetric flask and dilute to mark with distilled water.

Dilute the 0.01 M lead perchlorate titrant 1:1 with methanol-formaldehyde (3 drops of 37% formaldehyde to 1000 ml reagent grade methanol).

Pipet 25 ml of distilled water, 1 ml of ISA, and 25 ml of methanol-formaldehyde solution into a 100 ml beaker. Stir thoroughly throughout titration.

Using a 10 ml burette, add five 0.5 ml increments of titrant, recording mV after each addition.

Draw a straight line through the points. The line should intersect the horizontal axis at 0 ml. If the line does not intersect at 0 ml, calculate the concentration of the blank as follows and subtract if from the concentration of the sample:

$$Cb = Ct \frac{Vt}{Vb}$$

Where:

Cb = Concentration of blank

Ct = Concentration titrant before dilution

Vb = Volume blank before dilution

Vt = Volume titrant at endpoint from graph

Repeat (1) for the sample

Fill the 10 ml burette with titrant

Let titrant run slowly into the sample until the mV reading on the meter is near the value recorded for the first ml added in the blank. If the burette reading is between 0.5 ml markings, add more titrant to bring burette reading to the next 0.5 reading.

Continue adding 0.5 ml increments of titrant, recording mV values after 0.5 ml addition. Stop when mV readings on the meter are near the value recorded for 2.5 ml in the blank.

Draw the best straight line through the points. The line will intercept the horizontal axis at the endpoint.

Calculate the sulfate concentration, Cs, as follows:

$$Cs = Ct \frac{Vt}{Vx}$$

Where:

Ct = Concentration titrant before dilution

Vt = Volume of titrant at endpoint

Vx = Volume of sample before dilution with methanol

Appendix E

ENRICHMENT MODEL

Table E-1: Formulas in spreadsheet PROGRAM.XLS

(Column A, Rows 1-35)

	A
1	**Theoretical Enrichment Factor Model**
2	
3	
4	
5	
6	**Initial Conditions:**
7	
8	O2 content in reaction gas (%)
9	Reactor temperature (C)
10	
11	**Inorganics Concentrations (mol):**
12	
13	NaCl
14	KCl
15	Na2CO3
16	K2CO3
17	NaX
18	KX
19	
20	**Temperature Estimations:**
21	
22	Particle surface temperature (C)
23	
24	**Calculations:**
25	
26	Total potassium released by volatilization (mol)
27	NaCl released by volatilization (mol)
28	Total chloride released by volatilization (mol)
29	Sodium released by carbonate reduction (mol)
30	Potassium released by carbonate reduction (mol)
31	
32	**Enrichment Factors after 0.1s:**
33	
34	Chloride
35	Potassium

Table E-2: Formulas in spreadsheet PROGRAM.XLS

(Column B, Rows 1-35)

	B
1	
2	
3	
4	
5	
6	
7	
8	0
9	700.069991999299
10	
11	
12	Input
13	0.0000000001865
14	0.000000000003052
15	0.0000000045
16	0.00000000007772
17	=B13+2*B15+0.000000000003312*2
18	=B14+2*B16
19	
20	
21	
22	700.0699919993
23	
24	
25	
26	
27	
28	
29	
30	
31	
32	
33	
34	=D28/(D27+D29)*((22.65/23)/(0.67/35.5))
35	=(D26+D30)/(D27+D29)*((22.65/23)/(0.62/39))

Table E-3: Formulas in spreadsheet PROGRAM.XLS (Column C, Rows 1-30)

	C
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	Output
13	=B13-C27
14	=B14-C28+C27
15	=B15-C29/2
16	=B16-C30/2
17	=B17-C27-C29
18	=B18-C26-C30
19	
20	
21	
22	
23	
24	
25	
26	=Volatilization(E22,B22,E14,E8,74.5,B14)
27	=Volatilization(E22,B22,E15,E8,58.5,B13)
28	=C27+Volatilization(E22,B22,E16,E8,74.5,B14)
29	=Carbonate(E22,B22,E17,E8,23,B15)
30	=Carbonate(E22,B22,E18,E8,39,B16)

Table E-4: Formulas in spreadsheet PROGRAM.XLS (Column D, Rows 1-30)

	D
1	
2	
3	
4	
5	
6	
7	
8	Diameter of char particle (m)
9	Residence Time (s)
10	
11	**Partial Pressure at Equilibrium (bar):**
12	
13	
14	Potassium species
15	NaCl
16	KCl
17	Na (vapor)
18	K (vapor)
19	
20	
21	
22	Reactor temperature (C)
23	
24	
25	Acumulated:
26	=C26
27	=C27
28	=C28
29	=C29
30	=C30

Table E-5: Formulas in spreadsheet PROGRAM.XLS (Column E, Rows 1-22)

	E
1	
2	E.F.
3	Chloride
4	Potassium
5	
6	
7	
8	0.0003
9	0.5
10	
11	
12	
13	
14	0.0000002402
15	0.0000001115
16	0.00000013
17	0.0002303
18	0.00003024
19	
20	
21	
22	=B22-TEMP(B9,B22,B8,E8)

Table E-6: Formulas in spreadsheet PROGRAM.XLS (Column F, Rows 1-10)

	F
1	
2	
3	=B34
4	=B35
5	
6	
7	
8	
9	
10	

Table E-7: Formulas in spreadsheet PROGRAM.XLS (User-defined functions)

```
Option Explicit

' Define variables and constants

Dim Tg ' Tg is reactor's temperature (C)
Dim Tp ' Tp is the particle surface temperature (C)
Dim Salt ' Salt is the initial amount of the salt in the stage (mol)
Dim PO2 ' PO2 is the O2 content in the reaction gas (%)
Dim Psalt ' Psalt is the partial pressure of the salt at equilibrium using HSC
      (bar)
Dim Pvapor ' Pvapor is the partial pressure of alkali metal at equilibrium
      using HSC (bar)
Dim CO3 ' CO3 is the alkali carbonate concentration (mol)
Dim Dp ' Dp is the diameter of the particle (m)
Dim Tf ' Tf is the film temperature as an average between Tgas and
      Tparticle (C)
Dim Rate 'Rate is the rate of reaction of carbon with O2 around the
      particle (mol/m2.sec)
Dim Rmt 'Rmt is the rate of alkali metal mass transfer from the particle
      surface to the gas phase (mol/s)
Dim Rkinetic ' Rkinetic is the chemical kinetic rate of the carbonate
      reduction mechanism (mol/s)
Dim OverallRate 'OverallRate is the overall rate of alkali release by
      carbonate reduction mechanism (mol/s)
Dim heff 'heff is effective heat transfer coefficient (J/sec.m2.K)
Dim k ' k is thermal conductivity coefficient (J/sec.m.K)
Dim MW ' MW is the molecular weight (g)
```

Table E-7: Formulas in spreadsheet PROGRAM.XLS (User-defined functions) Continuation

```
' Diff is the diffusivity of molecule in N2 at given temperature (m2/s)
Dim vgas 'vgas is the gas velocity relative to the particle (m/s)
Dim Visc 'Visc is the gas kinematic viscosity (m2/s)
Dim Gr 'Gr is the Grashf number
Dim Re 'Re is the Reynolds number

Const DeltaHr = 110525 ' DeltaHr is the heat of reaction of CO (J/mol)
Const R = 0.08314 ' R is the constant of gases (bar*liter/mol*K)
Const Sh = 2 ' Sh is the assumed Sherwood number
Const Nu = 2 ' Nu is the assumed Nusselt number
Const Sigma = 0.0000000567 ' Sigma is the Stefan-Boltzmann constant
        (J/(sec.m2.K4))
Const Time = 0.1 'Time is the time interval between iterations (s)



' ------------------------------------------------------------------------
-----
' Function TEMP - Used for PARTICLE SURFACE TEMPERATURE
calculation:
'
' This routine estimates the difference between the particle surface temperature
and furnace temperature during its combustion.
'
' ------------------------------------------------------------------------
----
```

Table E-7: Formulas in spreadsheet PROGRAM.XLS (User-defined functions) Continuation

```
Function TEMP(Tg, Tp, PO2, Dp)
Const R = 0.08314 ' R is the constant of gases (bar*liter/mol*K)
Const DeltaHr = 110525 ' DeltaHr is the heat of reaction of CO (J/mol)
Const Sigma = 0.0000000567 ' Sigma is the Stefan-Boltzmann constant
      (J/(sec.m2.K4))
Const Nu = 2 ' Nu is the assumed Nusselt number
   If PO2 = 0 Then
      TEMP = 0
   Else
      Tf = (Tg + Tp) / 2
      Rate = kg(Tf, Dp, 32) * (PO2 / 100) / (R / 1000 * (Tf + 273.15))
       'Calculates the rate of reaction of C with O2 around the particle
       (mol/m2.sec)
      k = 0.0238 + 0.0000685 * Tf - 0.00000001614 * (Tf) ^ 2 'Calculates the
       thermal conductivity coefficient (J/sec.m.K)
      vgas = 0 'This is the gas velocity relative to the particle (m/s)
      Visc = 0.000000211 * (Tf + 273.15) - 0.0000866 'Calculates the gas
       kinematic viscosity (m2/s)
      Gr = 9.8 * (Tp - Tg) * Dp ^ 3 / (Tf * Visc ^ 2) 'Calculates the Grashf
       number
      Re = vgas * Dp / Visc 'Calculates the Reynolds number
      heff = k / Dp * (2 + 0.39 * Gr ^ 0.25 + 0.37 * Re ^ 0.6) + Sigma * ((Tp
       + 273.15) ^ 4 - (Tg + 273.15) ^ 4) / (Tp - Tg) 'Calculates the effective
       heat transfer coefficient around the particle (J/sec.m2.K)
       TEMP = (-DeltaHr) * (-Rate) / heff 'Calculates the difference between
Tp and Tg (C)
   End If
End Function
```

Table E-7: Formulas in spreadsheet PROGRAM.XLS (User-defined functions) Continuation

```
' ------------------------------------------------------------------------------
-----
' Function Volatilization - Calculates the amount of SALT VOLATILIZED:
'
' This routine calculates the amount of salt released by volatilization
mechanisms. The release of volatiles is equal to the product of the rate of
release (mol/m2.sec, the residence time (s), and the external surface area (m2).
The unit of Volatilization is mol.
' ------------------------------------------------------------------------------
----

Function Volatilization(Tg, Tp, Psalt, Dp, MW, Salt)
Const R = 0.08314 ' R is the constant of gases (bar*liter/mol*K)
Const Time = 0.1 'Time is the time interval between iterations (s)
   Tf = (Tg + Tp) / 2 'Calculates the film temperature (C)
   Rate = kg(Tf, Dp, MW) * Psalt / (R / 1000 * (Tf + 273.15)) 'Calculates the
      rate of reaction of C with O2 around the particle (mol/m2.sec)
   Volatilization = Rate * Time * 3.1416 * Dp ^ 2 'Calculates the amount of
      salt volatilized during that time interval (mol)
   If Volatilization > Salt Then
      Volatilization = Salt
   End If
End Function
```

Table E-7: Formulas in spreadsheet PROGRAM.XLS (User-defined functions) Continuation

```
' ------------------------------------------------------------------------------
----
' Function Carbonate - Calculates the amount of alkali released by
CARBONATE REDUCTION:
'
' This routine calculates the amount of salt released by carbonate reduction
mechanisms. The' release of alkali metals (sodium or potassium) is equal to the
product of the rate of release' of these elements by carbonate reduction
mechanism (mol/s) and the residence time (s).
' The unit of Carbonate is mol.
' ------------------------------------------------------------------------------
----

Function Carbonate(Tg, Tp, Pvapor, Dp, MW, CO3)
Const R = 0.08314 ' R is the constant of gases (bar*liter/mol*K)
Const Time = 0.1 'Time is the time interval between iterations (s)
   Tf = (Tg + Tp) / 2 'Calculates the film temperature (C)
   Rmt = kg(Tf, Dp, MW) * Pvapor / (R / 1000 * (Tf + 273.15)) * 3.1416 *
      Dp ^ 2 'Calculates the rate of alkali metal mass transfer from the
particle surface to the gas phase (mol/s)
   Rkinetic = 2 * 10 ^ 9 * CO3 * Exp(-244000 / 8.314 / (Tp + 273.15)) '
      Calculates the chemical kinetic rate of the carbonate reduction
      mechanism (mol/s)
   OverallRate = 1 / ((1 / Rmt) + (1 / Rkinetic)) 'Calculates the overall rate of
alkali release by carbonate reduction mechanism (mol/s)
```

Table E-7: Formulas in spreadsheet PROGRAM.XLS (User-defined functions) Continuation

```
   Carbonate = OverallRate * Time 'Calculates the amount of alkali released
       by carbonate reduction mechanism during that time interval (mol)
   If Carbonate > CO3 Then
      Carbonate = CO3
   End If
End Function



' ------------------------------------------------------------------------------
-----
' Function kg - Calculates MASS TRANSFER COEFFICIENT:
'
' This routine estimates the mass transfer coefficient given the film
temperature (Tf), diameter of the particle (Dp), and the molecular weight
(MW)of      molecule diffusing in the reaction gas.
' ------------------------------------------------------------------------------
----


Function kg(Tf, Dp, MW)
Const Sh = 2 ' Sh is the assumed Sherwood number
   kg = Sh * Diff(MW, Tf) / Dp 'Calculates the mass transfer coefficient (m/s)
End Function
```

Table E-7: Formulas in spreadsheet PROGRAM.XLS (User-defined functions) Continuation

```
' ------------------------------------------------------------------------------
----
' Function Diff - Calculates the DIFFUSIVITY OF MOLECULES IN N2:
'
' This routine estimates the diffusivity of molecules in N2 based on their
molecular weight. This equation was obtained by fitting a curve on the
diffusivity data available in Perry (Chemical Engineer's Handbook).
' ------------------------------------------------------------------------------
----

Function Diff(MW, Tf)
    Diff = 0.00010662 * (MW) ^ -0.4834 * ((Tf + 273.15) / 273.15) ^ 1.75
'Diffusivity of
      'molecules in N2 (m2/s)
End Function
```

Table E-8: Spreadsheet PROGRAM.XLS at 700°C, 0% O_2, and 0.1 sec.

	A	B	C	D	E
6	**Initial Conditions:**				
7					
8	O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
9	Reactor temperature (C)	700		Residence Time (s)	0.5
10					
11	**Inorganics Concentrations (mol):**			**Partial Pressure at Equilibrium (bar):**	
12		**Input**	**Output**		
13	NaCl	1.865E-10	1.865E-10		
14	KCl	3.052E-12	3.015E-12	Potassium species	2.402E-07
15	Na2CO3	4.500E-09	4.500E-09	NaCl	1.115E-07
16	K2CO3	7.772E-11	7.772E-11	KCl	1.300E-07
17	NaX	9.849E-09	9.849E-09	Na (vapor)	2.303E-04
18	KX	1.585E-10	1.584E-10	K (vapor)	3.024E-05
19					
20	**Temperature Estimations:**				
21					
22	Particle surface temperature (C)	700		Reactor temperature (C)	700
23					
24	**Calculations:**				
25				Accumulated	
26	Total potassium released by volatilization (mol)		6.861E-14	6.861E-14	
27	NaCl released by volatilization (mol)		3.579E-14	3.579E-14	
28	Total chloride released by volatilization (mol)		7.293E-14	7.293E-14	
29	Sodium released by carbonate reduction (mol)		7.208E-14	7.208E-14	
30	Potassium released by carbonate reduction (mol)		1.245E-15	1.245E-15	
31					
32	**Enrichment Factors after 0.1s:**				
33					
34	Chloride	35.3			
35	Potassium	40.1			

Table E-9: Spreadsheet PROGRAM.XLS at 700°C, 0% O_2, and 0.2 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.865E-10	1.864E-10		
KCl	3.015E-12	2.978E-12	Potassium species	2.402E-07
Na2CO3	4.500E-09	4.500E-09	NaCl	1.115E-07
K2CO3	7.772E-11	7.772E-11	KCl	1.300E-07
NaX	9.849E-09	9.849E-09	Na (vapor)	2.303E-04
KX	1.584E-10	1.584E-10	K (vapor)	3.023E-05
Temperature Estimations:				
Particle surface temperature (C)	700		Reactor temperature (C)	700
Calculations:				
			Accumulated	
Total potassium released by volatilization (mol)		6.860E-14	1.372E-13	
NaCl released by volatilization (mol)		3.579E-14	7.159E-14	
Total chloride released by volatilization (mol)		7.292E-14	1.458E-13	
Sodium released by carbonate reduction (mol)		7.188E-14	1.439E-13	
Potassium released by carbonate reduction (mol)		1.242E-15	2.487E-15	
Enrichment Factors after 0.2s:				
Chloride	35.3			
Potassium	40.2			

Table E-10: Spreadsheet PROGRAM.XLS at 700°C, 0% O_2, and 0.3 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.864E-10	1.864E-10		
KCl	2.978E-12	2.941E-12	Potassium species	2.401E-07
Na2CO3	4.500E-09	4.500E-09	NaCl	1.114E-07
K2CO3	7.772E-11	7.772E-11	KCl	1.299E-07
NaX	9.849E-09	9.849E-09	Na (vapor)	2.303E-04
KX	1.584E-10	1.583E-10	K (vapor)	3.023E-05
Temperature Estimations:				
Particle surface temperature (C)	700		Reactor temperature (C)	700
Calculations:				
			Accumulated	
Total potassium released by volatilization (mol)		6.857E-14	2.058E-13	
NaCl released by volatilization (mol)		3.576E-14	1.073E-13	
Total chloride released by volatilization (mol)		7.286E-14	2.187E-13	
Sodium released by carbonate reduction (mol)		7.188E-14	2.158E-13	
Potassium released by carbonate reduction (mol)		1.242E-15	3.729E-15	
Enrichment Factors after 0.3s:				
Chloride	35.3			
Potassium	40.2			

Table E-11: Spreadsheet PROGRAM.XLS at 700°C, 0% O_2, and 0.4 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.864E-10	1.864E-10		
KCl	2.941E-12	2.904E-12	Potassium species	2.401E-07
Na2CO3	4.500E-09	4.500E-09	NaCl	1.114E-07
K2CO3	7.772E-11	7.772E-11	KCl	1.299E-07
NaX	9.849E-09	9.848E-09	Na(vapor)	2.303E-04
KX	1.583E-10	1.582E-10	K(vapor)	3.023E-05
Temperature Estimations:				
Particle surface temperature (C)	700		Reactor temperature (C)	700
Calculations:				
			Accumulated	
Total potassium released by volatilization (mol)		6.857E-14	2.744E-13	
NaCl released by volatilization (mol)		3.576E-14	1.431E-13	
Total chloride released by volatilization (mol)		7.286E-14	2.916E-13	
Sodium released by carbonate reduction (mol)		7.188E-14	2.877E-13	
Potassium released by carbonate reduction (mol)		1.242E-15	4.971E-15	
Enrichment Factors after 0.4s:				
Chloride	35.3			
Potassium	40.2			

Table E-12: Spreadsheet PROGRAM.XLS at 700°C, 0% O_2, and 0.5 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.864E-10	1.863E-10		
KCl	2.904E-12	2.866E-12	Potassium species	2.40OE-07
Na2CO3	4.500E-09	4.500E-09	NaCl	1.114E-07
K2CO3	7.772E-11	7.772E-11	KCl	1.298E-07
NaX	9.848E-09	9.848E-09	Na(vapor)	2.303E-04
KX	1.582E-10	1.581E-10	K(vapor)	3.022E-05
Temperature Estimations:				
Particle surface temperature (C)	700		Reactor temperature (C)	700
Calculations:				
			Accumulated	
Total potassium released by volatilization (mol)		6.854E-14	3.429E-13	
NaCl released by volatilization (mol)		3.576E-14	1.789E-13	
Total chloride released by volatilization (mol)		7.283E-14	3.644E-13	
Sodium released by carbonate reduction (mol)		7.188E-14	3.595E-13	
Potassium released by carbonate reduction (mol)		1.242E-15	6.213E-15	
Enrichment Factors after 0.5s:				
Chloride	35.3			
Potassium	40.2			

Table E-13: Spreadsheet PROGRAM.XLS at 700°C, 4% O_2, and 0.1 sec.

	A	B	C	D	E
6	**Initial Conditions:**				
7					
8	O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
9	Reactor temperature (C)	700		Residence Time (s)	0.5
10					
11	**Inorganics Concentrations (mol):**			**Partial Pressure at Equilibrium (bar):**	
12		**Input**	**Output**		
13	NaCl	1.865E-10	1.840E-10		
14	KCl	3.052E-12	1.071E-12	Potassium species	6.794E-06
15	Na2CO3	4.500E-09	4.499E-09	NaCl	7.548E-06
16	K2CO3	7.772E-11	7.771E-11	KCl	6.683E-06
17	NaX	9.849E-09	9.845E-09	Na (vapor)	2.383E-03
18	KX	1.585E-10	1.565E-10	K (vapor)	6.713E-05
19					
20	**Temperature Estimations:**				
21					
22	Particle surface temperature (C)	799		Reactor temperature (C)	700
23					
24	**Calculations:**				
25				Accumulated	
26	Total potassium released by volatilization (mol)		2.014E-12	2.014E-12	
27	NaCl released by volatilization (mol)		2.515E-12	2.515E-12	
28	Total chloride released by volatilization (mol)		4.496E-12	4.496E-12	
29	Sodium released by carbonate reduction (mol)		1.173E-12	1.173E-12	
30	Potassium released by carbonate reduction (mol)		2.027E-14	2.027E-14	
31					
32	**Enrichment Factors after 0.1s:**				
33					
34	Chloride	63.6			
35	Potassium	34.2			

Table E-14: Spreadsheet PROGRAM.XLS at 700°C, 4% O_2, and 0.2 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.840E-10	1.815E-10		
KCl	1.071E-12	0.000E+00	Potassium species	6.631E-06
Na2CO3	4.499E-09	4.499E-09	NaCl	7.380E-06
K2CO3	7.771E-11	7.770E-11	KCl	6.521E-06
NaX	9.845E-09	9.842E-09	Na (vapor)	2.383E-03
KX	1.565E-10	1.554E-10	K (vapor)	6.713E-05
Temperature Estimations:				
Particle surface temperature (C)	799		Reactor temperature (C)	700
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		1.071E-12	3.085E-12	
NaCl released by volatilization (mol)		2.459E-12	4.974E-12	
Total chloride released by volatilization (mol)		3.530E-12	8.026E-12	
Sodium released by carbonate reduction (mol)		1.173E-12	2.347E-12	
Potassium released by carbonate reduction (mol)		2.027E-14	4.054E-14	
Enrichment Factors after 0.2s:				
Chloride	57.2			
Potassium	26.4			

Table E-15: Spreadsheet PROGRAM.XLS at 700°C, 4% O_2, and 0.3 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.815E-10	1.791E-10		
KCl	0.000E+00	0.000E+00	Potassium species	6.512E-06
Na2CO3	4.499E-09	4.498E-09	NaCl	7.240E-06
K2CO3	7.770E-11	7.769E-11	KCl	6.401E-06
NaX	9.842E-09	9.838E-09	Na(vapor)	2.383E-03
KX	1.554E-10	1.553E-10	K(vapor)	6.713E-05
Temperature Estimations:				
Particle surface temperature (C)	799		Reactor temperature (C)	700
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.085E-12	
NaCl released by volatilization (mol)		2.413E-12	7.387E-12	
Total chloride released by volatilization (mol)		2.413E-12	1.044E-11	
Sodium released by carbonate reduction (mol)		1.173E-12	3.520E-12	
Potassium released by carbonate reduction (mol)		2.027E-14	6.080E-14	
Enrichment Factors after 0.3s:				
Chloride	49.9			
Potassium	17.9			

Table E-16: Spreadsheet PROGRAM.XLS at 700°C, 4% O_2, and 0.4 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.791E-10	1.767E-10		
KCl	0.000E+00	0.000E+00	Potassium species	6.446E-06
Na2CO3	4.498E-09	4.498E-09	NaCl	7.136E-06
K2CO3	7.769E-11	7.768E-11	KCl	6.335E-06
NaX	9.838E-09	9.834E-09	Na (vapor)	2.383E-03
KX	1.553E-10	1.553E-10	K (vapor)	6.713E-05
Temperature Estimations:				
Particle surface temperature (C)	799		Reactor temperature (C)	700
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.085E-12	
NaCl released by volatilization (mol)		2.378E-12	9.765E-12	
Total chloride released by volatilization (mol)		2.378E-12	1.282E-11	
Sodium released by carbonate reduction (mol)		1.173E-12	4.693E-12	
Potassium released by carbonate reduction (mol)		2.026E-14	8.107E-14	
Enrichment Factors after 0.4s:				
Chloride	46.3			
Potassium	13.6			

Table E-17: Spreadsheet PROGRAM.XLS at 700°C, 4% O_2, and 0.5 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.767E-10	1.744E-10		
KCl	0.000E+00	0.000E+00	Potassium species	6.379E-06
Na2CO3	4.498E-09	4.497E-09	NaCl	7.037E-06
K2CO3	7.768E-11	7.767E-11	KCl	6.268E-06
NaX	9.834E-09	9.831E-09	Na(vapor)	2.383E-03
KX	1.553E-10	1.553E-10	K(vapor)	6.713E-05
Temperature Estimations:				
Particle surface temperature (C)	799		Reactor temperature (C)	700
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.085E-12	
NaCl released by volatilization (mol)		2.345E-12	1.211E-11	
Total chloride released by volatilization (mol)		2.345E-12	1.516E-11	
Sodium released by carbonate reduction (mol)		1.173E-12	5.866E-12	
Potassium released by carbonate reduction (mol)		2.026E-14	1.013E-13	
Enrichment Factors after 0.5s:				
Chloride	44.0			
Potassium	11.0			

Table E-18: Spreadsheet PROGRAM.XLS at 700°C, 21% O_2, and 0.1 sec.

	A	B	C	D	E
6	**Initial Conditions:**				
7					
8	O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
9	Reactor temperature (C)	700		Residence Time (s)	0.5
10					
11	**Inorganics Concentrations (mol):**			**Partial Pressure at Equilibrium (bar):**	
12		**Input**	**Output**		
13	NaCl	1.865E-10	1.629E-10		
14	KCl	3.052E-12	0.000E+00	Potassium species	5.430E-05
15	Na2CO3	4.500E-09	4.141E-09	NaCl	6.286E-05
16	K2CO3	7.772E-11	7.212E-11	KCl	2.815E-05
17	NaX	9.849E-09	9.108E-09	Na (vapor)	4.453E-03
18	KX	1.585E-10	1.442E-10	K (vapor)	7.166E-05
19					
20	**Temperature Estimations:**				
21					
22	Particle surface temperature (C)	1149		Reactor temperature (C)	700
23					
24	**Calculations:**				
25				Accumulated	
26	Total potassium released by volatilization (mol)		3.052E-12	3.052E-12	
27	NaCl released by volatilization (mol)		2.358E-11	2.358E-11	
28	Total chloride released by volatilization (mol)		2.663E-11	2.663E-11	
29	Sodium released by carbonate reduction (mol)		7.170E-10	7.170E-10	
30	Potassium released by carbonate reduction (mol)		1.120E-11	1.120E-11	
31					
32	**Enrichment Factors after 0.1s:**				
33					
34	Chloride	1.9			
35	Potassium	1.2			

Table E-19: Spreadsheet PROGRAM.XLS at 700°C, 21% O_2, and 0.2 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.629E-10	1.424E-10		
KCl	0.000E+00	0.000E+00	Potassium species	4.945E-05
Na2CO3	4.141E-09	3.804E-09	NaCl	5.464E-05
K2CO3	7.212E-11	6.679E-11	KCl	2.380E-05
NaX	9.108E-09	8.413E-09	Na (vapor)	4.453E-03
KX	1.442E-10	1.336E-10	K (vapor)	7.166E-05
Temperature Estimations:				
Particle surface temperature (C)	1149		Reactor temperature (C)	700
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		2.050E-11	4.408E-11	
Total chloride released by volatilization (mol)		2.050E-11	4.713E-11	
Sodium released by carbonate reduction (mol)		6.746E-10	1.392E-09	
Potassium released by carbonate reduction (mol)		1.066E-11	2.186E-11	
Enrichment Factors after 0.2s:				
Chloride	1.7			
Potassium	1.1			

Table E-20: Spreadsheet PROGRAM.XLS at 700°C, 21% O_2, and 0.3 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.424E-10	1.243E-10		
KCl	0.000E+00	0.000E+00	Potassium species	4.586E-05
Na2CO3	3.804E-09	3.488E-09	NaCl	4.819E-05
K2CO3	6.679E-11	6.173E-11	KCl	2.057E-05
NaX	8.413E-09	7.762E-09	Na (vapor)	4.453E-03
KX	1.336E-10	1.235E-10	K (vapor)	7.166E-05
Temperature Estimations:				
Particle surface temperature (C)	1149		Reactor temperature (C)	700
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.808E-11	6.216E-11	
Total chloride released by volatilization (mol)		1.808E-11	6.521E-11	
Sodium released by carbonate reduction (mol)		6.329E-10	2.024E-09	
Potassium released by carbonate reduction (mol)		1.012E-11	3.198E-11	
Enrichment Factors after 0.3s:				
Chloride	1.6			
Potassium	1.0			

Table E-21: Spreadsheet PROGRAM.XLS at 700°C, 21% O_2, and 0.4 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.243E-10	1.084E-10		
KCl	0.000E+00	0.000E+00	Potassium species	4.255E-05
Na2CO3	3.488E-09	3.192E-09	NaCl	4.249E-05
K2CO3	6.173E-11	5.694E-11	KCl	1.770E-05
NaX	7.762E-09	7.154E-09	Na (vapor)	4.453E-03
KX	1.235E-10	1.139E-10	K (vapor)	7.166E-05
Temperature Estimations:				
Particle surface temperature (C)	1149		Reactor temperature (C)	700
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.594E-11	7.809E-11	
Total chloride released by volatilization (mol)		1.594E-11	8.115E-11	
Sodium released by carbonate reduction (mol)		5.921E-10	2.617E-09	
Potassium released by carbonate reduction (mol)		9.573E-12	4.155E-11	
Enrichment Factors after 0.4s:				
Chloride	1.6			
Potassium	1.0			

Table E-22: Spreadsheet PROGRAM.XLS at 700°C, 21% O_2, and 0.5 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	700		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.084E-10	9.435E-11		
KCl	0.000E+00	0.000E+00	Potassium species	3.946E-05
Na2CO3	3.192E-09	2.915E-09	NaCl	3.746E-05
K2CO3	5.694E-11	5.243E-11	KCl	1.515E-05
NaX	7.154E-09	6.588E-09	Na (vapor)	4.453E-03
KX	1.139E-10	1.049E-10	K (vapor)	7.166E-05
Temperature Estimations:				
Particle surface temperature (C)	1149		Reactor temperature (C)	700
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.405E-11	9.215E-11	
Total chloride released by volatilization (mol)		1.405E-11	9.520E-11	
Sodium released by carbonate reduction (mol)		5.525E-10	3.169E-09	
Potassium released by carbonate reduction (mol)		9.036E-12	5.059E-11	
Enrichment Factors after 0.5s:				
Chloride	1.5			
Potassium	1.0			

Table E-23: Spreadsheet PROGRAM.XLS at 900°C, 0% O_2, and 0.1 sec.

	A	B	C	D	E
6	**Initial Conditions:**				
7					
8	O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
9	Reactor temperature (C)	900		Residence Time (s)	0.5
10					
11	**Inorganics Concentrations (mol):**			**Partial Pressure at Equilibrium (bar):**	
12		**Input**	**Output**		
13	NaCl	1.865E-10	1.810E-10		
14	KCl	3.052E-12	2.528E-12	Potassium species	1.678E-06
15	Na2CO3	4.500E-09	4.494E-09	NaCl	1.501E-05
16	K2CO3	7.772E-11	7.761E-11	KCl	1.595E-06
17	NaX	9.849E-09	9.831E-09	Na (vapor)	4.401E-03
18	KX	1.585E-10	1.577E-10	K (vapor)	7.193E-05
19					
20	**Temperature Estimations:**				
21					
22	Particle surface temperature (C)	900		Reactor temperature (C)	900
23					
24	**Calculations:**				
25				Accumulated	
26	Total potassium released by volatilization (mol)		5.513E-13	5.513E-13	
27	NaCl released by volatilization (mol)		5.544E-12	5.544E-12	
28	Total chloride released by volatilization (mol)		6.068E-12	6.068E-12	
29	Sodium released by carbonate reduction (mol)		1.226E-11	1.226E-11	
30	Potassium released by carbonate reduction (mol)		2.114E-13	2.114E-13	
31					
32	**Enrichment Factors after 0.1s:**				
33					
34	Chloride	17.8			
35	Potassium	2.7			

Table E-24: Spreadsheet PROGRAM.XLS at 900°C, 0% O_2, and 0.2 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.810E-10	1.756E-10		
KCl	2.528E-12	2.021E-12	Potassium species	1.626E-06
Na2CO3	4.494E-09	4.488E-09	NaCl	1.453E-05
K2CO3	7.761E-11	7.751E-11	KCl	1.543E-06
NaX	9.831E-09	9.814E-09	Na (vapor)	4.401E-03
KX	1.577E-10	1.570E-10	K (vapor)	7.193E-05
Temperature Estimations:				
Particle surface temperature (C)	900		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		5.341E-13	1.085E-12	
NaCl released by volatilization (mol)		5.366E-12	1.091E-11	
Total chloride released by volatilization (mol)		5.873E-12	1.194E-11	
Sodium released by carbonate reduction (mol)		1.222E-11	2.448E-11	
Potassium released by carbonate reduction (mol)		2.107E-13	4.220E-13	
Enrichment Factors after 0.2s:				
Chloride	17.6			
Potassium	2.6			

Table E-25: Spreadsheet PROGRAM.XLS at 900°C, 0% O_2, and 0.3 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.756E-10	1.704E-10		
KCl	2.021E-12	1.531E-12	Potassium species	1.573E-06
Na2CO3	4.488E-09	4.482E-09	NaCl	1.406E-05
K2CO3	7.751E-11	7.740E-11	KCl	1.491E-06
NaX	9.814E-09	9.796E-09	Na (vapor)	4.401E-03
KX	1.570E-10	1.563E-10	K (vapor)	7.193E-05
Temperature Estimations:				
Particle surface temperature (C)	900		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		5.169E-13	1.602E-12	
NaCl released by volatilization (mol)		5.193E-12	1.610E-11	
Total chloride released by volatilization (mol)		5.683E-12	1.762E-11	
Sodium released by carbonate reduction (mol)		1.220E-11	3.668E-11	
Potassium released by carbonate reduction (mol)		2.104E-13	6.324E-13	
Enrichment Factors after 0.3s:				
Chloride	17.4			
Potassium	2.6			

Table E-26: Spreadsheet PROGRAM.XLS at 900°C, 0% O_2, and 0.4 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.704E-10	1.654E-10		
KCl	1.531E-12	1.057E-12	Potassium species	1.524E-06
Na2CO3	4.482E-09	4.476E-09	NaCl	1.361E-05
K2CO3	7.740E-11	7.730E-11	KCl	1.442E-06
NaX	9.796E-09	9.779E-09	Na (vapor)	4.401E-03
KX	1.563E-10	1.555E-10	K (vapor)	7.193E-05
Temperature Estimations:				
Particle surface temperature (C)	900		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		5.007E-13	2.103E-12	
NaCl released by volatilization (mol)		5.026E-12	2.113E-11	
Total chloride released by volatilization (mol)		5.500E-12	2.312E-11	
Sodium released by carbonate reduction (mol)		1.219E-11	4.887E-11	
Potassium released by carbonate reduction (mol)		2.101E-13	8.425E-13	
Enrichment Factors after 0.4s:				
Chloride	17.2			
Potassium	2.6			

Table E-27: Spreadsheet PROGRAM.XLS at 900°C, 0% O_2, and 0.5 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.654E-10	1.605E-10		
KCl	1.057E-12	5.991E-13	Potassium species	1.476E-06
Na2CO3	4.476E-09	4.469E-09	NaCl	1.317E-05
K2CO3	7.730E-11	7.719E-11	KCl	1.394E-06
NaX	9.779E-09	9.762E-09	Na (vapor)	4.401E-03
KX	1.555E-10	1.549E-10	K (vapor)	7.193E-05
Temperature Estimations:				
Particle surface temperature (C)	900		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		4.849E-13	2.588E-12	
NaCl released by volatilization (mol)		4.864E-12	2.599E-11	
Total chloride released by volatilization (mol)		5.322E-12	2.845E-11	
Sodium released by carbonate reduction (mol)		1.217E-11	6.104E-11	
Potassium released by carbonate reduction (mol)		2.098E-13	1.052E-12	
Enrichment Factors after 0.5s:				
Chloride	17.1			
Potassium	2.6			

Table E-28: Spreadsheet PROGRAM.XLS at 900°C, 4% O_2, and 0.1 sec.

	A	B	C	D	E
6	**Initial Conditions:**				
7					
8	O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
9	Reactor temperature (C)	900		Residence Time (s)	0.5
10					
11	**Inorganics Concentrations (mol):**			**Partial Pressure at Equilibrium (bar):**	
12		**Input**	**Output**		
13	NaCl	1.865E-10	1.698E-10		
14	KCl	3.052E-12	0.000E+00	Potassium species	3.609E-05
15	Na2CO3	4.500E-09	4.467E-09	NaCl	4.411E-05
16	K2CO3	7.772E-11	7.715E-11	KCl	2.999E-05
17	NaX	9.849E-09	9.765E-09	Na (vapor)	4.431E-03
18	KX	1.585E-10	1.543E-10	K (vapor)	7.176E-05
19					
20	**Temperature Estimations:**				
21					
22	Particle surface temperature (C)	986		Reactor temperature (C)	900
23					
24	**Calculations:**				
25				Accumulated	
26	Total potassium released by volatilization (mol)		3.052E-12	3.052E-12	
27	NaCl released by volatilization (mol)		1.674E-11	1.674E-11	
28	Total chloride released by volatilization (mol)		1.979E-11	1.979E-11	
29	Sodium released by carbonate reduction (mol)		6.672E-11	6.672E-11	
30	Potassium released by carbonate reduction (mol)		1.142E-12	1.142E-12	
31					
32	**Enrichment Factors after 0.1s:**				
33					
34	Chloride	12.4			
35	Potassium	3.1			

Table E-29: Spreadsheet PROGRAM.XLS at 900°C, 4% O_2, and 0.2 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.698E-10	1.548E-10		
KCl	0.000E+00	0.000E+00	Potassium species	3.342E-05
Na2CO3	4.467E-09	4.434E-09	NaCl	3.931E-05
K2CO3	7.715E-11	7.658E-11	KCl	2.721E-05
NaX	9.765E-09	9.684E-09	Na (vapor)	4.431E-03
KX	1.543E-10	1.532E-10	K (vapor)	7.176E-05
Temperature Estimations:				
Particle surface temperature (C)	986		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.492E-11	3.166E-11	
Total chloride released by volatilization (mol)		1.492E-11	3.471E-11	
Sodium released by carbonate reduction (mol)		6.624E-11	1.330E-10	
Potassium released by carbonate reduction (mol)		1.133E-12	2.275E-12	
Enrichment Factors after 0.2s:				
Chloride	11.0			
Potassium	2.0			

Table E-30: Spreadsheet PROGRAM.XLS at 900°C, 4% O_2, and 0.3 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.548E-10	1.413E-10		
KCl	0.000E+00	0.000E+00	Potassium species	3.158E-05
Na2CO3	4.434E-09	4.401E-09	NaCl	3.556E-05
K2CO3	7.658E-11	7.602E-11	KCl	2.522E-05
NaX	9.684E-09	9.605E-09	Na (vapor)	4.431E-03
KX	1.532E-10	1.520E-10	K (vapor)	7.176E-05
Temperature Estimations:				
Particle surface temperature (C)	986		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.349E-11	4.515E-11	
Total chloride released by volatilization (mol)		1.349E-11	4.820E-11	
Sodium released by carbonate reduction (mol)		6.576E-11	1.987E-10	
Potassium released by carbonate reduction (mol)		1.125E-12	3.400E-12	
Enrichment Factors after 0.3s:				
Chloride	10.3			
Potassium	1.6			

Table E-31: Spreadsheet PROGRAM.XLS at 900°C, 4% O_2, and 0.4 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.413E-10	1.291E-10		
KCl	0.000E+00	0.000E+00	Potassium species	2.987E-05
Na2CO3	4.401E-09	4.368E-09	NaCl	3.224E-05
K2CO3	7.602E-11	7.546E-11	KCl	2.337E-05
NaX	9.605E-09	9.528E-09	Na (vapor)	4.431E-03
KX	1.520E-10	1.509E-10	K (vapor)	7.176E-05
Temperature Estimations:				
Particle surface temperature (C)	986		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.223E-11	5.738E-11	
Total chloride released by volatilization (mol)		1.223E-11	6.044E-11	
Sodium released by carbonate reduction (mol)		6.529E-11	2.640E-10	
Potassium released by carbonate reduction (mol)		1.117E-12	4.518E-12	
Enrichment Factors after 0.4s:				
Chloride	9.8			
Potassium	1.5			

Table E-32: Spreadsheet PROGRAM.XLS at 900°C, 4% O_2, and 0.5 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.291E-10	1.180E-10		
KCl	0.000E+00	0.000E+00	Potassium species	2.823E-05
Na2CO3	4.368E-09	4.336E-09	NaCl	2.928E-05
K2CO3	7.546E-11	7.491E-11	KCl	2.162E-05
NaX	9.528E-09	9.452E-09	Na (vapor)	4.431E-03
KX	1.509E-10	1.498E-10	K (vapor)	7.176E-05
Temperature Estimations:				
Particle surface temperature (C)	986		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.111E-11	6.850E-11	
Total chloride released by volatilization (mol)		1.111E-11	7.155E-11	
Sodium released by carbonate reduction (mol)		6.481E-11	3.288E-10	
Potassium released by carbonate reduction (mol)		1.109E-12	5.627E-12	
Enrichment Factors after 0.5s:				
Chloride	9.4			
Potassium	1.4			

Table E-33: Spreadsheet PROGRAM.XLS at 900°C, 21% O_2, and 0.1 sec.

	A	B	C	D	E
6	**Initial Conditions:**				
7					
8	O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
9	Reactor temperature (C)	900		Residence Time (s)	0.5
10					
11	**Inorganics Concentrations (mol):**			**Partial Pressure at Equilibrium (bar):**	
12		**Input**	**Output**		
13	NaCl	1.865E-10	1.553E-10		
14	KCl	3.052E-12	0.000E+00	Potassium species	3.888E-05
15	Na2CO3	4.500E-09	3.467E-09	NaCl	7.504E-05
16	K2CO3	7.772E-11	6.379E-11	KCl	1.875E-05
17	NaX	9.849E-09	7.752E-09	Na (vapor)	4.542E-03
18	KX	1.585E-10	1.276E-10	K (vapor)	7.220E-05
19					
20	**Temperature Estimations:**				
21					
22	Particle surface temperature (C)	1297		Reactor temperature (C)	900
23					
24	**Calculations:**				
25				Accumulated	
26	Total potassium released by volatilization (mol)		3.052E-12	3.052E-12	
27	NaCl released by volatilization (mol)		3.116E-11	3.116E-11	
28	Total chloride released by volatilization (mol)		3.421E-11	3.421E-11	
29	Sodium released by carbonate reduction (mol)		2.066E-09	2.066E-09	
30	Potassium released by carbonate reduction (mol)		2.786E-11	2.786E-11	
31					
32	**Enrichment Factors after 0.1s:**				
33					
34	Chloride	0.9			
35	Potassium	0.9			

Table E-34: Spreadsheet PROGRAM.XLS at 900°C, 21% O_2, and 0.2 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.553E-10	1.290E-10		
KCl	0.000E+00	0.000E+00	Potassium species	3.145E-05
Na2CO3	3.467E-09	2.519E-09	NaCl	6.341E-05
K2CO3	6.379E-11	5.054E-11	KCl	1.361E-05
NaX	7.752E-09	5.830E-09	Na (vapor)	4.542E-03
KX	1.276E-10	1.011E-10	K (vapor)	7.220E-05
Temperature Estimations:				
Particle surface temperature (C)	1297		Reactor temperature (C)	900
Calculations:				
			Accumulated	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		2.633E-11	5.749E-11	
Total chloride released by volatilization (mol)		2.633E-11	6.054E-11	
Sodium released by carbonate reduction (mol)		1.895E-09	3.962E-09	
Potassium released by carbonate reduction (mol)		2.650E-11	5.436E-11	
Enrichment Factors after 0.2s:				
Chloride	0.8			
Potassium	0.9			

Table E-35: Spreadsheet PROGRAM.XLS at 900°C, 21% O_2, and 0.3 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.290E-10	1.065E-10		
KCl	0.000E+00	0.000E+00	Potassium species	2.522E-05
Na2CO3	2.519E-09	1.685E-09	NaCl	5.434E-05
K2CO3	5.054E-11	3.818E-11	KCl	9.779E-06
NaX	5.830E-09	4.138E-09	Na (vapor)	4.542E-03
KX	1.011E-10	7.636E-11	K (vapor)	7.220E-05
Temperature Estimations:				
Particle surface temperature (C)	1297		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		2.256E-11	8.005E-11	
Total chloride released by volatilization (mol)		2.256E-11	8.310E-11	
Sodium released by carbonate reduction (mol)		1.669E-09	5.631E-09	
Potassium released by carbonate reduction (mol)		2.472E-11	7.908E-11	
Enrichment Factors after 0.3s:				
Chloride	0.8			
Potassium	0.9			

Table E-36: Spreadsheet PROGRAM.XLS at 900°C, 21% O_2, and 0.4 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.065E-10	8.720E-11		
KCl	0.000E+00	0.000E+00	Potassium species	1.945E-05
Na2CO3	1.685E-09	9.983E-10	NaCl	4.636E-05
K2CO3	3.818E-11	2.699E-11	KCl	6.679E-06
NaX	4.138E-09	2.746E-09	Na (vapor)	4.542E-03
KX	7.636E-11	5.397E-11	K (vapor)	7.220E-05
Temperature Estimations:				
Particle surface temperature (C)	1297		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.925E-11	9.930E-11	
Total chloride released by volatilization (mol)		1.925E-11	1.024E-10	
Sodium released by carbonate reduction (mol)		1.373E-09	7.003E-09	
Potassium released by carbonate reduction (mol)		2.239E-11	1.015E-10	
Enrichment Factors after 0.4s:				
Chloride	0.8			
Potassium	0.9			

Table E-37: Spreadsheet PROGRAM.XLS at 900°C, 21% O_2, and 0.5 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	900		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	8.720E-11	7.093E-11		
KCl	0.000E+00	0.000E+00	Potassium species	1.437E-05
Na2CO3	9.983E-10	4.991E-10	NaCl	3.918E-05
K2CO3	2.699E-11	1.734E-11	KCl	4.311E-06
NaX	2.746E-09	1.732E-09	Na (vapor)	4.542E-03
KX	5.397E-11	3.467E-11	K (vapor)	7.220E-05
Temperature Estimations:				
Particle surface temperature (C)	1297		Reactor temperature (C)	900
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.627E-11	1.156E-10	
Total chloride released by volatilization (mol)		1.627E-11	1.186E-10	
Sodium released by carbonate reduction (mol)		9.983E-10	8.002E-09	
Potassium released by carbonate reduction (mol)		1.930E-11	1.208E-10	
Enrichment Factors after 0.5s:				
Chloride	0.8			
Potassium	0.9			

Table E-38: Spreadsheet PROGRAM.XLS at 1100°C, 0% O_2, and 0.1 sec.

	A	B	C	D	E
6	**Initial Conditions:**				
7					
8	O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
9	Reactor temperature (C)	1100		Residence Time (s)	0.5
10					
11	**Inorganics Concentrations (mol/particle):**			**Partial Pressure at Equilibrium (bar):**	
12		**Input**	**Output**		
13	NaCl	1.865E-10	1.592E-10		
14	KCl	3.052E-12	1.016E-12	Potassium species	5.511E-06
15	Na2CO3	4.500E-09	4.297E-09	NaCl	6.559E-05
16	K2CO3	7.772E-11	7.440E-11	KCl	5.505E-06
17	NaX	9.849E-09	9.417E-09	Na (vapor)	4.445E-03
18	KX	1.585E-10	1.498E-10	K (vapor)	7.158E-05
19					
20	**Temperature Estimations:**				
21					
22	Particle surface temperature (C)	1100		Reactor temperature (C)	1100
23					
24	**Calculations:**				
25				Accumulated	
26	Total potassium released by volatilization (mol)		2.038E-12	2.038E-12	
27	NaCl released by volatilization (mol)		2.726E-11	2.726E-11	
28	Total chloride released by volatilization (mol)		2.930E-11	2.930E-11	
29	Sodium released by carbonate reduction (mol)		4.051E-10	4.051E-10	
30	Potassium released by carbonate reduction (mol)		6.640E-12	6.640E-12	
31					
32	**Enrichment Factors after 0.1s:**				
33					
34	Chloride	3.5			
35	Potassium	1.2			

Table E-39: Spreadsheet PROGRAM.XLS at 1100°C, 0% O_2, and 0.2 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol/particle):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.592E-10	1.363E-10		
KCl	1.016E-12	0.000E+00	Potassium species	4.636E-06
Na2CO3	4.297E-09	4.103E-09	NaCl	5.519E-05
K2CO3	7.440E-11	7.120E-11	KCl	4.631E-06
NaX	9.417E-09	9.005E-09	Na (vapor)	4.445E-03
KX	1.498E-10	1.424E-10	K (vapor)	7.158E-05
Temperature Estimations:				
Particle surface temperature (C)	1100		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		1.016E-12	3.054E-12	
NaCl released by volatilization (mol)		2.294E-11	5.020E-11	
Total chloride released by volatilization (mol)		2.395E-11	5.325E-11	
Sodium released by carbonate reduction (mol)		3.887E-10	7.938E-10	
Potassium released by carbonate reduction (mol)		6.398E-12	1.304E-11	
Enrichment Factors after 0.2s:				
Chloride	3.3			
Potassium	1.2			

Table E-40: Spreadsheet PROGRAM.XLS at 1100°C, 0% O_2, and 0.3 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol/particle):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.363E-10	1.169E-10		
KCl	0.000E+00	0.000E+00	Potassium species	3.942E-06
Na2CO3	4.103E-09	3.916E-09	NaCl	4.674E-05
K2CO3	7.120E-11	6.812E-11	KCl	3.937E-06
NaX	9.005E-09	8.612E-09	Na (vapor)	4.445E-03
KX	1.424E-10	1.362E-10	K (vapor)	7.158E-05
Temperature Estimations:				
Particle surface temperature (C)	1100		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.054E-12	
NaCl released by volatilization (mol)		1.943E-11	6.962E-11	
Total chloride released by volatilization (mol)		1.943E-11	7.267E-11	
Sodium released by carbonate reduction (mol)		3.734E-10	1.167E-09	
Potassium released by carbonate reduction (mol)		6.170E-12	1.921E-11	
Enrichment Factors after 0.3s:				
Chloride	3.1			
Potassium	1.1			

Table E-41: Spreadsheet PROGRAM.XLS at 1100°C, 0% O_2, and 0.4 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol/particle):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.169E-10	1.003E-10		
KCl	0.000E+00	0.000E+00	Potassium species	3.397E-06
Na2CO3	3.916E-09	3.737E-09	NaCl	3.990E-05
K2CO3	6.812E-11	6.514E-11	KCl	3.393E-06
NaX	8.612E-09	8.237E-09	Na (vapor)	4.445E-03
KX	1.362E-10	1.303E-10	K (vapor)	7.158E-05
Temperature Estimations:				
Particle surface temperature (C)	1100		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.054E-12	
NaCl released by volatilization (mol)		1.658E-11	8.621E-11	
Total chloride released by volatilization (mol)		1.658E-11	8.926E-11	
Sodium released by carbonate reduction (mol)		3.585E-10	1.526E-09	
Potassium released by carbonate reduction (mol)		5.946E-12	2.515E-11	
Enrichment Factors after 0.4s:				
Chloride	2.9			
Potassium	1.1			

Table E-42: Spreadsheet PROGRAM.XLS at 1100°C, 0% O_2, and 0.5 sec.

Initial Conditions:				
O2 content in reaction gas (%)	0		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol/particle):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.003E-10	8.613E-11		
KCl	0.000E+00	0.000E+00	Potassium species	2.927E-06
Na2CO3	3.737E-09	3.565E-09	NaCl	3.408E-05
K2CO3	6.514E-11	6.228E-11	KCl	2.923E-06
NaX	8.237E-09	7.879E-09	Na (vapor)	4.445E-03
KX	1.303E-10	1.246E-10	K (vapor)	7.158E-05
Temperature Estimations:				
Particle surface temperature (C)	1100		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.054E-12	
NaCl released by volatilization (mol)		1.416E-11	1.004E-10	
Total chloride released by volatilization (mol)		1.416E-11	1.034E-10	
Sodium released by carbonate reduction (mol)		3.441E-10	1.870E-09	
Potassium released by carbonate reduction (mol)		5.728E-12	3.088E-11	
Enrichment Factors after 0.5s:				
Chloride	2.7			
Potassium	1.1			

Table E-43: Spreadsheet PROGRAM.XLS at 1100°C, 4% O_2, and 0.1 sec.

	A	B	C	D	E
6	**Initial Conditions:**				
7					
8	O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
9	Reactor temperature (C)	1100		Residence Time (s)	0.5
10					
11	**Inorganics Concentrations (mol/particle):**			**Partial Pressure at Equilibrium (bar):**	
12		**Input**	**Output**		
13	NaCl	1.865E-10	1.589E-10		
14	KCl	3.052E-12	0.000E+00	Potassium species	5.344E-05
15	Na2CO3	4.500E-09	4.021E-09	NaCl	6.505E-05
16	K2CO3	7.772E-11	7.037E-11	KCl	2.682E-05
17	NaX	9.849E-09	8.864E-09	Na (vapor)	4.463E-03
18	KX	1.585E-10	1.407E-10	K (vapor)	7.173E-05
19					
20	**Temperature Estimations:**				
21					
22	Particle surface temperature (C)	1175		Reactor temperature (C)	1100
23					
24	**Calculations:**				
25				Accumulated	
26	Total potassium released by volatilization (mol)		3.052E-12	3.052E-12	
27	NaCl released by volatilization (mol)		2.758E-11	2.758E-11	
28	Total chloride released by volatilization (mol)		3.064E-11	3.064E-11	
29	Sodium released by carbonate reduction (mol)		9.577E-10	9.577E-10	
30	Potassium released by carbonate reduction (mol)		1.471E-11	1.471E-11	
31					
32	**Enrichment Factors after 0.1s:**				
33					
34	Chloride	1.6			
35	Potassium	1.1			

Table E-44: Spreadsheet PROGRAM.XLS at 1100°C, 4% O_2, and 0.2 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol/particle):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.589E-10	1.354E-10		
KCl	0.000E+00	0.000E+00	Potassium species	4.766E-05
Na2CO3	4.021E-09	3.578E-09	NaCl	5.539E-05
K2CO3	7.037E-11	6.345E-11	KCl	2.185E-05
NaX	8.864E-09	7.954E-09	Na (vapor)	4.463E-03
KX	1.407E-10	1.269E-10	K (vapor)	7.173E-05
Temperature Estimations:				
Particle surface temperature (C)	1175		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		2.349E-11	5.107E-11	
Total chloride released by volatilization (mol)		2.349E-11	5.412E-11	
Sodium released by carbonate reduction (mol)		8.862E-10	1.844E-09	
Potassium released by carbonate reduction (mol)		1.383E-11	2.854E-11	
Enrichment Factors after 0.2s:				
Chloride	1.5			
Potassium	1.0			

Table E-45: Spreadsheet PROGRAM.XLS at 1100°C, 4% O_2, and 0.3 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol/particle):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.354E-10	1.151E-10		
KCl	0.000E+00	0.000E+00	Potassium species	4.324E-05
Na2CO3	3.578E-09	3.170E-09	NaCl	4.786E-05
K2CO3	6.345E-11	5.697E-11	KCl	1.814E-05
NaX	7.954E-09	7.118E-09	Na (vapor)	4.463E-03
KX	1.269E-10	1.139E-10	K (vapor)	7.173E-05
Temperature Estimations:				
Particle surface temperature (C)	1175		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		2.029E-11	7.136E-11	
Total chloride released by volatilization (mol)		2.029E-11	7.442E-11	
Sodium released by carbonate reduction (mol)		8.153E-10	2.659E-09	
Potassium released by carbonate reduction (mol)		1.295E-11	4.149E-11	
Enrichment Factors after 0.3s:				
Chloride	1.4			
Potassium	1.0			

Table E-46: Spreadsheet PROGRAM.XLS at 1100°C, 4% O_2, and 0.4 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol/particle):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.151E-10	9.761E-11		
KCl	0.000E+00	0.000E+00	Potassium species	3.918E-05
Na2CO3	3.170E-09	2.798E-09	NaCl	4.132E-05
K2CO3	5.697E-11	5.094E-11	KCl	1.494E-05
NaX	7.118E-09	6.355E-09	Na (vapor)	4.463E-03
KX	1.139E-10	1.019E-10	K (vapor)	7.173E-05
Temperature Estimations:				
Particle surface temperature (C)	1175		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.752E-11	8.889E-11	
Total chloride released by volatilization (mol)		1.752E-11	9.194E-11	
Sodium released by carbonate reduction (mol)		7.457E-10	3.405E-09	
Potassium released by carbonate reduction (mol)		1.206E-11	5.355E-11	
Enrichment Factors after 0.4s:				
Chloride	1.4			
Potassium	1.0			

Table E-47: Spreadsheet PROGRAM.XLS at 1100°C, 4% O_2, and 0.5 sec.

Initial Conditions:				
O2 content in reaction gas (%)	4		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol/particle):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	9.761E-11	8.250E-11		
KCl	0.000E+00	0.000E+00	Potassium species	3.542E-05
Na2CO3	2.798E-09	2.459E-09	NaCl	3.564E-05
K2CO3	5.094E-11	4.536E-11	KCl	1.218E-05
NaX	6.355E-09	5.662E-09	Na (vapor)	4.463E-03
KX	1.019E-10	9.072E-11	K (vapor)	7.173E-05
Temperature Estimations:				
Particle surface temperature (C)	1175		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.052E-12	
NaCl released by volatilization (mol)		1.511E-11	1.040E-10	
Total chloride released by volatilization (mol)		1.511E-11	1.071E-10	
Sodium released by carbonate reduction (mol)		6.780E-10	4.083E-09	
Potassium released by carbonate reduction (mol)		1.117E-11	6.472E-11	
Enrichment Factors after 0.5s:				
Chloride	1.3			
Potassium	1.0			

Table E-48: Spreadsheet PROGRAM.XLS at 1100°C, 21% O_2, and 0.1 sec.

	A	B	C	D	E
6	**Initial Conditions:**				
7					
8	O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
9	Reactor temperature (C)	1100		Residence Time (s)	0.5
10					
11	**Inorganics Concentrations (mol):**			**Partial Pressure at Equilibrium (bar):**	
12		**Input**	**Output**		
13	NaCl	1.865E-10	1.462E-10		
14	KCl	3.052E-12	8.686E-13	Potassium species	1.121E-05
15	Na2CO3	4.500E-09	3.000E-09	NaCl	8.864E-05
16	K2CO3	7.772E-11	5.886E-11	KCl	5.400E-06
17	NaX	9.849E-09	6.809E-09	Na (vapor)	4.594E-03
18	KX	1.585E-10	1.177E-10	K (vapor)	7.272E-05
19					
20	**Temperature Estimations:**				
21					
22	Particle surface temperature (C)	1448		Reactor temperature (C)	1100
23					
24	**Calculations:**				
25				Accumulated	
26	Total potassium released by volatilization (mol)		3.052E-12	3.052E-12	
27	NaCl released by volatilization (mol)		4.028E-11	4.028E-11	
28	Total chloride released by volatilization (mol)		4.247E-11	4.247E-11	
29	Sodium released by carbonate reduction (mol)		2.999E-09	2.999E-09	
30	Potassium released by carbonate reduction (mol)		3.771E-11	3.771E-11	
31					
32	**Enrichment Factors after 0.1s:**				
33					
34	Chloride	0.7			
35	Potassium	0.8			

Table E-49: Spreadsheet PROGRAM.XLS at 1100°C, 21% O_2, and 0.2 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.462E-10	1.150E-10		
KCl	8.686E-13	0.000E+00	Potassium species	1.069E-05
Na2CO3	3.000E-09	1.562E-09	NaCl	6.867E-05
K2CO3	5.886E-11	4.037E-11	KCl	4.485E-06
NaX	6.809E-09	3.901E-09	Na (vapor)	4.594E-03
KX	1.177E-10	7.988E-11	K (vapor)	7.272E-05
Temperature Estimations:				
Particle surface temperature (C)	1448		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		8.686E-13	3.921E-12	
NaCl released by volatilization (mol)		3.121E-11	7.149E-11	
Total chloride released by volatilization (mol)		3.208E-11	7.454E-11	
Sodium released by carbonate reduction (mol)		2.877E-09	5.876E-09	
Potassium released by carbonate reduction (mol)		3.698E-11	7.469E-11	
Enrichment Factors after 0.2s:				
Chloride	0.7			
Potassium	0.8			

Table E-50: Spreadsheet PROGRAM.XLS at 1100°C, 21% O_2, and 0.3 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	1.150E-10	9.077E-11		
KCl	0.000E+00	0.000E+00	Potassium species	1.105E-05
Na2CO3	1.562E-09	7.809E-10	NaCl	5.334E-05
K2CO3	4.037E-11	2.254E-11	KCl	4.010E-06
NaX	3.901E-09	2.315E-09	Na (vapor)	4.594E-03
KX	7.988E-11	4.421E-11	K (vapor)	7.272E-05
Temperature Estimations:				
Particle surface temperature (C)	1448		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.921E-12	
NaCl released by volatilization (mol)		2.424E-11	9.573E-11	
Total chloride released by volatilization (mol)		2.424E-11	9.878E-11	
Sodium released by carbonate reduction (mol)		1.562E-09	7.438E-09	
Potassium released by carbonate reduction (mol)		3.567E-11	1.104E-10	
Enrichment Factors after 0.3s:				
Chloride	0.7			
Potassium	0.9			

Table E-51: Spreadsheet PROGRAM.XLS at 1100°C, 21% O_2, and 0.4 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	9.077E-11	7.147E-11		
KCl	0.000E+00	0.000E+00	Potassium species	9.045E-06
Na2CO3	7.809E-10	3.904E-10	NaCl	4.246E-05
K2CO3	2.254E-11	1.127E-11	KCl	2.865E-06
NaX	2.315E-09	1.515E-09	Na (vapor)	4.594E-03
KX	4.421E-11	2.167E-11	K (vapor)	7.272E-05
Temperature Estimations:				
Particle surface temperature (C)	1448		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.921E-12	
NaCl released by volatilization (mol)		1.930E-11	1.150E-10	
Total chloride released by volatilization (mol)		1.930E-11	1.181E-10	
Sodium released by carbonate reduction (mol)		7.809E-10	8.219E-09	
Potassium released by carbonate reduction (mol)		2.254E-11	1.329E-10	
Enrichment Factors after 0.4s:				
Chloride	0.7			
Potassium	1.0			

Table E-52: Spreadsheet PROGRAM.XLS at 1100°C, 21% O_2, and 0.5 sec.

Initial Conditions:				
O2 content in reaction gas (%)	21		Diameter of char particle (m)	3.00E-04
Reactor temperature (C)	1100		Residence Time (s)	0.5
Inorganics Concentrations (mol):			**Partial Pressure at Equilibrium (bar):**	
	Input	**Output**		
NaCl	7.147E-11	5.599E-11		
KCl	0.000E+00	0.000E+00	Potassium species	5.815E-06
Na2CO3	3.904E-10	1.952E-10	NaCl	3.406E-05
K2CO3	1.127E-11	5.635E-12	KCl	1.645E-06
NaX	1.515E-09	1.109E-09	Na (vapor)	4.594E-03
KX	2.167E-11	1.040E-11	K (vapor)	7.272E-05
Temperature Estimations:				
Particle surface temperature (C)	1448		Reactor temperature (C)	1100
Calculations:				
			Accumulated:	
Total potassium released by volatilization (mol)		0.000E+00	3.921E-12	
NaCl released by volatilization (mol)		1.548E-11	1.305E-10	
Total chloride released by volatilization (mol)		1.548E-11	1.336E-10	
Sodium released by carbonate reduction (mol)		3.904E-10	8.610E-09	
Potassium released by carbonate reduction (mol)		1.127E-11	1.442E-10	
Enrichment Factors after 0.5s:				
Chloride	0.8			
Potassium	1.0			

Appendix F

DIFFUSIVITY ESTIMATION

MW	Temp (C)	Diff (T)	Diff (0C)			
39.94	20	0.194	0.219551	A		
112.41	0	0.17	0.17	Cd		
44.01	20	0.163	0.184468	CO2		
84.16	15	0.076	0.083458	Cyclohexane		
142.28	90	0.0841	0.138468	n-Decane		
170.33	126	0.0813	0.157946	Dodecane		
4	20	0.705	0.797853	Helium		
86.17	15	0.0757	0.083128	n-Hexane		
2	0	0.697	0.697	Hydrogen		
253.84	0	0.07	0.07	Iodine		
200.61	0	0.13	0.13	Mercury		
85.13	15	0.0758	0.083238	Methyl Cyclopentane		
114.22	30	0.071	0.085212	n-Octane		
32	0	0.181	0.181	Oxigen		
115.13	30	0.0705	0.084611	2,2,4,trimetyl pentane		
145.2	90	0.0684	0.112618	2,2,3, trimetyl heptane