

CHAR BURNING

Project 3473-6

**Summary Technical Report
to
AMERICAN PAPER INSTITUTE
RECOVERY BOILER COMMITTEE**

February 22, 1985

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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TABLE OF CONTENTS

	Page
1. EXECUTIVE SUMMARY	1-1
Results	1-3
Char Characterization	1-4
Char Burning	1-5
Fume Formation	1-7
Implications	1-8
Bed Burning	1-8
Reduction	1-9
Fume Control	1-10
Bed Temperature	1-11
Air/Fuel Distribution	1-11
2. BACKGROUND	2-1
Overview of Black Liquor Burning	2-1
Recovery Boiler	2-1
Burning Process	2-2
Burning in Furnace	2-5
Flow Paths in Recovery Boilers	2-6
Need for Knowledge of Char Burning	2-11
Importance	2-11
Needs	2-12
Benefits	2-13
Previous Work Leading to the Project	2-14
Work at IPC	2-15
Work at ADL	2-15
Control Project	2-17
Approach to the Problem	2-18

Objectives	2-19
Program Structure	2-20
Support and Oversight	2-20
Original Plan	2-21
Revised Plan	2-21
Reporting	2-25
Report Structure	2-26
3. CHAR	3-1
Char Formation	3-1
Definitions	3-1
Process <u>vs.</u> Bed	3-2
Description of Char	3-3
Laboratory Procedures	3-3
Physical Properties of Char	3-6
ADL Data	3-6
Char Density	3-8
Chemical Composition	3-9
ADL Data	3-9
Other Data	3-10
IPC Data	3-12
Interpretation of Composition Data	3-16
Simplified Chemical Composition	3-17
Char Stoichiometry	3-19
Simplified View	3-19
General Case	3-24
Other Interactions with Surroundings	3-26
Interpretation of Air Requirements	3-27

Char Thermochemistry	3-29
Heating Value of Char	3-30
Heating Value of Smelt	3-33
Gasification Heating Values	3-34
4. CHAR BURNING	4-1
Sulfate-Sulfide Cycle	4-2
Description	4-2
Background	4-5
Quantitative Treatment of Sulfate-Sulfide Cycle	4-7
Sulfate Reaction Rates	4-10
Carbon-Sulfate Reactions	4-10
Sulfate Reduction by Carbon Monoxide	4-17
Reduction by Hydrogen Gas	4-18
Other Paths to Sulfide	4-19
Absorption of Hydrogen Sulfide	4-19
Thiosulfate Decomposition	4-22
CO-CO ₂ Distribution	4-22
Oxidation Rates	4-24
Experimental System	4-25
Sulfide Oxidation	4-25
Direct Carbon Oxidation	4-27
Carbon Oxidation with Sulfur Present	4-28
Significance	4-30
Theory of Char Burning	4-32
Unlimited Oxygen Access	4-34
Oxygen Limited Burning	4-35

General Case	4-36
Application to a Char Particle	4-42
Temperature Effects	4-44
Char Particle Burning	4-45
Burning Geometry	4-46
Single Particle Burning System	4-47
Burning Rate Curves	4-53
Interpretation	4-57
Conclusions	4-58
5. FUME FORMATION	5-1
Background	5-1
Definition of Fume	5-1
Volatiles	5-3
Existing Knowledge	5-4
Approach	5-5
Experimental	5-6
Oxidative Fuming	5-9
Definition and Significance	5-9
Results	5-9
Char Burns	5-12
Chemistry of Oxidative Fuming	5-16
Reductive Fuming	5-20
Results	5-20
Chemistry	5-21
Fume Summary	5-22
Major Findings	5-22
Further Work	5-23

6. OPERATIONAL IMPLICATIONS	6-1
Application to Furnace	6-1
Char Beds and Char Burning	6-1
Overall View	6-2
Specific Operating Objectives	6-6
Burning Rates	6-6
Bed Temperature	6-10
Bed Stability	6-13
Reduction Efficiency	6-15
Unburned Carbon in Smelt	6-19
Fume Control	6-21
Air/Fuel Distribution	6-24
Spray Size	6-24
Air/Fuel Coupling	6-27
Bed Air Supply	6-28
Stationary Firing	6-29
7. ACKNOWLEDGMENTS	7-1
8. LITERATURE CITED	8-1

LIST OF TABLES

<u>Table</u>		Page
1-1	Main Results of Study	1-3
2-1	Project Background	2-14
2-2	Location of Research Areas	2-19
3-1	Thermal Property Data	3-7
3-2	Analysis of Char Bed Samples	3-9
3-3	Composition Data on Weyerhaeuser Char	3-11
3-4	Elemental Analyses of IPC Chars	3-12
3-5	Inorganic Content of Char	3-13
3-6	Relative Char Composition	3-15
3-7	Calculated HHV for Simplified Char	3-31
3-8	Heating Value for Simplified Char - Actual Conditions	3-32
4-1	Heats of Carbon-Sulfate Reactions	4-11
4-2	Rate Parameters for Carbon-Sulfate Reactions	4-13
4-3	Parameters for Modified Carbon-Sulfate Rate Equation	4-14
4-4	Equilibrium CO/CO ₂ Distribution	4-23
4-5	Direct Oxidation Rate Parameters	4-27
5-1	Major Variables Influencing Oxidative Fuming	5-12

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
2-1	Black Liquor Burning Stages	2-4
2-2	Sodium Flow Paths	2-7
2-3	Sulfur Flow Paths	2-8
2-4	Carbon Flow Paths	2-9
2-5	Anticipated Information Flow	2-22
2-6	Original Project Task Schedule	2-23
3-1	Picture Sequence Showing Char Formation	3-4
3-2	Reactions of Char Constituents	3-20
4-1	Schematic of Sulfate-Sulfide Cycle	4-4
4-2	Atomics International Molten Salt Reactor	4-6
4-3	Laboratory Experimental System	4-12
4-4	Effect of Parameters on Carbon-Sulfate Reaction Rate	4-16
4-5	Sulfide Oxidation Rates	4-26
4-6	Soda Char Burning Curves	4-31
4-7	Calculated Burning Curves at 1700°F	4-39
4-8	Calculated Burning Curves at 2420°F	4-41
4-9	Calculated Mass <u>vs.</u> Time Burning Curves at 2420°F	4-43
4-10	Schematic of Single Particle Reactor	4-48
4-11	Photographs of Single Particle Reactor	4-50
4-12	Picture Sequence Showing Char Burning	4-51
4-13	Kraft Char Particle Burning in Air	4-53
4-14	Kraft Char Particle Burning in 10% O ₂	4-54
4-15	Soda Char Particle Burning in Air	4-55

5-1	SEM Pictures of Fume Particles	5-2
5-2	Experimental System for Fume Studies	5-7
5-3	Range of Observed Fume Intensities	5-8
5-4	Fuming During a Kraft Char Burn	5-14
5-5	Fuming During a Soda Char Burn	5-15
6-1	New Lower Furnace Model	6-4
6-2	ADL Lower Furnace Models	6-5
6-3	Air Levels and Bed Stability	6-16
6-4	Factors Involved in Reduction Efficiency	6-20
6-5	Fume Production in the Furnace	6-25

EXECUTIVE SUMMARY

This report is the main technical report on a two-year fundamental study of char burning. The overall goal of the study was a quantitative understanding of the char burning process that can be used to analyze recovery furnace operation and identify changes that could lead to improved performance. The project was jointly supported by the API Recovery Boiler Committee and the IPC Dues Funded Research Program.

Char burning is only one aspect of the burning of black liquor in a recovery furnace. Ten areas, where critical knowledge was lacking, were identified by the Recovery Boiler Committee in 1981. This work on char burning addressed two of those areas. Most of the remainder are being addressed in an ongoing effort at The Institute of Paper Chemistry, the National Bureau of Standards, and the University of Maine at Orono. Primary support for this overall program is from the U.S. Department of Energy. Support is also provided by the API Recovery Boiler Committee, the IPC Dues-Funded Research Program, and six private companies.

Although char burning is only part of the complex process of black liquor combustion, knowledge of char burning is valuable in itself. Such knowledge provides a basis for informed decisions on how to meet recovery boiler operating objectives such as improved reduction, optimum fume production, bed control, and blackout prevention. The greatest potential benefit would be the ability to achieve enhanced burning rates of large particles of liquor, which in turn would allow increased hearth loadings with minimum carryover. This could result in significant capacity improvement.

Char burning is concerned with the rates of carbon burnup and simultaneous sulfide formation and fume generation in smelt-char systems similar to char beds in recovery boilers. The complex rate processes in char burning were interpreted by synthesizing rate data from more fundamental process steps obtained in simpler systems. The approach which was taken was to obtain experimental data on the individual processes under controlled laboratory conditions, use this fundamental information to interpret experimental data on char burning under controlled laboratory conditions, and, finally, translate the results to char beds in recovery furnaces.

The specific objectives of the study were to

1. Obtain fundamental data on the chemistry of the reduction of sulfate to sulfide and develop quantitative rate equations that include all important variables
2. Obtain fundamental data and rate equations for oxidation processes in molten carbonate systems
3. Obtain fundamental data on the chemistry of fume forming processes and develop appropriate rate equations
4. Obtain experimental data on the combustion of char under controlled conditions and interpret the behavior in terms of the underlying fundamental processes
5. Examine the implications of the results of the work on furnace operations

The results of all of the work are covered in this report. Details of the work on the fundamental processes and the development of rate equations are given separately in a series of IPC Progress Reports to be listed later. In

addition, a relatively nontechnical, applications oriented report to communicate the results of the work to operations personnel is being prepared.

RESULTS

The results of the study are summarized in Table 1-1. These items are then expanded on in the remainder of this section.

Table 1-1. Main results of study.

Char Characterization:

- Data on char composition
- Simplified chemical description
- Combustion air requirements
- Heating values

Reduction:

- Char carbon-sulfate rate equation
- Carbon monoxide-sulfate rate equation
- Reduction by hydrogen not significant
- Thiosulfate decomposition

Oxidation:

- Sulfide oxidation rates
- Carbon oxidation rate equation (without sulfur)
- Carbon oxidation rate equation (with sulfur)
- Oxidation via sulfate/sulfide cycle
- Quantitative treatment of sulfate/sulfide cycle

Char Burning:

- Experimental data on char burning
- Agreement with sulfate/sulfide cycle theory
- Importance of temperature

Fume Formation:

- Phenomenon of oxidative fuming
- Possible explanations for oxidative fuming
- Fuming during char burning

Char Characterization

Char is the residual solid product from black liquor pyrolysis. It is a black, porous, friable material containing essentially all of the sodium and about one-half the carbon in the incoming black liquor. For most purposes, char can be considered to consist of three inorganic salts: sodium carbonate, sodium sulfide and sodium sulfate, along with carbon and bound hydrogen. Because the black liquor fired into the recovery furnace contains a large amount of recirculated sodium sulfate from the precipitator and dust hoppers, the sulfate content of the char will be high. A representative composition for kraft char before char burning reactions occur is

		moles/mole Na ₂	Wt. %
Sodium sulfide	Na ₂ S	1/6	9.0
Sodium sulfate	Na ₂ SO ₄	1/6	16.4
Sodium carbonate	Na ₂ CO ₃	2/3	49.0
Carbon	C	3	24.9
Bound hydrogen	H	1	0.7

From a chemical standpoint, carbon is the dominant species in the char. Carbon is the excess reactant. There is more than enough carbon present to reduce all of the sulfate to sulfide. Conversely, there is not enough oxygen present in the sulfate to burn off the carbon. Most of the oxygen needed to burn off the carbon in the char must come from combustion air. Hydrogen is a minor species and can be ignored for most purposes.

The most significant parameter governing the stoichiometric air requirement for char is the relative proportion of carbon monoxide (CO) and carbon dioxide (CO₂) in the product gas. About twice as much air is needed if the

char carbon is burned to CO_2 rather than CO . The char burning air requirement is about 25 to 45% of the air required for burning all of the black liquor, depending on the CO/CO_2 split. Very limited data on the gas composition just above the bed in a recovery furnace gives $\text{CO}/\text{CO}_2 \approx 1/2$. This would correspond to a char air requirement of about 40% of the theoretical air required by the liquor solids.

Char burning is an exothermic (heat releasing) reaction. The heating value of char in a bomb calorimeter is about 4500 Btu/lb char. The effective heating value of char in the furnace will be significantly lower than this because of the net reduction of sulfate that occurs and because some CO will be formed. Heating values under various conditions for the representative kraft char are:

Bomb calorimeter (fully oxidized products):	4380 Btu/lb
Smelt fully reduced, all CO_2 :	3430 Btu/lb
Smelt fully reduced, all CO :	910 Btu/lb

Char Burning

Kraft char burns via a sulfate/sulfide cycle. The carbon in the char reacts with sulfate, reducing it to sulfide and forming CO_2 and CO . The sulfide in turn reacts with oxygen from the combustion air, reforming sulfate and completing the cycle. The sulfate/sulfide cycle acts to carry oxygen to the carbon which is burnt off. The importance of the sulfate/sulfide cycle is that it permits simultaneous sulfate reduction and carbon burnup in the presence of an oxygen-containing atmosphere as long as the rate limiting step during char burning is oxygen mass transfer to the burning char.

Char burning via the sulfate/sulfide cycle can be treated quantitatively. Rate expressions for the carbon-sulfate reaction and for sulfide oxidation are sufficient to allow prediction of the remaining carbon content and the state of reduction of the sulfur compounds as burning proceeds. These rate expressions were developed in the course of this program. The rate of the carbon-sulfate reaction depends on temperature, carbon concentration, and sulfate concentration. The temperature dependence is quite strong, with the rate doubling for a temperature increase of about 120°F. The dependence on carbon content is linear (first-order). The sulfate dependence is such that the rate is independent of sulfate until very low sulfate concentrations (equivalent to reduction efficiencies >95%) are reached. At low sulfate concentrations, the rate gradually becomes first-order in sulfate. The rate of sulfide oxidation is inherently a very rapid reaction and proceeds at the rate of oxygen supply until the sulfide is depleted. Thus the oxidation rate is normally controlled by the rate of oxygen mass transfer to the burning char. This is controlled mainly by factors external to the burning char.

If the rate of the carbon-sulfate reaction exceeds the rate of oxygen supply (for sulfide reoxidation), the reduction state of the sulfur compounds will increase and approach 100%. It will remain at this level until the gradual depletion of carbon slows down the carbon-sulfate reaction to the point that it is exceeded by the rate of oxygen supply. At that point net reoxidation of sulfide begins. Because the carbon-sulfate reaction rate is first order in carbon, a point will always be reached where carbon depletion causes the rate to be lower than any given oxygen supply rate. Net sulfide reoxidation can only be avoided by removing the inorganic smelt from the oxygen environment before all carbon is depleted. On the other hand, because of the temperature dependence of

the reaction rate, a temperature can always be found such that the rate of the carbon-sulfate reaction exceeds any given oxygen supply rate at any arbitrary carbon content. The desired goals of a high char burning rate and a high net degree of reduction are obtained by maintaining high oxygen transfer rates at sufficiently high burning temperatures, and by avoiding contact between air and carbon-depleted smelt.

Experimental burns of char particles suspended in air confirmed the predictions of the theory of the sulfate/sulfide cycle. The mass loss vs. time curves gave evidence of a mass transfer controlled burning rate with extensive sulfide reoxidation at the end of the burn. There was clear evidence that the sulfur was highly reduced during most of the burning even though the surrounding gas was highly oxidizing. The heat of reaction was sufficient to bring the burning temperature up to levels where the carbon-sulfate reaction was fast enough to maintain high reduction efficiencies. Total char burn times for kraft char in air were on the order of 10 to 20 seconds.

Fume Formation

Fume particles are produced in large quantities when sulfide is oxidized to sulfate in molten carbonate. These fume particles consist mainly of sodium carbonate. Fume production under these conditions was not expected. This new fuming process is called oxidative fuming. It appears to be a much more important source of fume, in kraft systems, than the generally recognized processes of sodium vaporization or sodium hydroxide vaporization.

The main source of fume during char burning is oxidative fume associated with the oxidation of sulfide to sulfate in the sulfate/sulfide cycle. Particulate can also be produced by the ejection of tiny smelt droplets during high intensity burning.

The chemistry of oxidative fuming is not well understood. Several possible explanations are under consideration. The lack of a basic understanding of the cause of oxidative fuming leads to some uncertainty in extrapolating the results of experiments to new conditions (e.g., inside the furnace). Nevertheless, all signs indicate oxidative fuming is very important in the furnace.

Reductive fuming is a term for fume caused by the production of metallic sodium and its subsequent vaporization. High partial pressures of sodium vapor are only obtained under very strong reducing conditions and high temperatures. The sodium producing reaction is endothermic and requires an external source of heat. Reductive fuming is suppressed when sulfate or CO_2 are present. It is unlikely that reductive fuming, per se, is very important in a kraft recovery furnace.

Addition of sizable quantities of sodium hydroxide to melts never gave an increase in fume production. Sodium hydroxide vapor is not likely to be a significant source of fume in kraft recovery operations.

IMPLICATIONS

One of the main goals of the study was to use the understanding gained to analyze recovery furnace operation and identify means for improving performance. The results obtained have several implications on furnace operation.

Bed Burning

Char burning is an exothermic reaction involving a sizable fraction (40-50%) of the heating value of the original black liquor solids. Our work indicates that a good deal of burning can, and should, take place on the surface of the char bed. Combustion air impinging on the bed and burning char does not

jeopardize reduction efficiency. A reducing gas atmosphere in the lower furnace is not essential for reduction. The capability to handle a greater fraction of the burning load on the char bed allows the use of coarser sprays with a concomitant decrease in entrainment.

There are two basic requirements for increasing the burning rate on the char bed:

1. The required amount of air to satisfy the stoichiometric needs of the bed material must be supplied under conditions that sufficiently high mass transfer rates are attained.
2. The reacting zone on the bed surface must be kept at a sufficiently high temperature. Air-bed contact must be maintained over the entire bed surface in proportion to the amount of fuel landing on any particular area of the bed. Bed temperatures are increased by increasing the fuel value of the material landing on the bed, increasing burning rates, and by keeping all heat sinks (e.g., wet liquor) away from the bed.

Measured burning rates of kraft char were much higher than those corresponding to typical design hearth loadings. This indicates there is a large potential to increase bed burning rates and, ultimately, total liquor solids throughput.

Reduction

High reduction efficiencies should be relatively easy to obtain. Reduction rates depend on the temperature and carbon content of the char. Reduction is a relatively rapid reaction. Given enough carbon, reduction can be completed with a residence time of a few minutes at 1700°F and within a few

seconds at 2100 to 2200°F. Reduction rates can always be increased by increasing temperature. If low reduction efficiencies are caused by low reduction rates, the cure is to increase the bed surface temperature. This can be achieved most readily by increasing the air supply to the bed to increase the bed burning rates.

Low reduction efficiencies in the furnace can also be caused by sulfide reoxidation before the smelt runs out of the furnace. The bed plays a protective role here, by providing a path for molten reduced smelt to move out of the active surface layer and away from the combustion air. A properly sized and shaped char bed can shield the smelt from the primary air. Anytime combustion air comes in direct contact with molten smelt, some reduction efficiency is being lost.

The smelt discharge temperature is not an effective measure of proper temperature levels for reduction. Reoxidation of smelt is exothermic and will raise the temperature of the smelt. Thus a process that causes a loss in reduction efficiency can also increase the smelt discharge temperature. (A small amount of reoxidation close to the spouts may sometimes be beneficial in raising smelt temperature and improving flow out the spouts). The critical temperature for effective reduction is the bed surface temperature.

Fume Control

Fuming has both detrimental and beneficial effects inside the furnace. Fuming contributes to particulate loads and thus influences sootblowing requirements and possible boiler fouling and plugging. Fume is also a sulfur scavenger and helps to reduce SO_2 and (SO_3) concentrations in the flue gases and helps alleviate sticky ash problems. Whether or not fuming rates should be increased or decreased is dependent on the given situation.

Because the fuming process is not completely understood, there is some uncertainty of interpreting what causes fuming in the furnace. The oxidative fuming phenomenon is real. Oxidative fume was observed during char burning, and the fuming rate was related to burning intensity. Thus we would expect that the main sources of fume are local areas of intense burning (hot spots). Smelt reoxidation would also lead to fume production. Fuming rates would be higher with higher bed surface temperatures. A high temperature reducing condition would not be needed.

Bed Temperature

The most important parameter for optimizing the processes occurring in the lower furnace is bed temperature. More specifically, it is the temperature in the thin, air-accessible, surface layer of the bed. Higher temperatures increase the potential burning rate and provide for better reduction efficiencies. Higher burning rates on the bed increase the tolerance for handling coarse sprays, which should lead to less entrainment. The only apparent detrimental effect of excessive bed temperature is increased fume production. This may not be a severe limit.

Bed temperature is determined by heat balance considerations involving coupling between the burning rate, the heat of reaction and radiation to and from the bed. Radiation to the waterwalls will tend to cool the bed surface, especially along the sides of the bed. Hotter bed surface temperatures could be sustained if the same burning rate were achieved on the part of the bed near the center of the furnace.

Air/Fuel Distribution

If the bed surface temperature is kept hot enough (we believe it should be at least 2000 to 2100°F), the chemical recovery functions in the furnace tend

to take care of themselves. No other special actions need to be taken to achieve acceptable reduction, sulfur scavenging and low residual carbon in smelt. The main additional requirement is to introduce the black liquor in such a way that all of the sodium salts end up on the hearth (minimum entrainment).

With the chemical functions thus self-established, the combustion process can be treated in essentially the same manner as it is for any other fuel. Each element of black liquor fuel has a requirement for a certain amount of air. The essence of good combustion control is to introduce the fuel (black liquor) and air into the furnace in such a manner that the air reaching a given location is proportional to the stoichiometric demand of the fuel at that location. This implies that the black liquor spray system and the air supply system should be coupled. The distribution of air to the bed must match the distribution of char landing on the bed. If most of the char is landing close to the walls, most of the air is needed near the walls. If the char is spread uniformly over the bed surface, the combustion air to the lower furnace should also be distributed evenly over the bed. Changes in liquor spray patterns without a parallel adjustment in air distribution will always result in less than optimum performance.

BACKGROUND

OVERVIEW OF BLACK LIQUOR BURNING

Recovery Boiler

The recovery boiler is the heart of the kraft chemical recovery system. It plays a dual role in the process, serving as both a chemical reactor and as a steam and power generator. Burning of black liquor within the recovery boiler causes separation of the inorganic pulping chemicals from the organic wood substances which are dissolved during pulping. The inorganic chemicals are converted to sodium carbonate and sodium sulfide, which can be subsequently causticized and returned to the digester for reuse as pulping chemicals. The organic substances in the black liquor are destroyed within the recovery furnace and their fuel value is recovered in the form of process steam and cogenerated electrical power.

The recovery boiler has undergone considerable evolution since the first Tomlinson-type unit was installed during the 1930's. Recovery boilers are designed basically as steam generators, and the development has been guided by concepts derived from coal-fired power boilers. Solutions to problems stemming from the unique characteristics of black liquor as a fuel have been based on considerable experience, much of it hard won. The modern recovery boiler that has resulted from this evolutionary process is an impressive piece of equipment. It does a more than adequate job of fulfilling its dual role of chemical recovery and steam and power production. The successful performance of these tasks, more than any other single factor, has led to the present dominance of the kraft pulping process.

Despite its successful process role, the modern recovery boiler still has some serious deficiencies. It is a very costly piece of equipment. There is much more heat transfer surface in a recovery boiler than in a fossil-fuel fired boiler of comparable steaming rate. It has been stated that there are more pounds of steel per pound of steam in a recovery boiler than in any other type of steam generator. Economies of scale favor the use of large, high-capacity units rather than a number of smaller units. This makes the entire process vulnerable to recovery boiler outages. Steam generation efficiencies are significantly lower than in power boilers, although this is a little bit misleading. Substantial improvements in steam efficiency are possible by firing liquor at higher solids content, by insuring complete combustion, and by minimizing steam usage within the recovery unit. The recovery boiler is a relatively vulnerable piece of process equipment. It is not only subject to the same risks as a power boiler, but also to the possibility of smelt/water explosions. A recent insurance analysis (1) indicated that over 50% of the monetary loss experience over the entire pulp and paper industry was associated with the recovery boiler. The recovery boiler is also a potential source of odorous gas emissions or particulate emissions and has come under rather stringent limits on these emissions in recent years. All of these deficiencies are related to the peculiar characteristics of black liquor as a fuel and the dual role of the recovery boiler in the kraft process.

Burning Process

There are two characteristics of black liquor that strongly influence its burning performance.

1. Black liquor is fired as an aqueous liquid at a solids content of about 65%. Thus a substantial amount of liquid

water (about 1/2 lb per lb of solids) is introduced into the combustion zone.

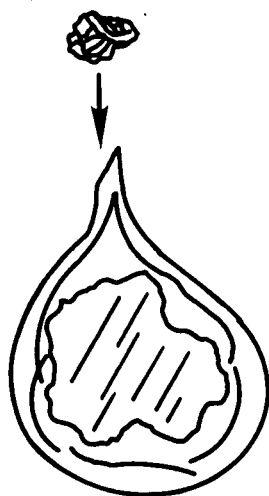
2. Black liquor solids contain 40 to 50% "ash." The "ash" is the inorganic coming from the spent pulping chemicals. Furthermore, these inorganic salts have relatively low melting points. This makes recovery boilers very susceptible to slagging and fouling.

Burning of a black liquor drop in air occurs in three distinct stages: drying, volatiles burning, and char burning (2). Although there is some overlap, these stages tend to occur sequentially. They are described in Fig. 2-1.

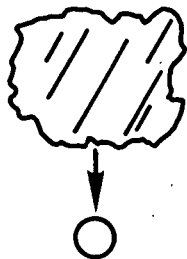
The drying process is straightforward. Volatiles burning consists of two distinct processes: pyrolysis and gaseous combustion. Pyrolysis is the thermal breakdown of the black liquor solids to yield combustible gases and a "solid" residual char. When a drop burns in air, pyrolysis and gaseous combustion occur simultaneously, and a visible flame surrounds the drop. However, if the drop is heated in the absence of oxygen, pyrolysis will still occur without combustion of the gases. Gaseous combustion may then occur at a point physically removed from the pyrolyzing drop. Pyrolysis is a major source of sulfur release to the furnace gases. Considerable swelling normally occurs during pyrolysis, resulting in a highly porous residual char particle. Char burning occurs as a heterogeneous reaction. There is no visible flame, but rather a glow at the reacting surface. The residual carbon burns away and the inorganic salts are reduced and smelted out. Char burning is also a source of volatile inorganics that lead to fume particles in the flue gas. Char burning does

Drying

Water in black liquor is evaporated
 Major heat sink - keeps temperatures down
 Rate governed by heat transfer
 Little volume expansion occurs
 Normally a relatively slow process

Volatiles Burning

Two processes - pyrolysis and gaseous combustion
 Pyrolysis yields combustible gases and residual char
 Gases burn when contacted by air
 Visible flame surrounds drop
 Considerable volume expansion occurs (swelling)
 Source of sulfur gases, H_2S and SO_2
 Rate governed by temperature
 Normally a relatively fast process

Char Burning

Burning occurs on particle - no flame
 Residual carbon is burned out
 Inorganics melt
 Sulfur compounds are reduced to sulfide
 Source of volatile inorganics (fuming)
 Rate governed by temperature and air supply
 Normally a relatively slow process

Figure 2-1. Black liquor burning stages.

not begin until volatile production ceases, permitting oxygen to reach the char particle.

Burning times are very strongly influenced by the size of the liquor drop. For drops of the size range encountered in the furnace, and for burning in air, burn times are about 5 to 10 sec. Drying and char burning stages tend to be the slowest (2).

Burning in Furnace

The burning process in the recovery furnace is much more complex because of the need to consider the spacial relationships between the burning liquor and the air supply, and their relation to the furnace structure. The goal is to have the inorganics go to the furnace hearth, where they are smelted out and removed, while the combustion gases move up in the furnace, through the heat traps and out the stack.

Liquor is sprayed into the furnace some 10 to 20 ft above the hearth, and falls by gravity to the hearth as it dries, pyrolyzes, and burns. The combustion air supply is split; part of it is introduced in the hearth zone below the liquor guns, with the remainder entering above the guns.

Part of the burning liquor is swept up by the combustion gases and entrained. Entrainment can occur at any stage in the burning process, and the burning process continues as the entrained particle moves with the gases. Entrainment results in part of the combustion load being carried to the upper furnace and causes inorganic salts, often in a molten state, to be carried into the heat traps, where they can foul the heat transfer surface. Entrainment is detrimental to optimum performance.

The unentrained liquor begins going through the burning stages as it falls to the hearth. The material reaching the hearth forms a char bed, where the burning process is completed. It is generally believed that the drying step should be completed before the liquor reaches the bed. It has not been conclusively established how much volatile burning and char burning occurs in flight and how much on the bed.

Significant amounts of sulfur gases are released in the furnace during volatile burning as H_2S and SO_2 . These contribute to air emissions unless oxidized completely to SO_2 and reacted with sodium compounds to form Na_2SO_4 . The sodium compounds that react with the sulfur are fume particles coming from volatile sodium compounds generated during char burning. The resulting Na_2SO_4 is recovered as dust from the ash hoppers and electrostatic precipitator and recycled to the black liquor coming to the furnace. This results in a large recirculating inorganic load around the recovery boiler.

Flow Paths in Recovery Boilers

Black liquor is made up of five major elements: sodium, sulfur, carbon, hydrogen, and oxygen. Combustion air contains nitrogen, oxygen, and a small amount of water vapor. The flow paths taken by sodium, sulfur, and carbon are shown in Fig. 2-2, 2-3, and 2-4, respectively.

Sodium enters the upper furnace from two sources: carryover of entrained droplets of black liquor which burn in suspension, and fume produced by volatilization processes. The sodium compounds in the upper furnace are responsible for dusting and slagging problems. The great bulk of these sodium compounds is recovered in the dust hoppers and precipitator and returned to the black liquor. This uncontrolled recirculating particulate load can be responsible for changes in as-fired liquor properties and heating values.

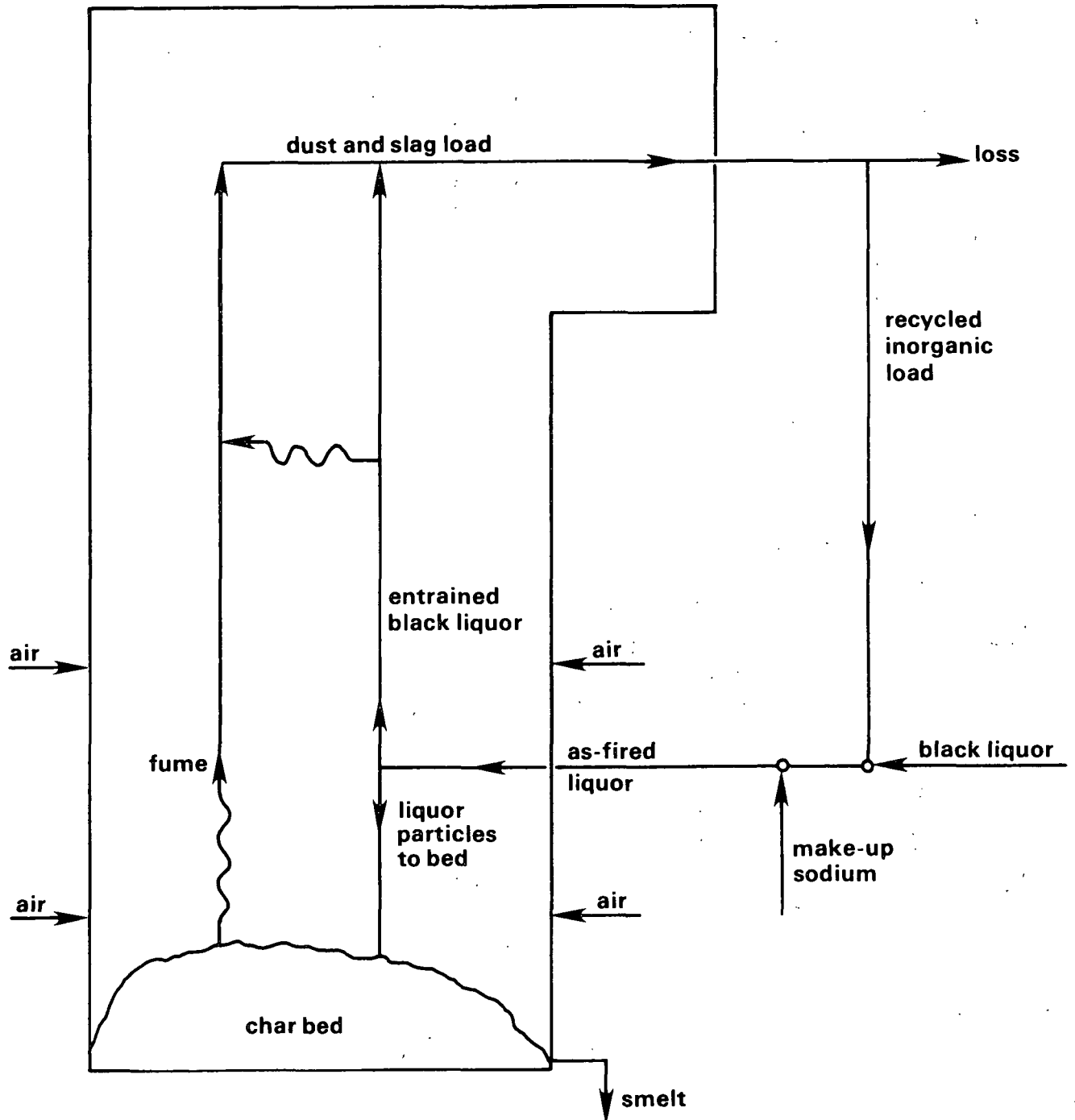


Figure 2-2. Sodium flow paths.

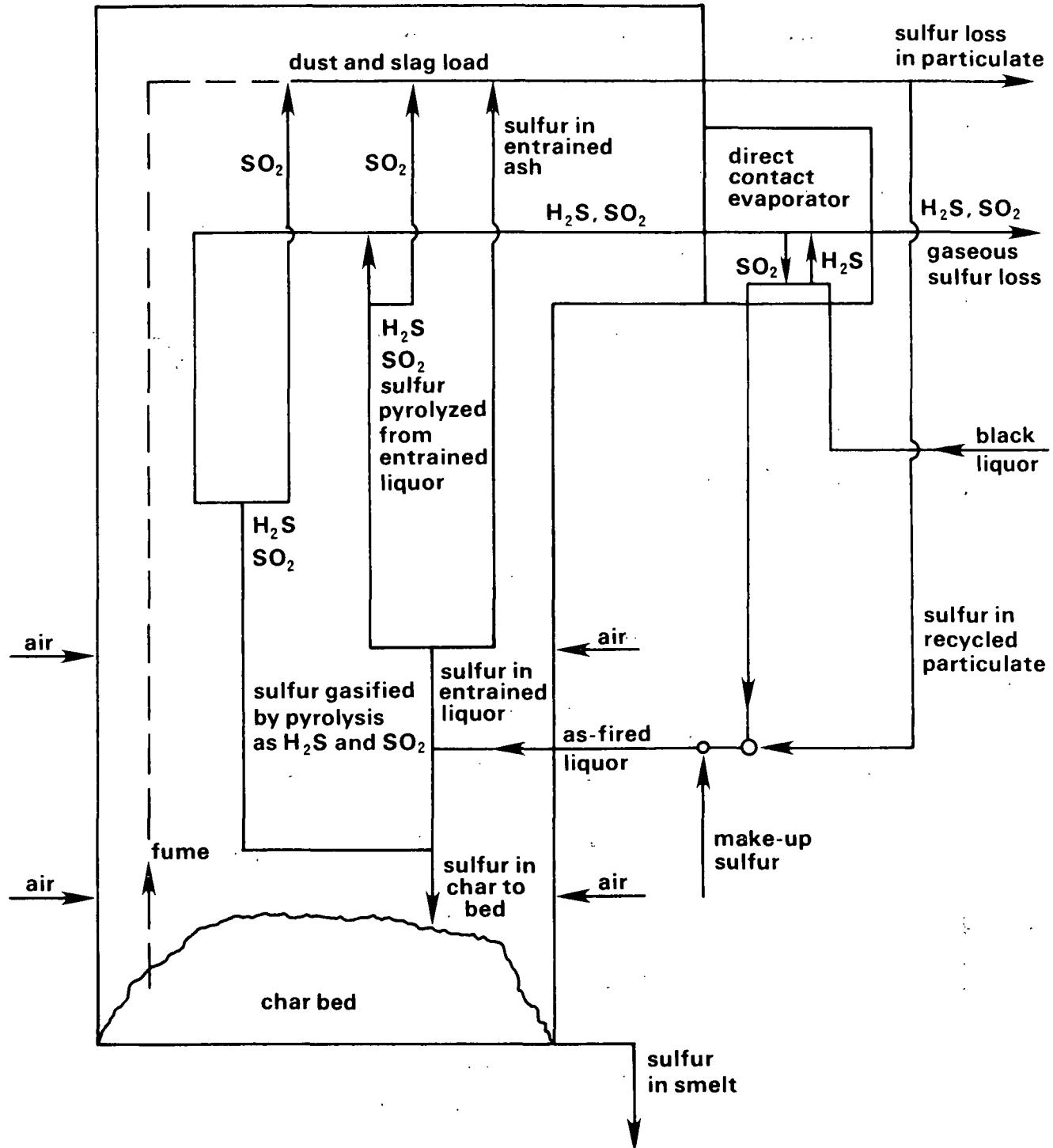


Figure 2-3. Sulfur flow paths.

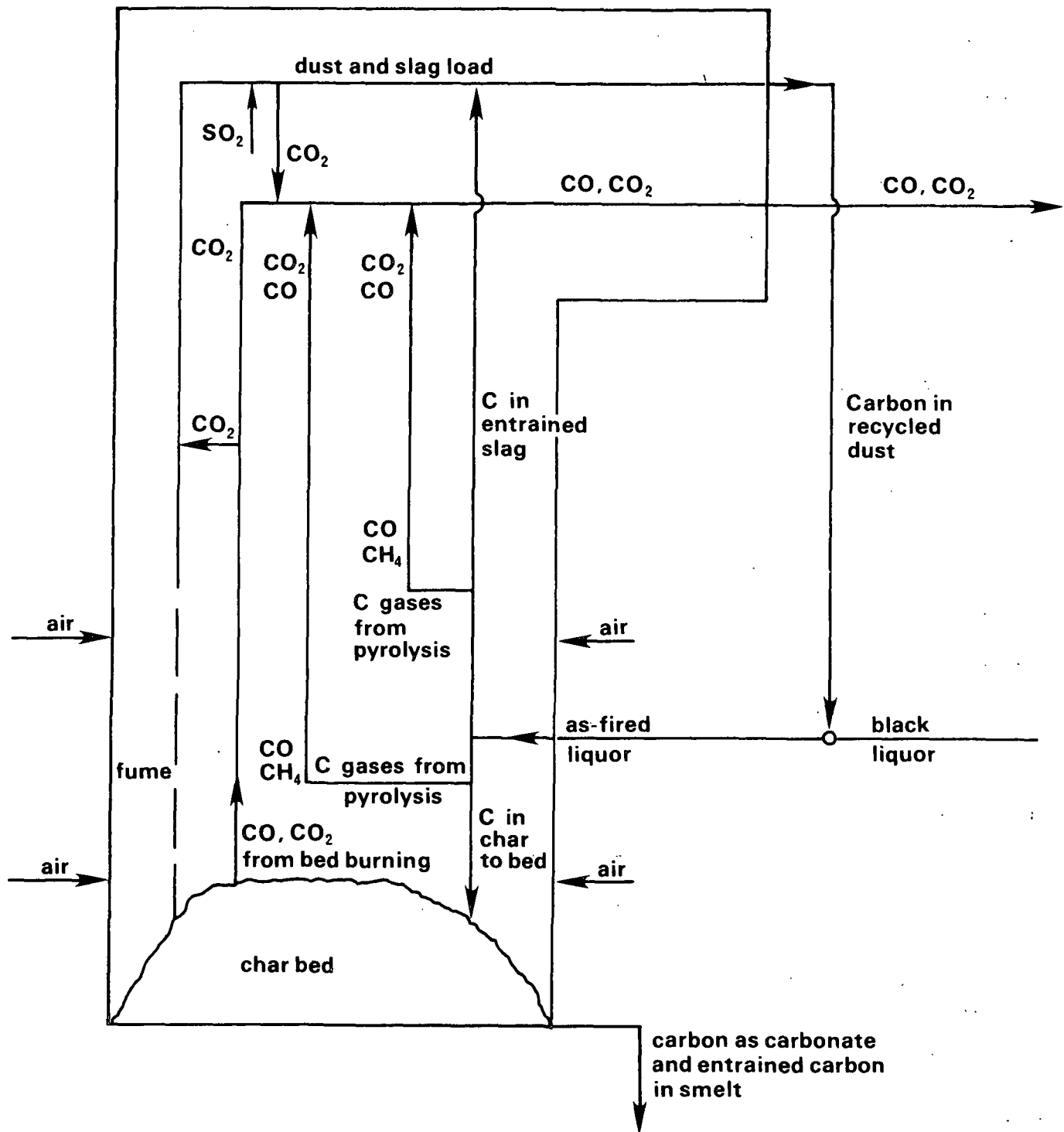


Figure 2-4. Carbon flow paths.

Sulfur flows are more complex. Sulfur can be gasified as H_2S and SO_2 by pyrolysis. This sulfur is freed from sodium and goes with the combustion gases. It is gradually oxidized to SO_2 , depending on the sufficiency of air addition. Sulfur is lost out of the stack unless it reacts with sodium fume components or is absorbed in black liquor in a direct contact evaporator. Only the sulfur that is present in the char reaching the char bed is able to leave with the smelt. The sulfur present in the entrained black liquor solids is only able to end up in the smelt if it is returned to the bed by recycle loops. Some of this entrained sulfur will be pyrolyzed in the upper furnace, and some will simply remain with the slag.

Carbon flows are also fairly complex. Of the carbon entering in the black liquor, a small amount leaves as carbonate and entrained carbon in the smelt. The great bulk leaves as CO_2 and unburned combustible. A certain amount of carbon must be present in the char reaching the bed - to supply the carbon needed for sulfate reduction and that needed to be burned to maintain bed temperatures. Most of this leaves the bed as CO_2 and combustible gases. A significant amount of carbon is gasified to combustibles by pyrolysis, and this is gradually oxidized to CO_2 as the gases move upward in the furnace. Part of the carbon in the entrained black liquor drops is pyrolyzed and gasified in the upper furnace and burned to CO_2 . Some remains with the entrained slag. There is relatively little interchange between CO_2 and sodium salts in the upper furnace. There is some tendency for SO_2 to replace CO_2 and convert Na_2CO_3 to Na_2SO_4 .

Hydrogen in the black liquor solids tends to follow a path similar to that of carbon, except that the amount of hydrogen tied up with sodium salts leaving the unit is negligible. Some hydrogen-containing combustibles reach the

bed and burn there as part of the char, and many hydrogen compounds are released by pyrolysis and burn to H_2O in the gas phase. The hydrogen in the water in the black liquor remains as water and enters the combustion gas as vapor as the black liquor dries.

Some oxygen enters with the black liquor solids, but the bulk enters with air. Ignoring the oxygen in the water in the black liquor, which tends to remain as water throughout the process, the ratio of oxygen in air to oxygen in black liquor is about 3.5 to 1. Oxygen tends to react with and increase the oxidation state of the combustion gases as it enters and moves through the furnace.

NEED FOR KNOWLEDGE OF CHAR BURNING

Importance

Although char burning is only one stage in black liquor combustion, it is very important.

1. Char burning tends to be one of the slowest steps in black liquor burning and may control the overall burning rate.
2. The final melting and separation of the inorganics occurs during char burning.
3. The oxidation state of the sulfur in the smelt (reduction efficiency) is determined during char burning.
4. Char burning is a source of volatile inorganic compounds which lead to fume formation.
5. Char burning conditions may determine the amount of unburned carbon present in the smelt.

Within the furnace, char burning occurs predominately in the char bed on the hearth. Bed processes and their control are very important to furnace operation. Blackouts, bed stability, unstable smelt discharge, low reduction efficiency, too much or too little fume production, high unburned carbon loss, and sometimes boiler fouling and plugging problems are all associated with bed burning behavior. Modern recovery boiler control strategies emphasize maximizing burning in the lower furnace. This requires intensive bed burning and increases the importance of understanding bed processes.

Char burning and bed burning are not identical. Char burning is the last stage in the black liquor burning process. It does occur on the bed, but may also occur as the liquor particle falls to the bed or is swept upward with the combustion gases. Bed burning, on the other hand, includes all processes occurring in and on the bed in the furnace. It includes char burning, but may also involve volatile burning and sometimes drying. The bed can be considered as an assemblage of particles, arriving at various degrees of completion of the burning process, and continuing to react (burn) on the bed. Nevertheless, bed burning is primarily char burning, and knowledge of char burning is directly applicable to interpreting bed behavior.

Needs

There is a general lack of knowledge about the basic processes which underlie char burning. Present operation is an art based on empiricism, fossil fuel burning experience, and limited chemical equilibrium analyses. Very little is known about rate processes in recovery boilers. The unit can be thought of as a large chemical reactor designed and operated without any data on reaction kinetics.

Among the questions for which answers are needed are the following:

1. How does the reduction of sulfur compounds to sulfide occur?
What are the important variables? What length of time is needed for reduction? Is a reducing atmosphere needed? How strong?
2. What causes fuming? What are the volatiles? How important is temperature in fuming? Are there any other important variables? Is fuming an equilibrium process?
3. What are the main variables that govern burning rates? Are there any intrinsic limits to faster burning rates? Can high burning rates be maintained without going to small drops? Is it possible to burn most of the organic on the bed at high loadings?
4. What are the critical factors that lead to blackout? What are the warning signs of incipient blackout?
5. What are the critical parameters to measure in a char bed?
6. What governs the amount of residual carbon in the smelt?
Is it possible to maintain very high reduction efficiencies and negligible carbon in the smelt?

Benefits

Although char burning is only a part of the complex process of black liquor combustion, knowledge of char burning is valuable in itself and not dependent on the ultimate understanding of the whole process. The benefits of work on char burning can be reaped while work on other aspects goes on.

Knowledge of char burning will provide a basis for informed decisions on how to meet recovery boiler operating objectives such as improved reduction, optimum fuming, bed control, and blackout prevention. Perhaps the greatest

potential benefit would be the ability to achieve enhanced burning rates of large drops or particles of liquor, which would allow increased hearth loadings with minimum carryover. This could result in significant capacity improvement.

PREVIOUS WORK LEADING TO THE PROJECT

This work was an outgrowth of three separate efforts.

1. Work on sulfate reduction kinetics at The Institute of Paper Chemistry (IPC)
2. API supported work at Arthur D. Little (ADL) which culminated in a recovery boiler model called Kraft 2.0
3. API effort to see if the Kraft 2.0 model provided a basis for an improved computer-based control system for a recovery boiler

The time scale of this previous work is detailed in Table 2-1.

Table 2-1. Project background.

API Studies

1976	ADL, Phase I - Char Bed Cooling
1977-79	ADL, Phase II - Char Bed Behavior (Kraft 1.0 - August, 1979)
1980	ADL, Cont. - Gun to Bed Processes (Kraft 2.0 - December, 1980)
1981	Recovery Boiler Control Project Feasibility

IPC Studies

1978-81	Sulfate Reduction Kinetics (Molten Salt Experimental Capability)
1981	Participant in Controls Project

Work at IPC

Work at IPC on the rates of key furnace reactions began in 1978 as part of our Dues Funded Research Program. The initial effort was directed at the rate of sulfate reduction by solid carbon in molten carbonate. By the end of 1981 we had developed experimental techniques for working with melts at high temperatures and obtaining quantitative rate data. A rate equation for sulfate reduction by carbon was developed that quantitatively described major variables, and a plausible reaction mechanism was proposed. This work is described in Ref. (3-5).

As a result of this early work we developed a versatile experimental system for studying rates of high temperature reactions which occur in char beds. The liquid and solid compounds were contained in a nonreactive ceramic vessel which was maintained at a controlled temperature. A sweep gas (either reactive or inert) passed through the reaction vessel at a measured rate, and the reaction products were monitored to follow the rate of reaction. The vessel was heated continuously by an induction coil. Techniques for extracting signals (such as thermocouple output) from within the induction field were developed. At that time carbon monoxide and carbon dioxide concentrations were measured. Subsequently sensors for oxygen, water vapor, and sodium fume were added.

Work at ADL

The Phase I ADL study was concerned with cooling of char beds following an emergency shutdown. Measurements were made of bed temperature profiles and thermal properties. A bed heat transfer model was developed and used to predict cooldown times. It was concluded that large beds could take as long as a week to cool down and that there was no safe way to accelerate the cooling process.

It was suggested that the only way to significantly shorten the cooldown time was to operate with small beds.

The Phase II study was aimed at finding out how to operate furnaces (especially B&W furnaces) with low beds without serious deterioration in performance. As part of this study a mathematical model of the furnace and char bed was developed (Kraft 1.0). This was basically a zonal equilibrium model with the exception that sulfate reduction was treated kinetically in the bed. The composition of the material landing on the bed and the extent of gas release in different zones was arbitrarily specified.

In order to relate furnace and bed behavior to externally controllable parameters, the study was extended to model gun to bed processes. This resulted in the Kraft 2.0 model which was documented and made available to the industry in December, 1980.

A number of concepts are embedded in the ADL model or tend to come out of its use.

1. There is little transfer of oxygen from combustion air to the bed.
2. Only a small amount of combustible can be allowed to reach the bed or the bed will grow. This is because there is insufficient oxygen in the bed to consume the carbon.
3. Extensive pyrolysis and gasification of liquor solids must occur before char lands on the bed. This follows directly from 2.
4. Bed processes are endothermic (heat absorbing). Heat flow is to the bed from the fireball above.

5. There is limited capacity for reduction in the bed. If there is not substantial reduction of sulfur before the char lands on the bed, reduction efficiencies will be low.
6. Fuming occurs by sodium evolution. This is treated as an endothermic equilibrium process and the effect is to thermostat the bed to a relatively low temperature.

These concepts, if valid, would have serious implications on how to run a boiler. However, they are not experimentally based but rather a product of assumptions made in developing the model. As will become evident in this report, the results of the char burning study suggest a very different version of what goes on in the furnace.

Control Project

In 1981, the Recovery Boiler Committee evaluated whether or not the ADL model (Kraft 2.0) provided a basis for a computer-based process control system for a kraft recovery boiler which would result in a major improvement in recovery boiler safety and economic performance. It was concluded that it did not. At the level of detail at which the ADL model was formulated, too much information was lacking which is critical to the model's formulation. The model and its evaluation did serve to identify in detail the critical knowledge and data which were lacking. Ten areas were identified (6).

1. Physical properties of black liquor
2. Predictors of droplet size and distribution
3. Mode of droplet drying and descriptors
4. Chemistry and kinetics of droplet pyrolysis and gasification
5. Chemistry and kinetics of bed reduction and combustion

6. Chemistry and kinetics of fume formation
7. Mechanics of smelt transport in the bed
8. Capability to describe bed movements, composition, and structure
9. Capability to describe gas motion and composition just above the bed
10. Capability to describe multiphase flow in the furnace cavity.

It was felt by the Recovery Boiler Committee that if this information were available, a significant improvement in the safe and efficient operation of a recovery boiler could be achieved. It was realized, however, that to achieve these results would require a substantial investment in research and a time span of probably five years or more.

Approach to the Problem

It was recognized that the entire effort was beyond the capability of the Recovery Boiler Committee, but that the Committee could serve as a catalyst in achieving this goal. The char burning project, which took advantage of existing capability and ongoing work at IPC, specifically addressed Items 5 and 6. This work could be initiated immediately in 1982 while the rest of the package was being put together.

At the present time eight of the areas of needed information are being addressed in a cooperative effort at the University of Maine, The Institute of Paper Chemistry, and the National Bureau of Standards. Altogether, this represents a five year research effort and a total investment of over \$4,000,000. Primary support for this program is from the U.S. Department of Energy. Support is also provided by six private companies that are contributing to the University of Maine "Black Liquor Characterization" study, by the API Recovery Boiler Committee, and by the IPC Funded Research Program. Table 2-2 indicates where each of the eight areas is being researched.

Table 2-2. Location of research areas.

• Physical properties of black liquor	University of Maine
• Predictors of droplet size and distribution	University of Maine
• Mode of droplet drying and predictors	IPC
• Chemistry and kinetics of droplet pyrolysis and gasification	IPC + NBS
• Chemistry and kinetics of bed reduction and combustion	IPC
• Chemistry and kinetics of fume formation	IPC
• Mechanics of smelt transport in bed	IPC
• Capability to described bed movements, composition, and structure	IPC (partially)
• Capability to describe gas motion and composition just above bed	
• Capability to describe multiphase flow in the furnace cavity	

OBJECTIVES

The overall goal of the char burning study is a quantitative theory of the char burning process that can be used to analyze recovery furnace operation and identify changes that could improve performance.

The project was a study of the rates of carbon burnup and simultaneous sulfide formation and fume generation in smelt-char systems similar to char beds in recovery boilers. The complex rate processes in char burning were interpreted by synthesizing rate data from more fundamental process steps obtained in simpler, more idealized systems. The approach which was taken was to obtain experimental data on the individual bed processes under controlled laboratory conditions, use this fundamental information to interpret experimental data on

char burning under controlled laboratory conditions, and finally to translate these results to char beds.

Specific objectives of the study are to

1. Obtain fundamental data on the chemistry of the reduction of sulfate to sulfide and develop quantitative rate equations that include all important variables
2. Obtain fundamental data and rate equations for oxidation processes in molten carbonate systems
3. Obtain fundamental data on the chemistry of fume forming processes and develop appropriate rate equations
4. Obtain experimental data on the combustion of char under controlled conditions and interpret the behavior in terms of the underlying fundamental processes
5. Examine the implications of the results of the work on furnace operations

The study was limited in scope and was concerned solely with the behavior of char after it is formed. The relationship between pyrolysis conditions and char composition and properties was beyond the scope of this project. This matter is, of course, being addressed as part of the overall research effort on black liquor combustion.

PROGRAM STRUCTURE

Support and Oversight

The char burning project was jointly supported by the API Recovery Boiler Committee and the IPC Dues Funded Research Program. API support was

\$85,000 per year for the two-year duration of the program. IPC support was about \$170,000 per year.

Progress was reviewed twice a year by the IPC Program Advisory Committee for Pulping and Bleaching. Status reports were given at each meeting of the API Recovery Boiler R&D Subcommittee. At the conclusion a special task group of the R&D Subcommittee provided a peer review of the technical content of the work and a critique of the draft report. This task group consisted of

D. R. Raymond - Union Camp - Chairman

P. E. Shick - Consultant

R. E. Harrison - Weyerhaeuser

D. A. Armstrong - Georgia Pacific

R. A. Thorman - International Paper

Original Plan

The original plan envisioned that all of the rate information needed could be obtained in the experimental system that had been developed for the sulfate reduction kinetic studies. It also assumed that the reduction process was pretty well understood and that relatively little work on reduction would be necessary in the char burning study. The original plan anticipated a need to continuously monitor the relative amounts of sulfate and sulfide as char burning occurred and proposed the development of an electrochemical probe to do this. The anticipated information flow is shown in Fig. 2-5, and the project task schedule in Fig. 2-6.

Revised Plan

As the work proceeded, it became obvious that the original work plan had to be revised. A summary of the major modifications and the reasons for

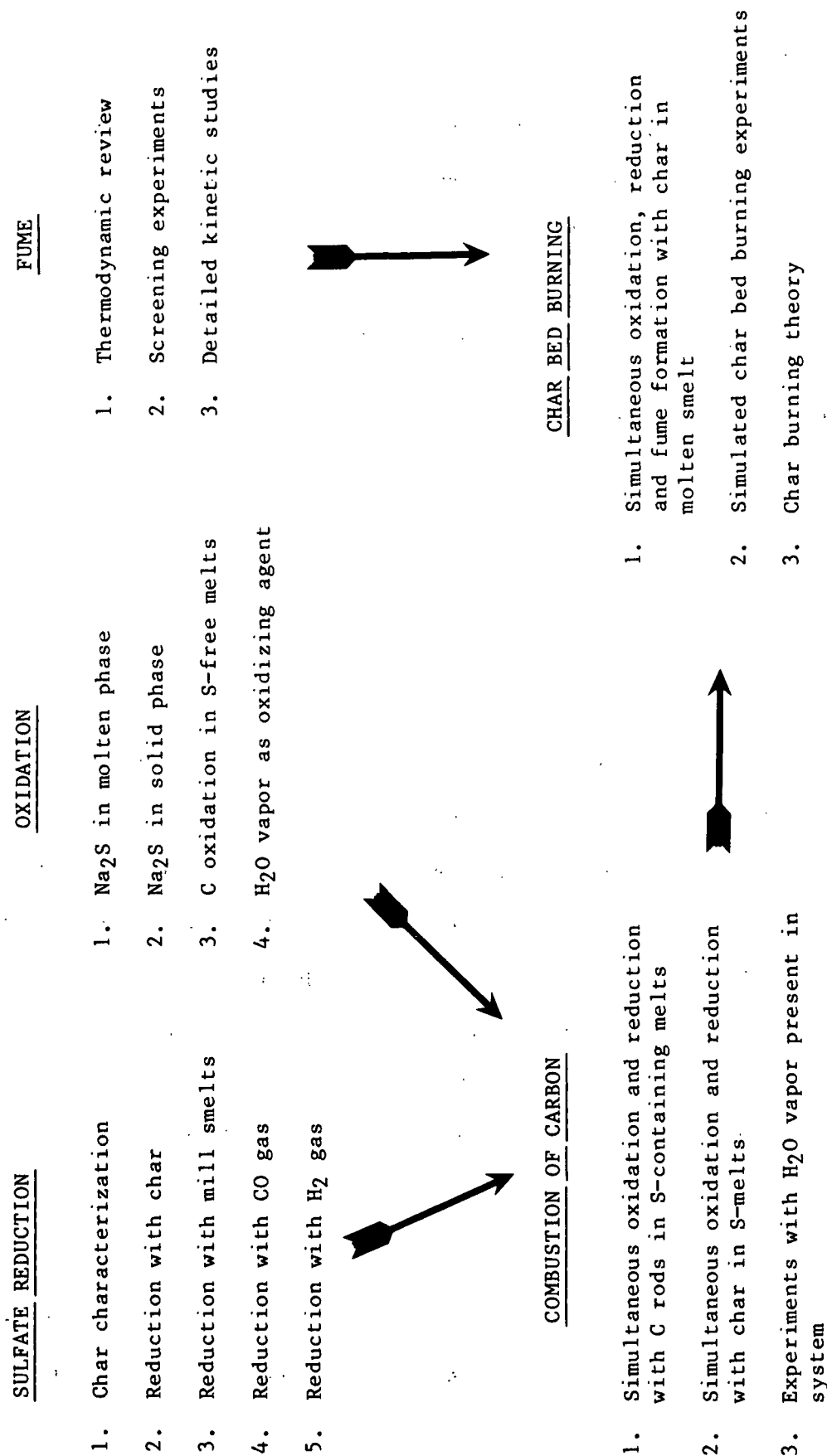


Figure 2-5. Information flow.

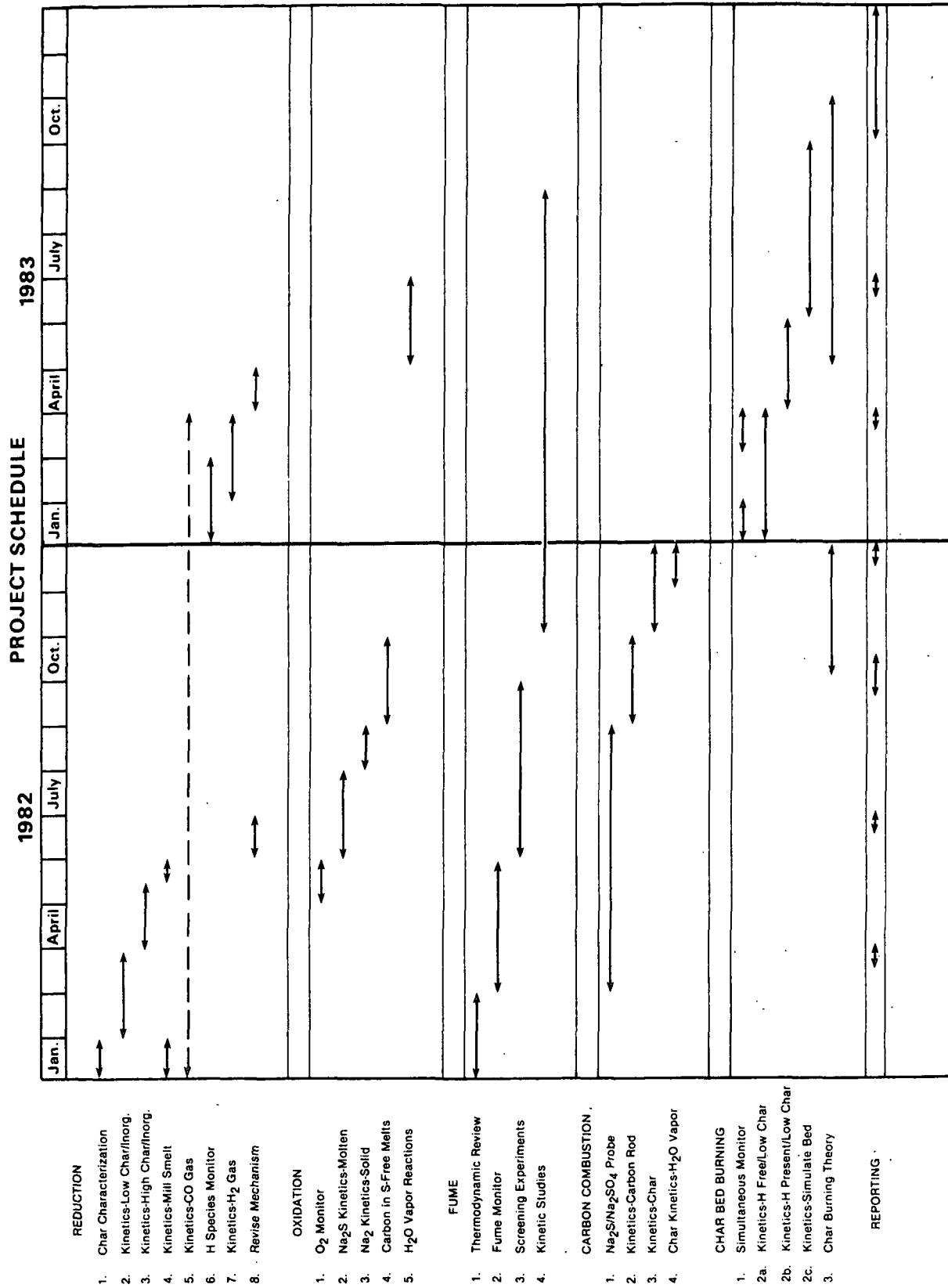


Figure 2-6. Original project task schedule.

them is given below. There were no modifications of overall goals, timetable, and budget.

1. The effort on sulfate reduction, specifically carbon-sulfate reactions, was greatly expanded over that envisioned at the start of the project. This was required when it was found that the kinetics of the char-carbon reaction with sulfate was considerably different from the carbon rod-sulfate behavior found previously. Clarification of this behavior became the number one priority because carbon-sulfate reactions underlie much of the char-burning process.
2. Quantitative oxidations in well-defined systems were delayed to allow greater emphasis on sulfate reduction.
3. The development of an electrochemical probe to follow the $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_4$ ratio was terminated based on an estimate of the difficulty of the task, a realization that the state of reduction of the reacting mass could be followed by oxygen and carbon material balances coupled with sudden quenching and analysis, and an appreciation that we needed a technique which would operate in the absence of a continuous smelt phase.
4. Fume experimentation and kinetic studies were delayed somewhat, due partly to the priority placed on reduction kinetics, but primarily to fuming being a more complex phenomenon than anticipated and not at all in accordance with prevailing theory and thermodynamic equilibrium predictions.
5. A single particle reactor to study char combustion quantitatively was designed, assembled, and used. This was not envisioned

in the original proposal. At that time we felt our molten salt reactor system would be adequate. The change to incorporate this additional experimental approach was made when it became apparent that we could not meet final project objectives without a means for studying char burning with real geometries and the char existing in a solidlike phase.

6. Hydrogen reactions were deemphasized because they did not appear to be of critical importance.

REPORTING

The work on this char burning project is reported as follows:

1. A very brief Executive Report aimed at CEO's. This describes what was done, cost, scope, and implications on operations.
2. A short Operators Report. This is relatively nontechnical and applications oriented. The objective is to communicate the results of the work to operators in a form which they can utilize.
3. A Main Technical Report (this report).
4. A series of IPC Progress Reports giving in-depth data on fundamental processes and the development of rate equations.

Progress Report One: Sulfate Reduction by Carbon (1981) (5)
 Progress Report Two: Sulfate Reduction by Carbon (1983) (19)
 Progress Report Three: Carbon Oxidation in Carbonate (1985) (24)
 Progress Report Four: Fume Formation (in preparation) (36)
 Progress Report Five: Char Particle Burning (in preparation) (44)

All of these reports are expected to be issued by the middle of 1985. Progress Reports One and Two have already been issued.

REPORT STRUCTURE

The remainder of the report is divided into four sections. These are

CHAR

CHAR BURNING

FUME FORMATION

OPERATIONAL IMPLICATIONS

The full benefit of the logic of the work is obtained by reading the report in sequence. However, each of the sections is largely self-contained, and can be understood as a separate entity.

CHAR

CHAR FORMATION

What is char? Char is the residual solid product resulting from black liquor pyrolysis. (Pyrolysis is the thermal decomposition of black liquor solids.) Pyrolysis is a very complex process involving competing fragmentation and polymerization reactions. Thus pyrolysis products are path dependent quantities, i.e., they depend on detailed conditions during the pyrolysis and not just the final conditions. The heating rate is important as well as the final temperature. Fast pyrolysis (higher heating rates) favors gas formation and less char, while slow pyrolysis tends to increase char formation. Because pyrolysis is a path dependent phenomenon, one expects a range of char compositions from any given liquor rather than a unique composition.

In the furnace, pyrolysis does not take place in isolation. The pyrolyzing liquor is in an oxygen containing atmosphere, and the combustible gases given off can burn in the close vicinity of the particle. It is impossible to specify exactly when pyrolysis ceases and gasification and burning begins in this case. In order to have well-defined systems, pyrolyses must be carried out under standardized conditions in inert atmospheres.

Definitions

In order to avoid confusion, the following nomenclature is followed in this report:

Char: Char is the entire residual product from black liquor pyrolysis. This includes both the carbonaceous material and the inorganic salts.

Char Carbon: This is the carbonaceous material in the char formed from the pyrolytic degradation of the organic compounds in the black liquor.

Inorganic: The sodium (and possibly potassium) salts in the char regardless of whether liquid or solid. Normally these are considered to consist of Na_2CO_3 , Na_2S , and Na_2SO_4 .

Smelt: A continuous molten salt phase substantially free of carbonaceous material.

Frozen Smelt: Solidified salts that had previously been a continuous molten salt phase.

Bed: (Also called char bed.) The pile of material lying on the furnace hearth. The bed is dynamic in nature with fresh material being continuously added and combustion gases and molten smelt continuously leaving.

Process vs. Bed

The definition of char used in this report puts it in a process context. Char is the residual solids after black liquor pyrolysis. It is not the material landing on the char bed. Char formation is an inherent step in the burning of black liquor. When the black liquor solids pyrolyze and the pyrolysis gases burn, char is formed. This can occur as droplets rise or fall in the furnace, on the wall, or in the char bed. Char burning takes place after char is formed and oxygen (from air) has an opportunity to reach the char. This can occur (and mostly occurs) on the char bed, but can occur in flight, on the walls, etc.

This study is concerned with char burning, not bed burning per se. The bed comes into play when interpreting the results in terms of the recovery furnace. This is a very important application of the results of the work and is covered in a separate section of the report. However, the focus is on char burning, not bed burning.

Description of Char

Char produced by black liquor pyrolysis is black, porous, papery, and friable. If crushed, it forms a black powder. Despite having a high inorganic content, crushed char looks a lot like carbon black. Considerable swelling of the liquor solids can take place during pyrolysis. This gives a very porous, low density char.

A series of pictures illustrating pyrolysis and char formation are shown in Fig. 3-1. A pellet of dry black liquor solids is suspended and exposed to hot nitrogen gas at 800°C. Gas flow is from the top (hook side) to the bottom. The initial pellet contains about 300 mg of solids and loses about 25% of its weight during the pyrolysis. It takes about 20 to 25 seconds for pyrolysis to be completed under these conditions. The volume of swollen particle is about 10 times that of the initial pellet. The swollen char has some of the characteristics of a cenosphere. Most of the mass is located in the exterior layer, while the interior is much more porous. However, there is some char present throughout the particle. The structure of the swollen char is similar to the fireworks "snakes" that are lit on the 4th of July.

Laboratory Procedures

Chars used in the fundamental kinetic studies in the molten salt reactor were produced by drying a quantity of liquor under vacuum at 105°C, and then

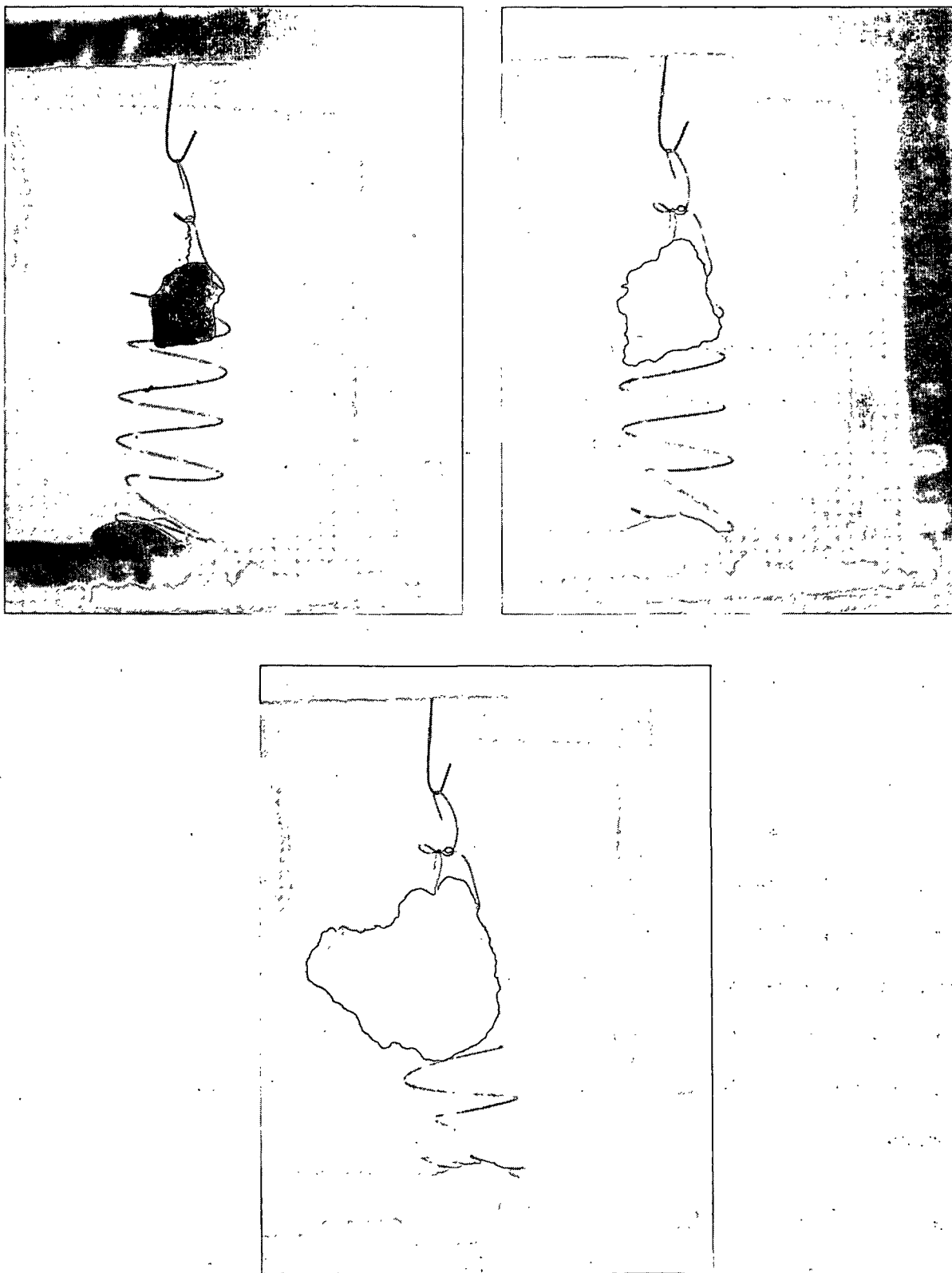


Figure 3-1. Picture sequence showing char formation.

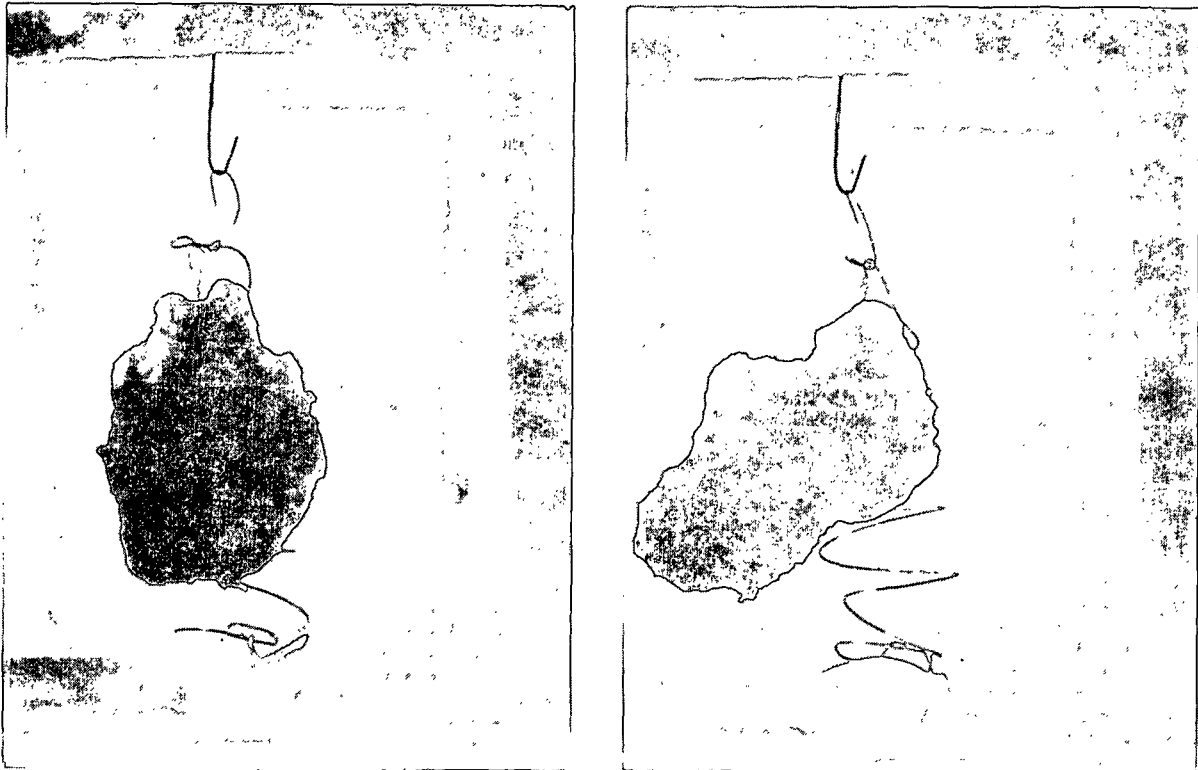


Figure 3-1 (Contd.). Picture sequence showing char formation.

pyrolyzing the dried solids in a covered ceramic crucible placed in a muffle furnace at 950°C for 7 minutes. This procedure is based on one recommended for determination of the volatile content of coal (7). Although the procedure is arbitrary, batches of char prepared in this manner were reproducible and provided consistent rate data.

Two types of char were used in the fundamental studies: a kraft char and a soda char. The kraft char was produced from a kraft black liquor obtained from Thilmany Pulp and Paper Co., Kaukauna, Wisconsin. The soda char was used in experiments where a sulfur-free char sample was needed. It was produced from a soda liquor from a laboratory soda cook carried out for that purpose.

For char burns in the single particle reactor, char was formed in place by pyrolyzing a pellet of liquor solids, suspended from the microbalance, in hot nitrogen. This is the process shown in Fig. 3-1. Typically the nitrogen was at 800°C, and the pyrolysis continued until weight loss ceased.

PHYSICAL PROPERTIES OF CHAR

There is little information available on the physical properties of black liquor char. Most of the data that does exist is for bed material in the furnace, and not on char per se.

ADL Data

Richardson and Merriam (8) obtained data on the thermal properties of char as part of the Phase I study of char bed cooling. Their data are summarized in Table 3-1. These data show that the bed density is significantly lower than the density of the inorganics (and the density of carbon). Thus the bed must be porous. The bed is a poor conductor of heat at low temperature, but becomes a much better conductor at high temperature.

Table 3-1. Thermal property data [from ADL Phase I Report (8)].

	Smelt		Char Bed	
	Liquid	Solid	Cold	Hot
Density, lb/ft ³	120	132	30-80	18-30
Specific heat, Btu/lb °F	0.32	0.34	0.3	0.3
Thermal conductivity, Btu/hr ft °F	0.26	0.48	0.05	0.16-0.22
Thermal diffusivity, ft ² /hr	0.007	0.011	0.002-0.006	0.02-0.04
Latent heat, Btu/lb	61			

The fact that the char bed thermal conductivity is a strong function of temperature was one of the most important findings in Phase I. This behavior occurs because the heat flow in the porous bed has a high radiative component across the pores at high temperatures. This makes the apparent thermal conductivity of bed material a strong function of temperature. Richardson and Merriam (8) were able to model the heat transfer in char beds by considering ordinary conduction and radiation acting in parallel. This led to the expression:

$$k = 0.05 + 4 \sigma \phi D_p T^3 \quad (3-1)$$

where k = apparent thermal conductivity of bed

σ = Boltzmann's radiation constant

ϕ = porosity of bed

D_p = average pore size

T = absolute temperature.

The value of 0.05 in the above expression is just the measured bed thermal conductivity at low temperature where radiation is unimportant.

Caution must be used in interpreting the above data as representing char data. The measurements were made on operating char beds with all of the uncertainty that the dynamic nature of char beds entails. Nevertheless, the ADL char bed data is certainly indicative of some of the main physical properties of char.

Char Density

Several authors have noted the tendency for black liquor to swell during pyrolysis, but there is little data available on char density or swollen volume. Kubes (9) has described a procedure for measuring swollen volume. Samples of dry liquor solids (0.5 g) are pyrolyzed at 400°C for 5 minutes. After cooling, the total volume of the swollen samples is measured by covering them with fine silica and determining the volume of silica displaced. Measured swollen volumes ranged from 6 to 54 cc/g of solids. Oye, et al. (10) used a similar procedure except that dried pulp balls were used to determine the volume displaced by the swollen particle. They reported values of swollen volume from 4 to over 50 mL/g total solids. Since dried black liquor solids have specific gravities of 1.6 to 1.7 and the inorganic smelt components have specific gravities of 2 to 2.2, the void fraction in the swollen char can range from 80 to 99%.

We did not attempt to measure char density or swollen volume. Most of the work was carried out with crushed char, so that the swollen volume did not enter the picture. Only the char burns on the single-particle reactor were carried out on swollen char as it was formed. Photographs taken of the pyrolysis process in the single particle reactor (e.g., Fig. 3-1) show considerable swelling. Volumetric expansions can easily approach a factor of ten, giving porosities of 90% or higher and particle densities on the order of 0.2 g/cm³.

CHEMICAL COMPOSITION

More information is available on the chemical composition of char than on its physical properties. A significant amount of composition data was obtained in the course of the ADL studies (8,11). Limited data have also been published by Borg et al. (12), Weyerhaeuser (13), and Feuerstein et al. (14).

ADL Data

Six samples of char bed material were obtained from two different boilers and analyzed during Phase I. The results are given in Table 3-2. All of the sodium compounds were removed from the samples by water leaching. The reported values were determined by anion analysis of the leachate according to TAPPI Procedures T 624 and T 625. Carbon was determined by ignition weight loss on the water insoluble material.

Table 3-2. Analysis of char bed samples (8) (all data in wt.%).

	A-1	A-3	A-5	T-5	T-9	T-11
Na ₂ CO ₃	64.6	64.7	64.4	68.1	66.6	68.4
Na ₂ SO ₄	2.9	6.5	1.8	3.6	4.6	1.3
Na ₂ S	13.1	1.5	11.5	1.5	1.0	12.4
Na ₂ S ₂ O ₃	4.9	5.2	6.7	10.3	3.9	5.6
Na ₂ SO ₃	0.4	1.2	0.1	0.1	1.6	0.9
Carbon	4.7	4.9	6.0	5.2	8.2	7.0
Insoluble ash	0.6	0.7	0.3	0.2	0.5	0.1
Total accounted	91.2	84.7	90.8	89.0	86.4	95.7

These data indicate that the great bulk of the bed material is simply inorganic sodium salts, mainly sodium carbonate (Na₂CO₃). Sulfur is present, to

a large extent, as a mixture of simple inorganic sulfur compounds of various oxidation states. The carbon content is only about 5 to 8% by weight. The unaccounted material is likely to be water soluble salts of low molecular weight organic acids such as acetates, etc.

Additional samples were taken from operating furnaces and analyzed during Phase II (11). A redesigned sampler was used to minimize oxidation of the samples after they were taken. Besides sampling bed material, some samples were taken of the material landing on the bed (fines). The results were generally similar to that found during Phase I. The major differences were:

1. Carbon contents of the "fines" tended to be higher than those of bed samples, ranging up to 15 wt.%.
2. The average oxidation state of sulfur compounds was higher in the "fines" than in bed samples. There was considerable variability in sulfur oxidation state from sample to sample. Most of the bed samples were highly reduced (over 90% reduction).
3. No significant amounts of sulfite were found in samples inerted during sampling.

It must be borne in mind that these were samples taken from operating furnaces. There was no control over the conditions from where they were obtained and there was a high degree of uncertainty as to what the local conditions were. Nevertheless, they are relevant to questions about char composition and char burning.

Other Data

Borg, Teder, and Warnqvist have reported on data obtained from field measurements inside a kraft recovery furnace (12). They report that besides the

major components, Na_2CO_3 and Na_2S , the bed contains a few percent Na_2SO_4 and NaOH , but no other sodium compounds. The carbon content of the bed was found to be around 5% by weight except in areas of unusually low temperature (cold spots) where the percentage is around 8%. These results are in general agreement with those of ADL.

Feuerstein, Thomas, and Brink (14) carried out laboratory pyrolyses of kraft black liquor. They did not analyze the residual char in detail. They reported char yields between 60 and 70% of the original black liquor solids, with a trend toward lower yields at higher temperature. They also found that only 20 to 40% of the sulfur was retained in the char. There was an indication of a minimum in sulfur retention at a pyrolysis temperature of about 700°C .

Composition data on char obtained during the development of the Weyerhaeuser dry solids pyrolysis process (13) are shown in Table 3-3. These are composite data summarizing their general experience. Information was not given on conditions, analytical methods, or other details.

Table 3-3. Composition data on Weyerhaeuser char (13).

(wt.% on char)	
Na_2CO_3	64.31
Na_2SO_4	3.63
Na_2S	1.99
Organic	
C	27.50
H	0.93
S	1.64
yield = 64.5%	
HHV \approx 4600 Btu/lb	

The data in Table 3-3 are for char produced under controlled conditions. They are char data and not bed data. Thus these data can be considered as more representative of char composition (as char is defined in this report) than the bed composition data discussed previously. It may be noted that the carbon content of the Weyerhaeuser char is much greater than that reported for bed samples (8,11,12).

IPC Data

Elemental analyses on the kraft char and soda char used in our fundamental kinetic studies are given in Table 3-4. These analyses were performed by Huffman Laboratories, Wheat Ridge, CO. All elements were determined directly. No information is available on the precision of each value. The deviation of the sum from 100% can be taken as an indication of the accuracy of the data.

Table 3-4. Elemental analyses of IPC chars.

	(wt.% on char)	
	Kraft Char	Soda Char
Carbon, C	29.36	33.39
Hydrogen, H	0.65	0.53
Oxygen, O	33.78	35.94
Sulfur, S	2.12	0.03
Chlorine, Cl	0.56	--
Potassium, K	3.39	0.27
Sodium, Na	<u>26.00</u>	<u>29.41</u>
	95.86	99.57

The kraft black liquor pyrolyzed had a sodium content of 18.0%. Since sodium should be conserved during pyrolysis, the calculated yield of char is $18.0/26.0 = 69\%$ of the original black liquor solids.

The results of carbonate, sulfide, and sulfate analyses on the kraft char, and an interpretation of this data in terms of the elemental composition are given in Table 3-5. It is possible to account for 100% of the alkali (Na + K) and 75% of the sulfur in the char by these three inorganic compounds.

Table 3-5. Inorganic content of char.

(wt.% on char)

Carbonate, as Na_2CO_3	59.8
Sulfide, as Na_2S	2.9
Sulfate, as Na_2SO_4	1.76

$$\text{M}_2 = \text{Na}_2 + \text{K}_2$$

$$\text{Carbonate: } 59.8/106 = 0.564 \text{ moles } \text{M}_2\text{CO}_3$$

$$\text{Sulfide: } 2.9/78 = 0.0372 \text{ moles } \text{M}_2\text{S}$$

$$\text{Sulfate: } 1.76/142 = \underline{0.0124} \text{ moles } \text{M}_2\text{SO}_4$$

$$0.6136 \text{ moles } \text{M}_2$$

$$0.0496 \text{ moles } \text{S}$$

$$\frac{\text{moles } \text{Na}_2}{\text{mole } \text{Na}_2 + \text{mole } \text{K}_2} = \frac{26.00/46.0}{26.00/46.0 + 3.39/78.2} = 0.929$$

	Calculated	Measured
Na in inorganic = $0.929 \times 0.6135 \times 46$	= 26.22%	26.00%
K in inorganic = $0.071 \times 0.6135 \times 78.2$	= 3.41%	3.43%
S in inorganic = 0.0496×32	= 1.59%	2.12%

These data indicate that char can be considered to be made up of inorganics (carbonate, sulfate, and sulfide), which account for all of the alkali and most of the sulfur, and a carbonaceous material. Similar conclusions could be derived from the ADL data on bed and "fines" composition.

It is possible to take these data one step further by expressing the composition in terms of moles. Mass relationships in chemical reactions involve discrete quantities of substances that are proportional to the molecular weight. It is convenient to use moles to describe such relationships. A mole of any substance is an amount, in any convenient set of mass units, that is numerically equal to the molecular weight. A mole involves a fixed number of molecules (e.g., one gram-mole contains 6.023×10^{23} molecules). Thus moles combine in simple proportions identical to the coefficients of the chemical formulas in a chemical reaction equation.

Table 3-6 shows char composition on a relative mole basis. The data on the Weyerhaeuser char are included along with our own char data. In the top portion of the table, the char composition is displayed as moles of each element per mole of Na_2 . In the middle portion, the inorganic alkali is assumed to be Na_2SO_4 , Na_2S , Na_2CO_3 , and K_2CO_3 (for our kraft char we assumed 75% of the sulfur was in the inorganic, equally split between sulfate and sulfide). In the bottom portion of the table the residual "char carbon" mole ratios are determined by difference.

All of these chars show strong similarities. The dominant chemical species is carbon in the "char carbon." The ratio of carbon to hydrogen is about 3 to 1 as is the ratio of carbon to alkali. Most of the oxygen in the char is accountable as carbonate and sulfate, and oxygen is a minor constituent

of the char carbon. The two IPC chars tend to be a little more oxygenated than the Weyerhaeuser char, but even here, 85% of the oxygen in the char is inorganic.

Table 3-6. Relative char composition.

moles/mole Na ₂	Kraft Char	Soda Char	Weyerhaeuser Char
C	4.33	4.35	4.40
H	1.15	0.83	1.41
O	3.74	3.51	2.92
S	0.12	--	0.16
Cl ₂	0.01	--	--
K ₂	0.08	0.01	--
Na ₂	1.00	1.00	1.00
Inorganic			
Na ₂ SO ₄	0.045	--	0.04
Na ₂ S	0.045	--	0.04
Na ₂ CO ₃	0.91	1.00	0.92
K ₂ CO ₃	0.08	0.01	--
Char Carbon			
C	3.34	3.34	3.48
H	1.15	0.83	1.41
O	0.59	0.48	--
S	0.03	--	0.08

Interpretation of Composition Data

There are consistent patterns in all of the available data on char composition. An interpretation of this data which leads to a simplified view of char is summarized below.

1. Char produced by pyrolyzing kraft black liquor has a yield in the range of 60 to 70% of the original black liquor solids. To a first approximation, about 1/2 of the carbon in the original liquor ends up in the char.
2. Char can be considered to consist of an intimate mixture of two substances; inorganic and "char carbon." The inorganic contains all of the alkali in the char and is primarily alkali carbonate. It also contains alkali-sulfur compounds in various oxidation states. The "char carbon" is primarily solid carbon with lesser amounts of hydrogen, oxygen, and sulfur.
3. The alkali in the inorganic consists of sodium and potassium salts with sodium the dominant constituent. Except where volatilization and melting point behavior is involved, sodium and potassium salts can be considered as equivalent. In this report we will consider the inorganic to consist solely of sodium salts except where specially noted.
4. The major sodium-sulfur salts are sulfate and sulfide. The other intermediate oxidation state sodium-sulfur compounds in the char can be considered as chemically equivalent to a mixture of sulfate and sulfide. These are the only stable sulfur compounds in molten carbonate (5).

5. The char carbon consists of solid carbon, bound hydrogen (probably as condensed aromatic hydrocarbons) and small amounts of organic sulfur and oxygen. More intense pyrolysis reduces the oxygen content. For many purposes it can be considered to be solid carbon (e.g., graphite).
6. The sulfur/sodium ratios in char samples from pyrolysis of black liquor are only about 1/2 the ratios usually found in smelt from recovery boilers. This is due to extensive release of sulfur gases during pyrolysis. Within the furnace this sulfur can react with fume and most of it returns to the black liquor as recycled Na_2SO_4 from the precipitator and ash hoppers. This recycle load can be 10 to 15% by weight of the original black liquor solids. The composition of char produced in the furnace must be adjusted to account for this recycled sulfate.
7. Because of the high recycle Na_2SO_4 load and the stability of Na_2SO_4 during pyrolysis (15), a substantial fraction of the sulfur in the char will be sulfate until conditions favorable for sulfate reduction are reached.
8. On a mole basis, the dominant chemical species in char is carbon. There is insufficient oxygen present in char to burn off the carbon, so that a significant amount of oxygen from combustion air is required.

Simplified Chemical Composition

It is possible to develop a simplified view of char composition by making the following assumptions.

1. All sodium and sulfur are present as the three inorganic compounds: carbonate, sulfate, and sulfide.
2. The relative amounts of sulfate and sulfide define the average oxidation state of the sulfur.
3. Hydrogen present as condensed aromatics is treated as "bound" hydrogen.
4. Carbon not present as sodium carbonate is treated as solid carbon.
5. All oxygen is accounted for by the inorganics.
6. The relative amounts of carbon, hydrogen, and alkali are close to those found in Table 3-6.

With these assumptions, along with an assumed S/Na₂ ratio of 1 to 3 and an initial state of reduction equivalent to a 50% reduction efficiency, a representative char composition, before char burning occurs, is the following

moles/mole Na ₂	
Na ₂ S	1/6
Na ₂ SO ₄	1/6
Na ₂ CO ₃	2/3
C	3
H	1

At the completion of char burning processes, the approximate composition would be

moles/mole Na ₂	
Na ₂ S	19/60
Na ₂ SO ₄	1/60
Na ₂ CO ₃	2/3
C	1/12
H	0

The latter set of numbers corresponds to a reduction efficiency of 95% and a residual carbon content in the smelt of 1% by weight.

CHAR STOICHIOMETRY

Stoichiometry means a description of the mass relationships between reactants and products in a chemical reaction. Such relationships are most conveniently described in terms of moles. Char stoichiometry is concerned with two situations.

1. Stoichiometric relationships between individual constituents in char.
2. Stoichiometric interactions between char and its surroundings, specifically relationships between combustion air and char components.

We will first apply stoichiometry to the simplified char composition discussed above. These calculations are straightforward and the results are easier to interpret. We will then consider the more general case of any particular char composition.

Simplified View

According to the simplified view, char consists of the three inorganic salts Na_2CO_3 , Na_2SO_4 , and Na_2S , along with carbon and bound hydrogen. There are typically 3 moles of carbon per mole of inorganic and 3 moles of carbon per mole of H.

Sodium carbonate, Na_2CO_3 , can be considered as an inert during char burning (this view must be weakened slightly when fuming reactions are considered). Thus the moles of Na_2CO_3 remain fixed during burning. The two

inorganic sulfur compounds can be converted back and forth to each other, but not to other compounds. Thus the sum of the moles of sulfate and sulfide remains constant and the only change occurring is the gain or loss of oxygen. Carbon can be oxidized to either carbon monoxide or carbon dioxide. Bound hydrogen can be oxidized to water vapor. These concepts are shown diagrammatically in Fig. 3-2.

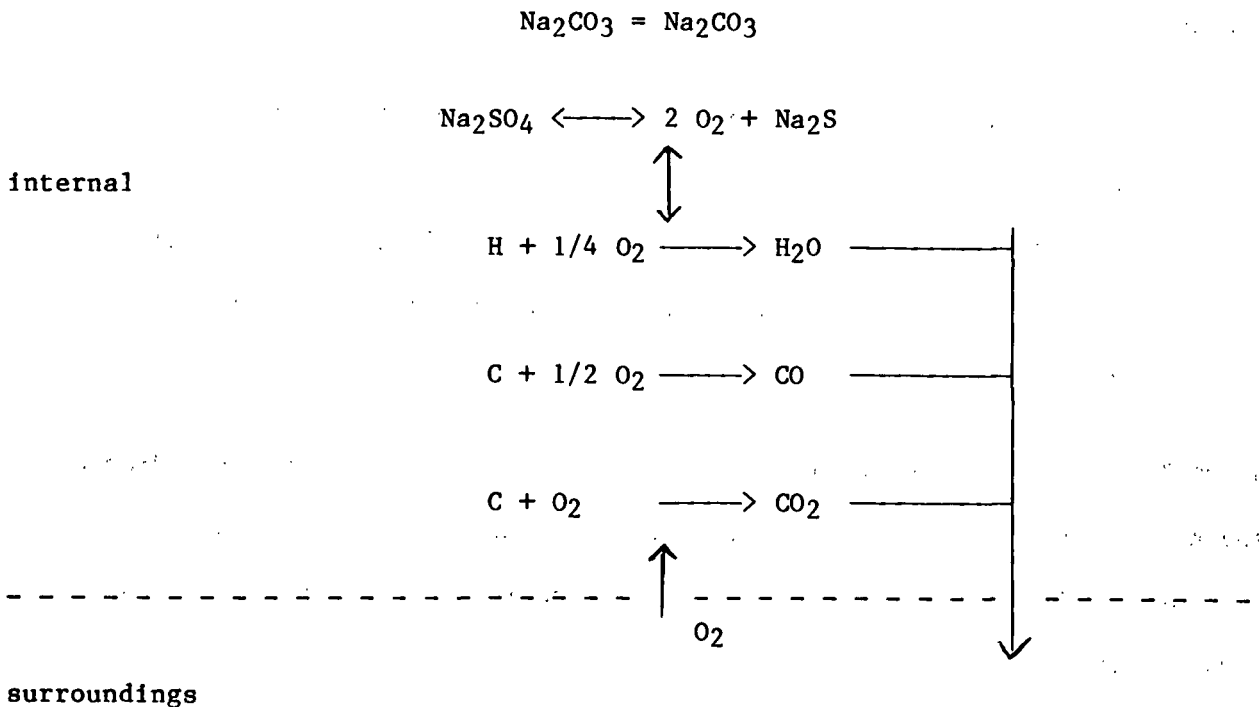
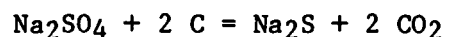
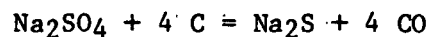
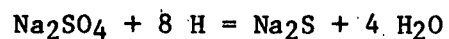


Figure 3-2. Reactions of char constituents (simplified view).

The only significant reaction occurring between the char constituents themselves is the transfer of oxygen from sulfate to oxidize carbon and bound hydrogen. This can be represented by the following three reactions.



Turning now to the simplified char composition, the 1 mole of H is capable of reducing $1/8$ mole of sulfate. However, the char contains $1/6$ mole of sulfate. There is not enough bound hydrogen present in the char to reduce all of the sulfate to sulfide. The 3 moles of C can reduce $3/4$ mole of sulfate if CO is the reaction product, or it can reduce 1.5 moles of sulfate if CO_2 is the reaction product. The amount of carbon present is far in excess of that needed to reduce the sulfate. This means that there is not enough oxygen present in the sulfate to burn off all of the carbon.

Consideration of the internal stoichiometry of the char leads to the following conclusions.

1. Carbon is the most important sulfate reducing agent.
2. Carbon balances dominate char stoichiometry.
3. The relative amount of CO and CO_2 produced is an important factor in carbon balances.
4. Interactions with the surroundings are essential for getting rid of the carbon content of the char.

The most straightforward interaction with the surroundings is the pick-up of oxygen. This is illustrated in Fig. 3-2. Oxygen comes into the char from the combustion air, and the oxidized gases (H_2O , CO, and CO_2) leave. This can be treated quantitatively. The char composition can be described by the following parameters:

s = molar ratio of sulfur to alkali, S/Na_2

r = molar ratio $\frac{Na_2S}{Na_2S + Na_2SO_4}$, state of reduction

$[C]$ = molar ratio of carbon (not as Na_2CO_3) to alkali

$[H]$ = molar ratio of bound hydrogen to alkali.

According to our assumptions, s remains constant during char burning, r can vary between 0 and 1, and $[C]$ and $[H]$ decrease toward zero as char burns. Letting the subscript i denote the initial composition and the subscript f the final composition we get

$$a = (1 - f/2) \{ [C]_i - [C]_f \} + 1/4 \{ [H]_i - [H]_f \} - 2s (r_f - r_i) \quad (3-2)$$

where a = moles O_2 from surroundings/mole alkali

and f = molar ratio $CO/(CO + CO_2)$.

Equation (3-2) states that the amount of oxygen coming in from the surroundings is the difference between that picked up by the carbon and bound hydrogen, and that supplied by the sulfate.

It is possible to define a "theoretical air" requirement for char analogous to that defined for the black liquor solids. We note that the desired end state is all carbon and bound hydrogen burned and the smelt (inorganic) completely reduced. Using this as a benchmark we can set $[C]_f = 0$, $[H]_f = 0$, and $r_f = 1$ in Eq. (3-2) and obtain

$$a_0 = (1 - f/2) [C]_i + 1/4 [H]_i - 2s (1 - r_i) \quad (3-3)$$

where a_0 = stoichiometric O_2 required from surroundings, moles O_2 /mole alkali.

For the simplified char composition discussed previously, $[C]_f = 3$, $[H]_f = 1$, $s = 1/3$, and $r_f = 1/2$. Then

$$a_o = 3 (1 - f/2) + 1/4 - 1/3 = 3 (1 - f/2) - 1/12 \quad (3-4)$$

Note that the O_2 requirement is strongly dependent on the parameter f (the mole fraction CO in the carbon gases). Since f could have any value between 0 and 1, a_o could vary from 17/12 to 35/12 or by more than a factor of two. Note also that the bound hydrogen and sulfate terms are much smaller than the carbon term and tend to cancel each other out. Two parameters, $[C]_f$ and f , are critical in determining the amount of O_2 needed from the surroundings. The dependence of char stoichiometry on the relative amounts of CO and CO_2 produced has important implications to the furnace which will be explored in a later section. Thus those factors which govern $CO/(CO + CO_2)$ are very important in understanding char burning behavior. This was one of the key questions which the char burning chemistry work focussed on.

One final point needs to be made. The amount of oxygen required from the surroundings is much greater than that originally present in the char as sulfate. The ratio of external to internal oxygen is given by

$$\frac{a_o}{2s (1-r_f)} = \frac{(1 - f/2) [C]_f + 1/4 [H]_f}{2s (1-r_f)} - 1 \quad (3-5)$$

Using the numbers for the simplified char composition gives

$$\frac{\text{external } O_2}{\text{internal } O_2} = \frac{3 (1 - f/2) + 1/4}{1/3} - 1 = 9 (1-f/2) - 1/4.$$

Thus it varies from 4.25 to 8.75 depending on f . From 80 to 90% of the oxygen needed to burn up a typical char must come from combustion air.

General Case

The general treatment of char stoichiometry allows the presence of "organic" sulfur and oxygen (i.e., sulfur and oxygen that is not present as carbonate, sulfate, and sulfide). We retain the concept that all alkali is present as the three inorganic salts. Compositions are expressed as mole ratios of the constituent per mole alkali (Na_2).

The char composition can be specified in terms of the following parameters.

[C] = moles of carbon (except for carbonate) per mole alkali

[H] = moles of bound hydrogen per mole alkali

[O] = moles of "organic" oxygen per mole alkali

[S_O] = moles of "organic" sulfur per mole alkali

[S_I] = moles of inorganic sulfur (sulfate + sulfide) per mole of alkali

r = molar ratio of $\text{Na}_2\text{S}/(\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4)$.

The presence of "organic" sulfur introduces ambiguity that cannot be resolved by stoichiometric principles alone. It is necessary to arbitrarily define what happens to "organic" sulfur during char burning. There are several possibilities. The "organic" S could come off as a gas such as SO_2 , H_2S , or COS as the char burns. The "organic" S could interact with sodium carbonate and end up as sulfate or sulfide (i.e., as inorganic sulfur). Or, there could be a combination of both gases evolved and inorganic sulfur produced. In sorting through these possibilities, it is helpful to note that, from a stoichiometric standpoint, nothing is gained by considering "organic" S being converted to inorganic S. That sulfur that ends up as sulfate or sulfide might just as well have been considered to have started as sulfate or sulfide. This leads us to an

operational definition of "organic" sulfur; "organic" sulfur in char is the sulfur converted to sulfur gases and given off to the surroundings as char burns. Now our task is reduced to specifying what sulfur gas(es) are evolved. We will arbitrarily assume this to be SO_2 .

Using the subscripts i and f for initial and final conditions of the char and f as the mole fraction CO in the carbon gases, as before, we can write

$$a = (1-f/2) \{ [C]_i - [C]_f \} + 1/4 \{ [H]_i - [H]_f \} + \{ [S_o]_i - [S_o]_f \} - 1/2 \{ [O]_i - [O]_f \} - 2 [S_I] (r_f - r_i) \quad (3-6)$$

where a = moles O_2 from surroundings/mole alkali.

Choosing the final state to be pure, fully-reduced inorganic as before gives

$$a_o = (1-f/2) [C]_i + 1/4 [H]_i + [S_o]_i - 1/2 [O]_i - 2 [S_I] (r_f - r_i) \quad (3-7)$$

a_o = general stoichiometric O_2 required from the surroundings, moles O_2 /mole alkali.

We can evaluate Eq. (3-7) for the IPC kraft char composition given in Table 3-6. The composition values in Table 3-6 must be divided by 1.08 to be put on the basis of moles/mole alkali, since there are 0.08 mole of K_2 present per mole of Na_2 . The composition parameters for the kraft char are

$$\begin{array}{ll} [C]_i \approx 3.09 & [S_o]_i = 0.028 \\ [H]_i \approx 1.06 & [S_I] = 0.083 \\ [O]_i \approx 0.55 & r_i = 0.50 \end{array}$$

$$\therefore a_o = 3.09 (1-f/2) + 0.265 + 0.028 - 0.275 - 0.083 = 3.09 (1-f/2) - 0.065$$

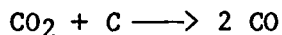
This is very close to the result obtained for the simplified char composition. All of the conclusions reached when considering the stoichiometry of the simplified char remain valid in the general case.

Other Interactions with Surroundings

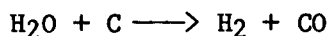
The preceding discussion limited the interaction between char and surroundings to the pickup of oxygen and the release of oxidized gases. We now want to examine if this is too restrictive and other interactions need to be considered. We will consider possible interactions with the following gases: H_2 , CO , CO_2 , and H_2O . All analyses will be based on the simplified char composition.

The first two gases, H_2 and CO , can be considered together. They are reducing gases and could reduce sulfate to sulfide. They are not capable of gasifying carbon and bound hydrogen. Thus they cannot play a major role in char burning, since they cannot get rid of the "char carbon." In addition, it is difficult to consider these gases as interacting with char in parallel with O_2 , since the O_2 would burn the reducing gases outside the char particle. Thus it is not necessary to consider interactions between H_2 or CO and char in char burning.

The second pair of gases, CO_2 and H_2O , can also be considered together. They are both fully oxidized species, and are not capable of reducing sulfate to sulfide. They are capable of gasifying carbon by reactions such as



and



Since these gasification reactions are capable of converting char carbon to gases, they do result in char ending up as inorganic that can be smelted and

removed. Thus they allow the char carbon to be "burned" off. There is no a priori reason to dismiss these gasification reactions as significant interactions during char burning.

The gasification reactions differ from combustion in one important regard. Gasification reactions are endothermic (heat absorbing) while combustion reactions are exothermic (heat releasing). As gasification reactions proceed they tend to cool the char, and the resulting lower temperatures tend to slow down or stop gasification. Combustion reactions tend to raise char temperatures and accelerate reaction rates. For this reason, combustion tends to dominate gasification whenever oxygen is available. It will be evident when we look at experimental char burning that combustion (reaction with O_2) is dominant. However, gasification reactions with CO_2 may influence the CO/CO_2 ratio in the product gases.

Interpretation of Air Requirements

The stoichiometric air requirement for char burning was given by Eq. (3-7) for the general case. For the simplified char composition which we have been considering, this reduced to $a_0 = 3(1 - f/2) - 1/12$ [Eq. (3-4)]. The stoichiometric O_2 requirement varied from 1.4 to 2.9 moles O_2 /mole alkali, depending on relative amounts of CO and CO_2 produced. It is useful to compare this amount of O_2 (air) needed for char burning, with that needed for complete burning of black liquor.

For a typical kraft black liquor, the theoretical (stoichiometric) oxygen demand is about 0.9 lb O_2 /lb of liquor solids. A typical black liquor also has an alkali content corresponding to about 20% by weight sodium on the liquor solids. Thus the total stoichiometric demand for complete burning of the liquor

is $\frac{0.9/32}{0.2/46} = 6.45$ moles O_2 /mole alkali. Thus the char burning requirement is $(1.4 \text{ to } 2.9)/6.45$ or 22 to 45% of the total stoichiometric air for the black liquor, depending on the CO/CO_2 split. Since there tends to be a one-to-one correspondence between oxygen requirements for complete combustion and fuel value, this would indicate that about 40 to 50% of the fuel value in the original liquor solids ends up in the char.

Char burning air requirements can also be compared with the air supply to the lower furnace (char bed zone). Normally the air supply to the lower furnace is 65 to 75% of the total air supply. Since the total air is normally about 115% of the stoichiometric air (15% excess air), the air supply to the lower furnace is 75 to 85% of the stoichiometric air. Thus the char burning air requirement is from 30 to 60% of the air supply to the lower furnace.

The wide range in the percent of the lower furnace air represented by char burning is due to the dependence on the CO/CO_2 ratio. Borg, Teder, and Warnqvist (12) measured gas composition just above the bed in an operating furnace, and reported 13% CO_2 and 6% CO . This would give $f = 0.32$ and $a_0 = 2.44$, and would correspond to $2.44/6.45 = 38\%$ of the stoichiometric air for complete combustion or 45 to 50% of the air supply to the lower furnace.

It seems reasonable to expect that most char burning takes place in the lower furnace. Extensive char burning in the upper furnace would lead to excessive entrainment of molten inorganic and would likely lead to severe plugging in the superheater and boiler bank. However, it is clear that char burning is not the only significant burning process occurring in the lower furnace. About twice as much air is put into the lower furnace than is needed for

char burning. Obviously, substantial pyrolysis and volatiles burning is also occurring in the lower furnace.

It is less clear how much of the burning, both volatile burning and char burning, takes place on the bed and how much takes place in flight. Caution must be exercised to avoid an a priori identification of char burning with bed burning. If pyrolysis is incomplete when the incoming material lands on the bed, bed air requirements would be greater than char burning requirements. If substantial char burning occurs before the material reaches the bed, bed air requirements will be less than char burning requirements.

These stoichiometric calculations, the configuration of the air supply with respect to the bed, and the response of the bed to changes in liquor spray or air supply, all indicate that it is reasonable to suppose that a significant portion of the air supply to the lower furnace actually interacts directly with the bed and causes combustion to occur in the bed. Under such conditions, burning could be controlled by the rate of air supply to the bed and burning rates could be increased by increasing air-bed contact. It will be shown later that when the rate of air supply controls the rate of burning, it is entirely possible for the sulfur to remain in a high state of reduction as burning proceeds.

CHAR THERMOCHEMISTRY

Thermochemistry deals with the changes of energy in chemical reactions. All chemical reactions are accompanied by energy changes which normally manifest themselves by either an absorption or evolution of heat. Endothermic reactions absorb heat and tend to lower the temperature of the system. Exothermic reactions evolve heat and tend to raise the temperature of the system.

Heats of reaction under defined conditions, when all reactants and products are identified, can be calculated from organized thermochemical data such as the JANAF Tables (16). If the starting material is not rigorously defined (such as char or black liquor), heats of reaction cannot be rigorously calculated and it is necessary to resort to experimental measurement or approximation.

Heating Value of Char

The heating value of a fuel is the heat of reaction for the fuel reacting with oxygen to give a prescribed set of combustion products. In North America it is most common to use the higher heating value (HHV) in which the combustion products are those obtained when the fuel is burned in an oxygen bomb calorimeter. For black liquor the HHV is based on the combustion products being Na_2CO_3 , Na_2SO_4 , CO_2 , and liquid H_2O . These same products would be the basis for the HHV of char. The actual heat release during char burning under furnace conditions is different from the HHV because the combustion products are different from those in the bomb calorimeter. There are four major differences:

1. The main sulfur product is sulfide not sulfate.
2. Water vapor is formed instead of liquid water.
3. Some CO may be present as well as CO_2 .
4. The reactions occur at high temperature, not at 25°C .

The only available reported data on char HHV's is for the Weyerhaeuser char (13). This gives a value of 4600 Btu/lb for the HHV of char at a char yield of 64.5% (by weight on original solids). If the heating value of the original black liquor solids is taken as 6600 Btu/lb solids, the heating value in the char is $0.645 \times 4600/6600 = 45\%$ of that in the original black liquor solids.

An estimate can be made of the HHV for the simplified char composition discussed previously. It is assumed that the carbon can be treated as if it is graphite and the "bound hydrogen" treated as if it were hydrogen gas. The calculations are given in Table 3-7. The calculated HHV of 4436 Btu/lb char agrees quite well with the reported value for the Weyerhaeuser char. This indicates the assumptions made here are reasonable.

Table 3-7. Calculated HHV for simplified char.

basis = 1 mole Na₂

$$\text{Na}_2\text{S} = 1/6 \text{ mole} = 78/6 = 13$$

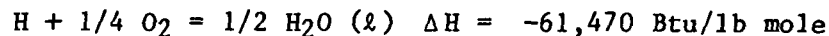
$$\text{Na}_2\text{SO}_4 = 1/6 \text{ mole} = 142/6 = 23.67$$

$$\text{Na}_2\text{CO}_3 = 2/3 \text{ mole} = 2 \times 106/3 = 70.67$$

$$\text{C} = 3 \text{ moles} = 3 \times 12 = 36$$

$$\text{H} = 1 \text{ mole} = 1 = \frac{1}{144.34 \text{ lb}}$$

Heats of reaction at 25°C



$$\text{HHV} = \frac{3 \times (-169,300) + (-61,470) + 1/6 (-425,500)}{144.34} = -4436 \frac{\text{Btu}}{\text{lb char}}$$

(The negative sign means the reaction is exothermic)

[Thermochemical data from JANAF Tables (16)]

The bomb calorimeter HHV's for char are quite exothermic. However, as noted previously, the effective heating values during char burning can be quite different from the value in Table 3-7. An expression to calculate the actual heating values for the simplified char at 1200°K (1700°F) is developed in Table 3-8. The heats of reaction are not strong functions of temperature, so this expression is adequate for all char burning temperatures.

Table 3-8. Heating value for simplified char - actual conditions.

basis = 1 mole Na₂



$$C \longrightarrow CO = 3 f (-48,710) = -146,130 f$$

$$C \longrightarrow CO_2 = 3(1-f)(-169,950) = -509,850 + 509,850 f$$

$$H \longrightarrow 1/2 H_2O (v) = (-53,570) = -53,570$$

$$\begin{aligned} Na_2S \longrightarrow Na_2SO_4 &= 1/3 (r_f - r_i)(-413,480) = +137,830 (r_f - r_i) \\ &= -563,420 + 363,720 f + 137,830 (r_f - r_i) \end{aligned}$$

Dividing through by 144.34 lb/mole Na₂ (see Table 3-7),

$$\Delta H = -3903 + 2520 f + 955 (r_f - r_i) \text{ Btu/lb char.}$$

The char heating value is given as

$$\Delta H \text{ char} = -3903 + 2520 f + 955 (r_f - r_i) \frac{\text{Btu}}{\text{lb char}} \quad (3-8)$$

where f = mole fraction CO in carbon gases,

r_i and r_f = initial and final reduction states of sulfur in char.

The simplified char which we have been considering had an assumed initial reduction state (r_1) = 0.5. Equation (3-8) can be evaluated for a number of special cases.

Fully oxidized: $f = 0$, $r_1 = 0.5$, $r_f = 0$ $\Delta H = -4381$ Btu/lb

Smelt reduced: $f = 0$, $r_1 = 0.5$, $r_f = 1$ $\Delta H = -3426$ Btu/lb

All CO and reduced smelt: $f = 1$, $r_1 = 0.5$, $r_f = 1$ $\Delta H = -906$ Btu/lb

Worst case: $f = 1$, $r_1 = 0$, $r_f = 1$ $\Delta H = -428$ Btu/lb

In all cases char burning remains exothermic, but the exothermicity becomes very marginal when carbon is burned only to CO and reduction loads are high.

Heating Value of Smelt

Reduced smelt, separated from char carbon, may have heating value because the sulfide can be oxidized to sulfate. If we let s be defined as the smelt sulfidity (mole S/mole Na_2) and r the prevailing reduction efficiency in the smelt, the amount of oxidation that occurs is $s(r_1 - r_f) = s \Delta r$, moles Na_2S oxidized/mole Na_2 . The heat of reaction is -413,480 Btu/lb mole Na_2S oxidized at 1700°F. Thus the heating value for smelt oxidation is -413,480 $s \Delta r$ Btu/mole Na_2 .

For example, for a smelt sulfidity of 30%, a 5% loss in reduction efficiency has a heating value of

$$-413,480 \times 0.3 \times 0.05 = -6200 \text{ Btu/mole } \text{Na}_2.$$

One mole of Na_2 in smelt corresponds to about 100 lb. Thus the heating value of a 30% sulfidity smelt is about 62 Btu/lb for each 5% loss in reduction efficiency. Although this seems to be a small number, it is capable of giving a considerable rise in smelt temperature. The specific heat of smelt is about

0.3 Btu/lb °F. If all of the heat of oxidation goes into raising the smelt temperature, a heat balance gives

$$0.3 \frac{\text{Btu}}{\text{lb } ^\circ\text{F}} \Delta T \text{ } ^\circ\text{F} = 62 \text{ Btu/lb or } \Delta T \approx 200^\circ\text{F}.$$

Thus a 5% loss of reduction efficiency by smelt reoxidation could lead to as much as a 200°F temperature increase. In actual fact, some of the heat evolved would heat the surrounding gases, and some would be radiated away. Nevertheless, large local temperature increases can occur when smelt is reoxidized. This is why air lances should not be used in recovery furnaces.

Gasification Heating Values

Char carbon can be gasified by reactions with CO₂ and water vapor. The relevant reactions and heating values at 1700°F are



Both of these are endothermic (heat absorbing) reactions.

CHAR BURNING

In the previous section, we saw that char could be considered as being made up of inorganic plus char carbon. The inorganic consists of sodium carbonate, which acts as an inert, and sodium sulfate and sulfide, which can be converted back and forth into each other. The char carbon contains carbon and bound hydrogen (and sometimes organic sulfur and oxygen). To a first approximation, char carbon can be considered to be solid carbon (graphite). This simplified description is adequate for treating char stoichiometry and thermochemistry. In this section we will see that it is also adequate for treating the char burning process and interpreting burning rates.

Char burning involves the interaction of the char with surrounding gases to remove the char carbon and retain the inorganic as a reduced (sulfide rich) melt. The primary interaction process is combustion, in which oxygen (O_2) comes from the air supplied to burn off the char carbon. Although other carbon gasification reactions are possible, it will be seen that char burning behavior is dominated by, and readily interpretable in terms of, combustion with oxygen. It will also be seen that reduction of sulfate to sulfide can occur simultaneously with char carbon burning, and there is no inherent contradiction in having high reduction efficiency when char carbon is burned with air.

This chapter is concerned with the char burning process. The information obtained includes the following:

1. The role of the "sulfate-sulfide cycle" in char burning
2. Reaction rates for char burning as well as rates for underlying fundamental processes

3. Identification and quantification of key parameters which influence reaction rates
4. Predictive methodology for following the sulfur reduction state during char burning
5. Data on CO/CO₂ ratios during char burning

SULFATE-SULFIDE CYCLE

Description

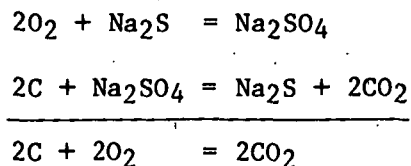
For a char containing carbonate, sulfate, sulfide, and carbon, there are two ways that carbon can be "burned":

1. The oxygen can react directly with the carbon, generating CO and CO₂.
2. The oxygen can react directly with the sulfide, oxidizing it to sulfate. The sulfate in turn reacts with carbon, producing CO and CO₂, and reforming sulfide.

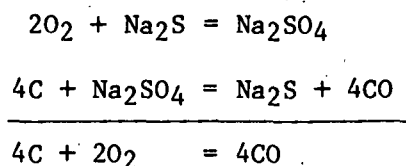
The first mode is essentially how carbon in coal or coke is burned. The second mode is the sulfate-sulfide cycle, and is the way that kraft char is burned. We have neglected a third possibility. Carbon could "burn" by reaction with CO₂ to form CO. This can be considered as influencing the CO/CO₂ ratio and ignored as a separate path.

The distinguishing feature between black liquor chars and coal or coke is the large amount of low melting inorganic in char. At the temperatures involved in char burning, the inorganic should be in the liquid phase and char carbon should be immersed in or wetted by molten smelt. Thus for O₂ to react with char carbon, it must first interact with the molten inorganic.

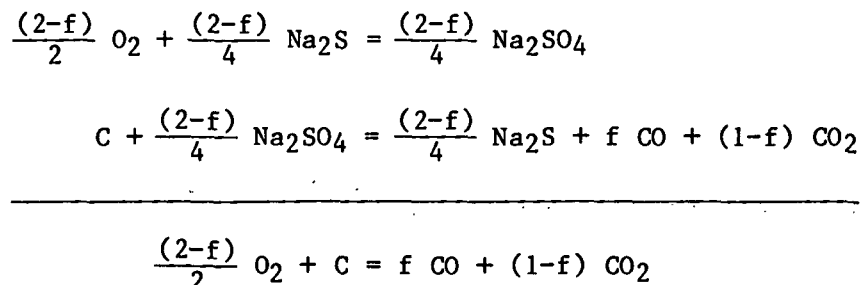
The stoichiometry of the sulfate-sulfide cycle can be represented as follows:



An analogous cycle can be written for CO as product.



The general stoichiometry for the sulfate/sulfide cycle can be written as



The net result of the cycle is simply the oxidation of carbon by air to give CO and CO₂.

The concept of the sulfate-sulfide cycle is illustrated in Fig. 4-1. Oxygen comes in from the combustion air and reacts with sulfide (Na₂S). This oxidizes sulfide to sulfate (Na₂SO₄). The sulfate carries the oxygen over to the carbon, where it reacts to form CO₂ and CO. The sulfate, in turn, is reduced back to sulfide, completing the cycle. The cycle can operate at any level of sulfur or average reduction state in the system. The operating sulfur reduction

state (reduction efficiency) during char burning is determined by the relative rates of sulfide oxidation and sulfate reduction. If the rate limiting step is the oxidation of sulfide by air (e.g., an oxygen mass transfer limit), the carbon will tend to react with sulfate as fast as it is formed and keep the concentration of sulfate low (high reduction efficiency). Conversely, if the rate limiting step is the reaction between sulfate and carbon, the sulfide will be oxidized as fast as it is formed and the sulfide concentration would be very low (low-reduction efficiency). It is evident that simultaneous carbon burning and sulfate reduction can occur if the rate limiting step is the oxidation.

Char burning via the sulfate-sulfide cycle is inherently a rate process. Reaction rate data must be used in interpreting char burning behavior. These rate processes are treated quantitatively later in this section.

Sulfate - Sulfide Cycle

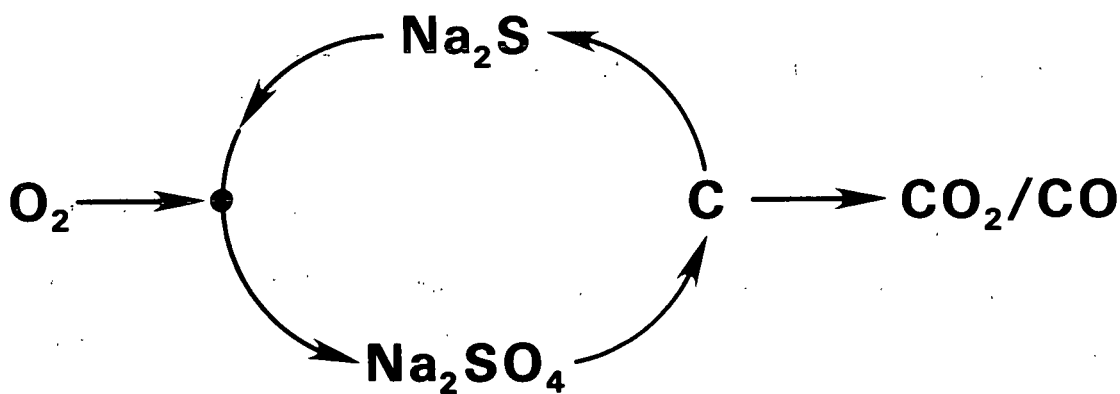


Figure 4-1. Schematic of sulfate-sulfide cycle.

Background

The concept of the sulfate-sulfide cycle for carbon burnup was first developed by workers at Atomics International (now Rockwell International), as part of their work on flue gas desulfurization processes involving molten salt (carbonate) reactors (17,18).

Gehri and Oldenkamp (17) discussed work involving simultaneous reduction of sulfate (and sulfite) and air oxidation of carbon in molten carbonate reactors. The reaction system is illustrated in Fig. 4-2. The objective was to reduce sulfate and sulfite (Na_2SO_3) obtained from a flue gas scrubber to sulfide so that the sulfur could subsequently be stripped off as H_2S for recovery. An excess of carbon was added and burned in the reactor to supply the heat needed to maintain reactor temperature. In operation, a mixture of Na_2SO_4 , Na_2SO_3 and carbon was air blown into a molten carbonate pool along with sufficient air to react with carbon to maintain the temperature. The temperature in the melt pool was maintained at 1700-1900°F. Less than 5% excess carbon (over reduction and heat generation requirements) was used to obtain 95% reduction of the feed salts. Reactor off-gas contained less than 1% O_2 and up to 35% carbon oxides with CO_2/CO ratios of 10/1 or greater. These results were obtained in laboratory reactors and corroborated by pilot scale tests in their Molten Salt Test Facility. The latter system had the capacity to obtain steady-state data at feed rates up to 300 lb/hour.

These results indicated that sulfate reduction rates with carbon were sufficiently fast to allow high reduction efficiencies in the presence of oxygen. The geometry of their system was such that most of the oxygen in the air would be picked up by the melt through oxidation of sulfide to sulfate. This strongly suggested the sulfate-sulfide cycle.

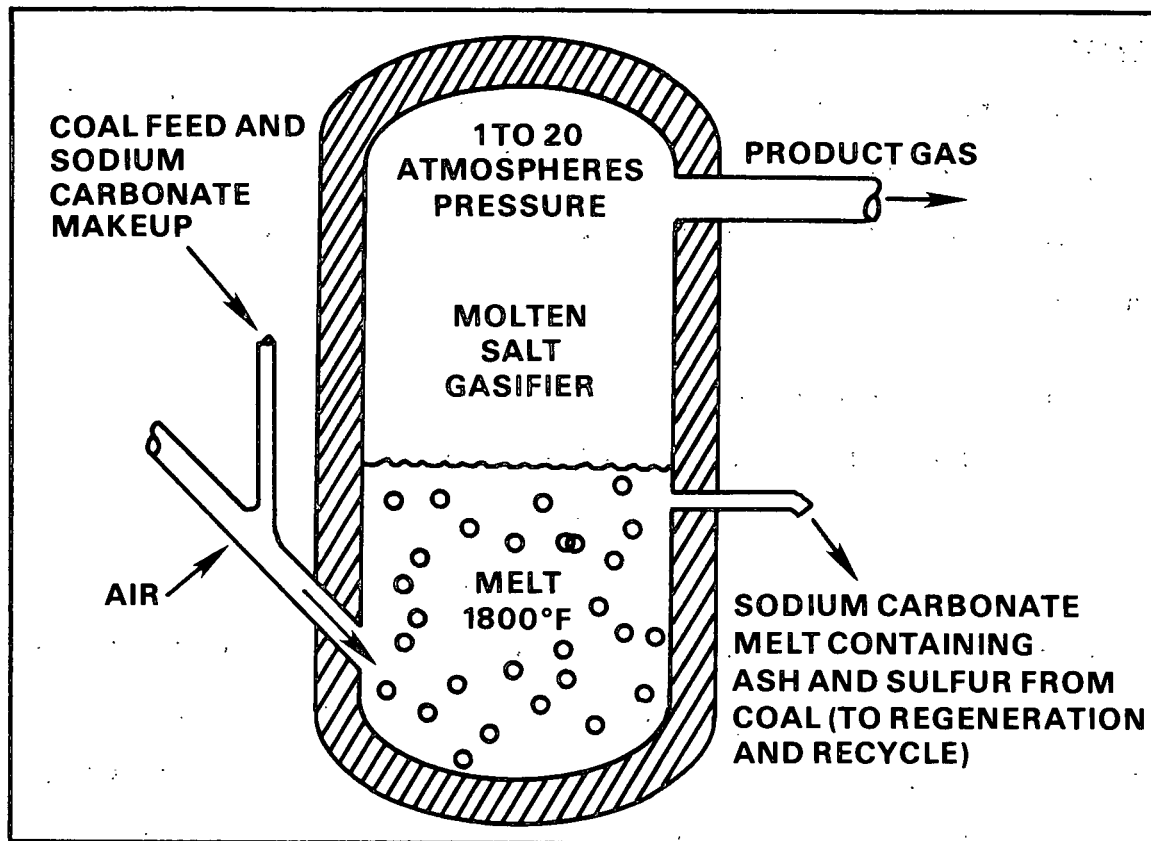


Figure 4-2. Atomics International Molten Salt Reactor (17).

Stelman, et al. (18) studied the air oxidation of graphite in molten salts. They found that the addition of a small amount of sulfate to a carbonate melt catalyzed the rate of carbon oxidation in the melt. A marked increase in burning rate was obtained when sulfur was present. This behavior was interpreted as being due to the sulfate-sulfide cycle.

Thus there was considerable evidence for the existence of a sulfate-sulfide cycle at the start of this char burning project. However, the Atomics International work was all on systems where a large excess of molten salt formed a continuous liquid phase, and the amount of carbon and air present at any time were much less. Thus it was not clear that the same cycle operated during char burning in a recovery furnace.

In order to interpret char burning when sufficient carbon was present that the char acted as a solid, we needed a quantitative treatment of the sulfate-sulfide cycle in terms of the rates of the individual steps. Fundamental data obtained on these rates of individual steps in very different geometries could then be applied to char burning.

Quantitative Treatment of Sulfate-Sulfide Cycle

The sulfate/sulfide cycle can be treated quantitatively. The following assumptions are made to facilitate this analysis:

1. The only significant chemical species in char are C, Na_2S , Na_2SO_4 , and Na_2CO_3 .
2. Fume formation and sulfur gasification are neglected.
3. The only gaseous species of interest are O_2 , CO_2 , and CO.

The second assumption is useful because it makes Na_2CO_3 and total alkali a constant and also makes the sum of Na_2S and Na_2SO_4 constant. This is a very good first approximation for treating char carbon burnup and sulfate reduction. Even though fuming is obviously significant in a recovery furnace, its effect on carbon burnup and reduction is minor.

The composition of the char is then completely specified by three variables:

$[C]$ = moles char carbon/mole Na_2 (alkali)

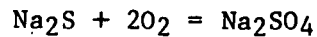
r = reduction efficiency = $\text{Na}_2\text{S}/(\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4)$ (in moles)

s = mole S/mole Na_2

Note that s is constant by assumption, and only two variables, $[C]$ and r , are functions of time.

The following reactions are considered to take place:

1. The only reaction between char species and O_2 is

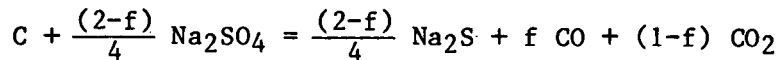


Let R_0 = rate of above oxidation in moles O_2 /mole Na_2 , time

then $1/2 R_0$ = rate of Na_2SO_4 production by this reaction

$1/2 R_0$ = rate of Na_2S depletion by this reaction.

2. Char carbon is oxidized by sulfate according to the reaction



where f is the mole fraction of CO in the product gas coming directly from this reaction.

Let R_C = rate of C - Na_2SO_4 reaction in moles C /mole Na_2 , time

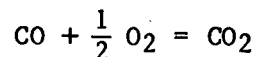
then $f R_C$ = rate of CO production by C - Na_2SO_4

$(1-f)R_C$ = rate of CO_2 production by C - Na_2SO_4

$\frac{(2-f)}{4}R_C$ = rate of Na_2SO_4 depletion by C - Na_2SO_4

$\frac{(2-f)}{4}R_C$ = rate of Na_2S production by C - Na_2SO_4

3. Since O_2 and CO can come in contact in the gas phase, the following reaction is allowed:

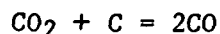


Let R_{CO} = rate of above reaction in moles CO /mole Na_2 , time

then $1/2 R_{CO}$ = rate of O_2 depletion by O_2 - CO

R_{CO} = rate of CO_2 production by O_2 - CO

4. Product CO_2 is allowed to react with C to give CO according to the reaction



Let R_{CO_2} = rate of above reaction in moles CO_2 /mole Na_2 , time

then R_{CO_2} = rate of C depletion by C- CO_2

$2R_{\text{CO}_2}$ = rate of CO production by C- CO_2

Material balances (in moles) can be written per unit mole of alkali in the form:

rate of production - rate of consumption = rate of accumulation.

Only two material balances are needed, given the assumptions that are made. Balances for carbon and sulfide totally describe the system (Na_2CO_3 doesn't change and Na_2SO_4 is known if Na_2S is known).

Carbon balance: Rate of production = 0

Rate of consumption = $R_C + R_{\text{CO}_2}$

Rate of accumulation = $\frac{d}{dt} [C]$

$$\therefore R_C + R_{\text{CO}_2} = \frac{-d[C]}{dt} \quad (4-1)$$

Sulfide balance: Rate of production = $\frac{(2-f)}{4} R_C$

Rate of consumption = $1/2 R_0$

Rate of accumulation = $\frac{d[\text{Na}_2\text{S}]}{dt} = s \frac{dr}{dt}$

$$\therefore \frac{(2-f)}{4} R_C - \frac{R_0}{2} = s \frac{dr}{dt} \quad (4-2)$$

Equations (4-1) and (4-2) describe how the carbon content and sulfur reduction state change during char burning. Given the assumptions made, these two equations contain all the information needed to describe char burning quantitatively. If suitable expressions for R_C , R_O , and R_{CO_2} are available, an analytical solution can be obtained. It is of interest that the rate of CO oxidation, R_{CO} , is not directly involved in char burning. In any given situation, it would affect the final CO/CO₂ ratio and the amount of oxygen actually reaching the char.

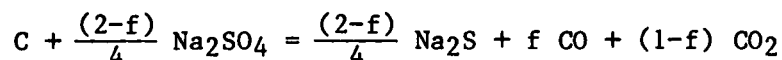
In the following sections quantitative expressions for R_C and R_O will be derived. Evidence will be presented to suggest that R_{CO_2} is not very important and that reactions between sulfate and reducing gases can be neglected. Finally, the results will be applied to burning of char particles.

SULFATE REACTION RATES

Reactions of sulfate during char burning result in its being reduced to sulfide. These are often referred to as reduction reactions. Reduction is a prime chemical recovery function in the recovery furnace, since sulfide is the desired pulping chemical (sulfate is inert during pulping). There are a number of potential reducing agents present within the furnace including carbon, hydrogen gas, and carbon monoxide. Carbon is by far the most important reducing agent.

Carbon-Sulfate Reactions

The stoichiometry of the reaction between carbon and sulfate is given by



It takes between 2 and 4 moles of carbon to reduce one mole of Na_2SO_4 , depending on the CO/CO_2 ratio in the product gases.

The reaction between carbon and sulfate is endothermic (heat absorbing). Heats of reactions calculated from standard heats of formation from the JANAF Tables (16) are given in Table 4-1. The reaction producing CO is about three times as endothermic as the reaction producing CO_2 . There is a very weak temperature dependence. The reactions become slightly less endothermic at increasing temperature. In general, the heat of reaction is a nonlinear function of the mole fraction CO. The nonlinearity occurs because twice as much sulfate is reduced per mole of CO_2 formed as is reduced per mole of CO formed.

Table 4-1. Heats of Carbon-Sulfate Reactions (in Btu/lb Na_2SO_4).

	1340°F 1000°K	1700°F 1200°K	2060°F 1400°K
$\text{Na}_2\text{SO}_4 + 2\text{C} \longrightarrow \text{Na}_2\text{S} + 2\text{CO}_2$	+542	+518	+495
$\text{Na}_2\text{SO}_4 + 4\text{C} \longrightarrow \text{Na}_2\text{S} + 4\text{CO}$	+1576	+1540	+1503

In the general case, the heats of reaction are

$$542 + 1034 f/(2-f) \text{ at } 1340^\circ\text{F};$$

$$518 + 1022 f/(2-f) \text{ at } 1700^\circ\text{F};$$

$$495 + 1008 f/(2-f) \text{ at } 2060^\circ\text{F}.$$

(positive values indicate an endothermic reaction)

Rates of reaction between carbon and sulfate in molten carbonate were determined in a special laboratory system. The laboratory system is shown schematically in Fig. 4-3. The reactor is a small crucible containing molten salt (primarily carbonate). Nitrogen gas was bubbled through the melt to agitate it and sweep out product gas. Reaction rates were measured by monitoring the rates

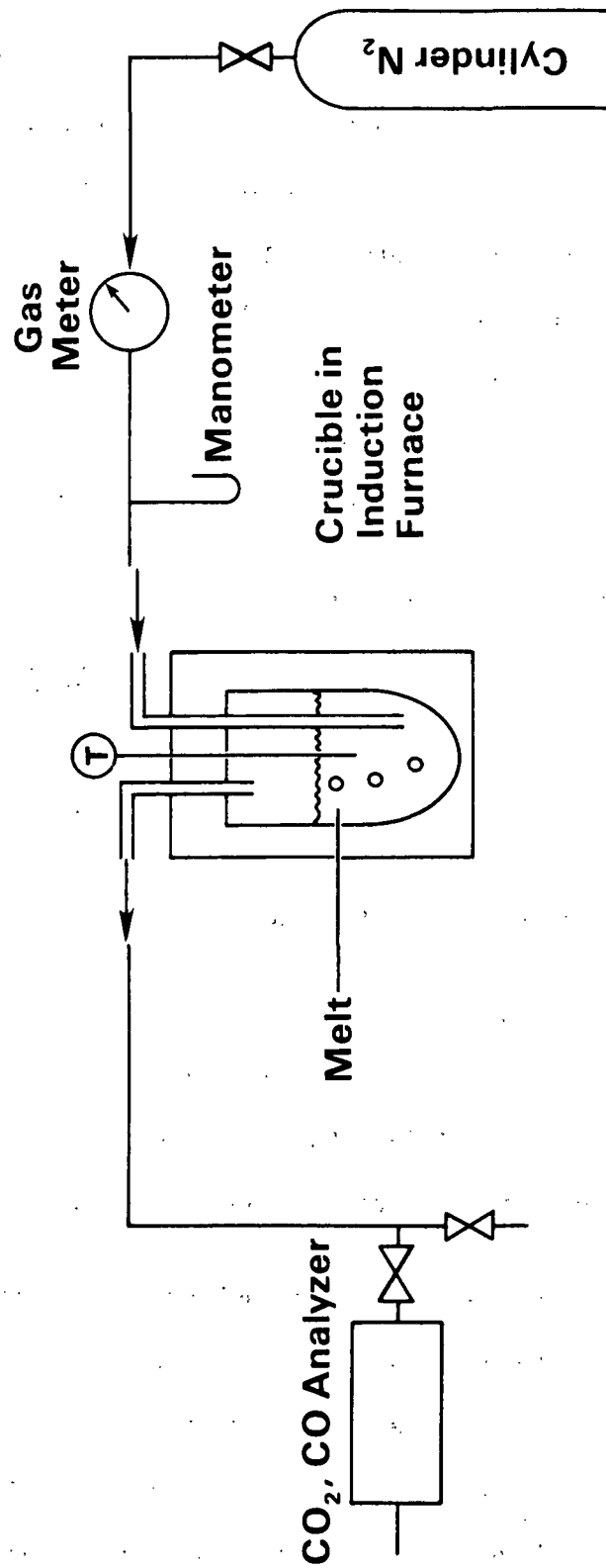


Figure 4-3. Experimental system.

of CO₂ and CO produced. The experimental system and data are described in detail elsewhere (5,19). Only a summary of the results is given in this report. The important features of the experimental system, which influence the interpretation of results, are the use of only small concentrations of carbon and sulfate, and a reaction medium that was clearly a liquid phase.

The rate of reduction between sulfate and three different types of carbon (pulverized graphite, kraft char, and soda char) can be represented by the expression

$$\frac{d[SO_4]}{dt} = - k_1 \left\{ \frac{[SO_4]}{k_2 + [SO_4]} \right\} [C] e^{-\Delta E/RT} \quad (4-3)$$

where [SO₄] = sulfate concentration

[C] = carbon concentration

k₁, k₂ = rate constants in Eq. (4-3)

ΔE = activation energy

R = gas constant

T = absolute temperature

Any consistent set of concentration units (e.g., moles per liter, moles/mole Na₂, etc.) can be used. Rate constant, k₁, has units of inverse time. Rate constant, k₂, must have units compatible with sulfate concentration. Best fit parameters for the constants in Eq. (4-3) are given in Table 4-2.

Table 4-2. Rate parameters for carbon-sulfate reactions.

Carbon Type	k ₁ , sec ⁻¹	k ₂ , mol/liter	ΔE, cal/mol
Kraft char	1.31 ± 0.41 × 10 ³	0.022 ± 0.008	29,200 ± 1000
Pulverized graphite	4.94 ± 0.82 × 10 ⁴	0.026 ± 0.005	44,000 ± 1200
Soda char	3.04 ± 0.73 × 10 ⁵	0.041 ± 0.012	39,850 ± 1500

Direct interpretation of k_1 cannot be made because a coupling between the activation energy and k_1 influences the magnitude of the rate. In order to eliminate this problem it is useful to express the activation energy term as a difference from a reference temperature (e.g., $1200^\circ\text{K} = 1700^\circ\text{F}$).

$$\frac{1}{T} = \frac{1}{T_R + \Delta T} = \frac{1}{T_R} - \frac{\Delta T}{T_R(T_R + \Delta T)} \quad (4-4)$$

Then

$$\frac{d[\text{SO}_4]}{dt} = -k_1 \left\{ \frac{[\text{SO}_4]}{k_2 + [\text{SO}_4]} \right\} [\text{C}] e^{-\Delta E/RT_R + \frac{\Delta E}{RT_R^2} \left(\frac{\Delta T}{1 + \Delta T/T_R} \right)} \quad (4-5)$$

or

$$\frac{d[\text{SO}_4]}{dt} = -k_1' \left\{ \frac{[\text{SO}_4]}{k_2 + [\text{SO}_4]} \right\} [\text{C}] e^{+k_3 \left(\frac{\Delta T}{1 + \Delta T/T_R} \right)} \quad (4-6)$$

where

$$k_1' = k_1 e^{-\Delta E/RT_R} \quad (4-7)$$

$$k_3 = \Delta E/RT_R^2 \quad (4-8)$$

Values of the constants in the modified rate equation are given in Table 4-3.

Interpretation of Eq. (4-6) in terms of the values of the parameters in Table 4-3 provides a good deal of information about sulfate reduction rates.

Table 4-3. Parameters for Modified Carbon-Sulfate Rate Equation.

$$\frac{d[\text{SO}_4]}{dt} = -k_1' \left\{ \frac{[\text{SO}_4]}{k_2 + [\text{SO}_4]} \right\} [\text{C}] e^{+k_3 \left(\frac{\Delta T}{1 + \Delta T/T_R} \right)}$$

($T_R = 1200^\circ\text{K}$, ΔT in $^\circ\text{C}$)

Carbon Type	k_1' , sec^{-1}	k_2 , mol/L	k_3 , $^\circ\text{C}^{-1}$
Kraft char	6.3×10^{-3}	0.022	0.0102
Pulverized graphite	4.8×10^{-4}	0.026	0.0154
Soda char	1.7×10^{-2}	0.041	0.0139

The time scale of the reaction is determined by k_1' . The larger the value of k_1' , the faster the reaction. At 1700°F (1200°K) the kraft char is 13 times as reactive as the pulverized graphite and 40% as reactive as the soda char. (No particular significance should be attached to the differences between kraft char and soda char.) A reaction "time constant" can be defined as $1/k_1'$. This has a value of about 150 seconds for kraft char, 60 seconds for soda char, and 2000 seconds for pulverized graphite. This provides a rough time frame for the reduction reaction at 1700°F.

The effect of sulfate is embodied in the term $\left\{ \frac{[SO_4]}{k_2 + [SO_4]} \right\}$. This term is bounded between zero and one. The parameter k_2 is equal to the sulfate concentration at which the term has a value of 1/2. For kraft char, when $[SO_4]$ equals 0.022 mole/liter, the reduction rate would be 1/2 that at infinitely high sulfate concentration. For a typical smelt, $[SO_4] = 0.022$ mole/L is reached when the reduction efficiency reaches 99.5%. The sulfate term is greater than 0.9 for all reduction efficiencies up to 95%. Thus for all practical purposes the sulfate term can be neglected and the rate of sulfate reduction considered to be independent of sulfate concentration until sulfate is exhausted.

The reaction rate is directly proportional to the carbon concentration (first order in carbon). Since carbon is consumed in the reaction in proportion to sulfate, the carbon dependence will result in an exponential decline in reaction rate with time.

The temperature dependence of the reduction rate is specified by k_3 . The value of k_3 for the kraft char is such that the reaction rate would increase by a factor of two for a 68°C (122°F) temperature rise. For the pulverized graphite, a temperature rise of 45°C (81°F) would double the reaction rate.

The rate of carbon burnup by carbon-sulfate reactions can be obtained from Eq. (4-6) by multiplying by the stoichiometric factor $4/(2-f)$.

$$R_C = \frac{4k_1'}{(2-f)} \left\{ \frac{[SO_4]}{k_2 + [SO_4]} \right\} [C] e^{+k_3 \left(\frac{\Delta T}{1+\Delta T/T_R} \right)} \quad (4-9)$$

The effect of carbon concentration, sulfate concentration, and temperature on the carbon-sulfate reaction rate is illustrated in Fig. 4-4.

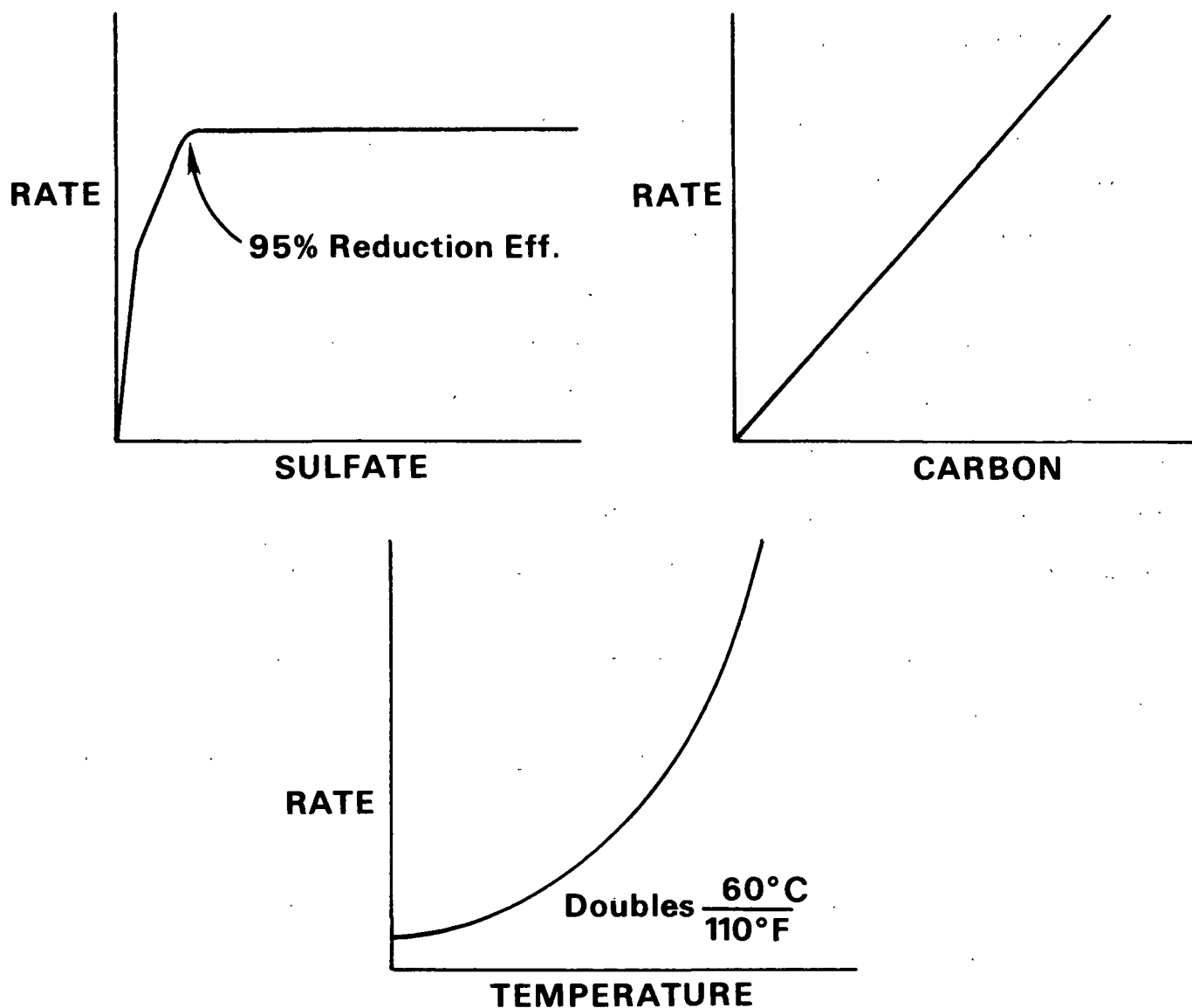


Figure 4-4. Equilibrium CO/CO₂ distribution.

Sulfate Reduction by Carbon Monoxide

The rate of reduction of sodium sulfate by carbon monoxide gas was studied by Sjöberg (20) by bubbling a CO containing gas stream through a sulfate-carbonate melt and measuring the rate of CO₂ production according to the reaction $\text{Na}_2\text{SO}_4 + 4\text{CO} \longrightarrow \text{Na}_2\text{S} + 4\text{CO}_2$. She found that the reduction rate could be described by

$$\frac{d[\text{SO}_4]}{dt} = -k_{\text{CO}} P_{\text{CO}} e^{-\Delta E_{\text{CO}}/RT} \quad (4-10)$$

where $k_{\text{CO}} = 31.7 \text{ moles/L atm. sec.}$

P_{CO} = partial pressure of CO, atm.

$\Delta E_{\text{CO}} = 27,500 \text{ cal/mole}$

and the remaining terms have been defined previously. The rate is dependent only on the partial pressure of CO and the temperature. It is independent of the sulfate concentration until sulfate is practically depleted. She also found that iron or iron salts did not catalyze the reaction.

The magnitude of the activation energy, experiments with different purge tube geometries, and the much higher reaction rates observed for sulfide oxidation by air in the same reaction system all indicate that the reduction rate in these experiments was not controlled by mass transfer of CO from gas to melt.

By using a reference temperature of 1200°K (1700°F), Eq. (4-10) can be converted to

$$\frac{d[SO_4]}{dt} = -k'_{CO} P_{CO} e^{+k''_{CO} \left(\frac{\Delta T}{1 + \Delta T/T_R} \right)} \quad (4-11)$$

with $k'_{CO} = 3.1 \times 10^{-4} \text{ sec}^{-1} \text{ atm}^{-1} \text{ mol/L}$

$k''_{CO} = 0.0096 \text{ } ^\circ\text{C}^{-1}$

$T_R = 1200^\circ\text{K} (1700^\circ\text{F})$

$\Delta T = T - T_R, \text{ } ^\circ\text{C}$

The relative rate of sulfate reduction by CO and by kraft char can be obtained by dividing Eq. (4-11) by Eq. (4-6). (It is assumed the sulfate term in Eq. (4-6) is equal to one).

$$\left(\frac{\text{Rate with CO}}{\text{Rate with kraft char}} \right)_{1700^\circ\text{F}} = \frac{3.1 \times 10^{-4} P_{CO}}{6.3 \times 10^{-3} [C]} \approx \frac{0.05 P_{CO}}{[C]}$$

where P_{CO} is in atm and $[C]$ is in moles/L. We might expect P_{CO} to be on the order of 0.1 atm inside the furnace. A carbon concentration of 1 mole/L would correspond to about 0.05 mole C/mole Na_2 . This would only be reached at the end of char burning after about 98% of the char carbon had burned off. Thus we can state with reasonable confidence that

$$\frac{\text{Rate of reduction with CO}}{\text{Rate of reduction with char}} < 0.005$$

This calculation supports the contention that sulfate reduction by CO gas in the furnace environment is insignificant and can be ignored.

Reduction by Hydrogen Gas

Limited data on the rate of reduction of sulfate in molten alkali carbonates by hydrogen gas have been published (21). The experiments were carried out in graphite crucibles which may have influenced the results to some extent. The findings can be summarized as follows:

1. The reaction rate was zero order in sulfate concentration.
2. The reaction order with respect to hydrogen was 0.67 (for CO the order was unity).
3. The reaction was catalyzed by iron. The catalyzed rate was 6 times faster at 600°C, but this difference was negligible at 1000°C).
4. The rate was 0.4 order in sulfide. This represents an autocatalytic behavior. (We never found any dependence on sulfide concentration in any of our work).
5. The activation energy is 26,300 cal/mole (this is about the same temperature dependence shown by CO).
6. At 840°C (1544°F) hydrogen reduction of sulfate was about 3.6 times as fast as reduction by carbon monoxide. This relative rate would not be very sensitive to temperature.

Although sulfate reduction by hydrogen may be somewhat faster than reduction by CO, it is still about two orders of magnitude slower than reduction by kraft char. Sulfate reduction by hydrogen can be ignored in char burning.

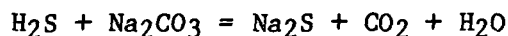
Other Paths to Sulfide

Although the main route to sulfide is through reduction of sulfate by carbon, two other pathways need to be examined. These are

1. Absorption of H₂S gas by molten Na₂CO₃
2. Thermal decomposition of thiosulfate

Absorption of Hydrogen Sulfide

Sodium sulfide can form by reaction between H₂S and Na₂CO₃.



This is more appropriately described as absorption of H_2S from the gas phase followed by reaction.

The equilibrium of the above reaction has been used to interpret the effect of lower furnace temperature on sulfur emissions (22). The equilibrium constant is given as

$$K = \frac{P_{CO_2} P_{H_2O} a_{Na_2S}}{P_{H_2S} a_{Na_2CO_3}} \quad (4-12)$$

where the P's are partial pressures of the gases in atm and the a's are activities of the sulfide and carbonate. Values of the equilibrium constant calculated from data in the JANAF Tables are as follows:

Temperature, °F	1340	1700	2060
K	2.32	30.2	323

It is apparent that the equilibrium shifts to the right as temperature increases. The significance of this equilibrium can be most easily seen by considering equilibrium partial pressures of H_2S expressed in ppm. In the furnace the partial pressures of CO_2 and H_2O will be on the order of 0.1 atm each and the ratio of concentrations of Na_2S to Na_2CO_3 will be about 1/2 to 1/3. Thus the equilibrium P_{H_2S} will be on the order of 3000/K ppm. At 1340°K, the equilibrium P_{H_2S} is about 1300 ppm. At 1700°F, it is in the range of 100 ppm, and at 2060°F it is around 10 ppm. As a bench mark, if all of the sulfur in the incoming black liquor solids was present as H_2S in flue gas, the concentration would be on the order of 5000 ppm.

The major source of H_2S in the black liquor combustion process is pyrolysis of the black liquor solids. Pyrolysis initiates at relatively low

temperatures and much of the sulfur can be driven off as H_2S if the pyrolysis is carried out at lower temperatures where the equilibrium is unfavorable for H_2S absorption. In this case, the reaction between H_2S and Na_2CO_3 would not be a significant source of sodium sulfide. The released sulfur would be oxidized to SO_2 or SO_3 in the upper furnace and partially reclaimed as recycled Na_2SO_4 added to the liquor being fired. However, if pyrolysis is carried out at high temperatures where at least the outer layer of the pyrolyzing particle is molten and the equilibrium is favorable, relatively little H_2S would be released and a good deal of sodium sulfide could be formed.

Borg et al. (12) reported the following relationship between the concentration of H_2S measured just above the bed and the bed surface temperature.

Bed Temperature, °C	H_2S (ppm) Above Bed
725(1335°F)	5250
825(1515°F)	750
860(1580°F)	250

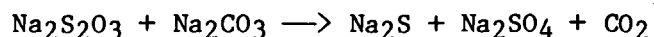
These data are in general agreement with the equilibrium predictions, and suggest that considerable pyrolysis is continuing on the bed in a furnace.

Release of H_2S and its readsorption by Na_2CO_3 will not be significant after the char has formed (particularly a well pyrolyzed char). H_2S absorption can play a role in determining the relative amounts of sulfate and sulfide in the char at the start of char burning. The reverse reaction should not be a major source of H_2S release at burning temperature. We have confirmed this. Sulfur retentions in a series of sequential reduction and oxidation experiments lasting over a week were greater than 95%

Thiosulfate Decomposition

Thiosulfate can be a significant constituent in the incoming black liquor. Although it has been shown that thiosulfate tends to decompose and release H_2S during pyrolysis with organic matter (15,23), some thiosulfate could enter the smelt. Thus it is of interest to examine the fate of thiosulfate in carbonate melts.

Addition of thiosulfate to molten carbonate results in the formation of sulfate and sulfide and the release of CO_2 . This can be explained by the reaction.



Thus thiosulfate is unstable in smelt and forms equal amounts of sulfide and sulfate. The decomposition is quite rapid and we have been unable to get reliable kinetic data on it. If thiosulfate is premixed with carbonate and then heated up to the melting point, the decomposition is essentially complete before temperature equilibrium is established. If thiosulfate is added to molten carbonate, the evolution of CO_2 is so violent that the addition must be strung out to prevent smelt boil over. By the time all of the thiosulfate is added, the decomposition is practically over.

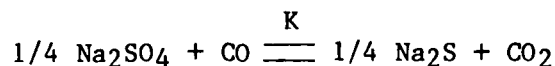
For all practical purposes thiosulfate decomposition can be taken as an infinitely fast reaction under furnace conditions, and thiosulfate may be treated as an equal mixture of sulfate and sulfide. There is no reason to believe that thiosulfate can exist for more than a few seconds in molten smelt.

CO-CO₂ Distribution

CO_2 was the dominant reaction product in the carbon-sulfate rate experiments. Typically, CO_2 rates were at least 10 times the CO rate. Generally, the

CO/CO₂ ratio increased with increasing temperature. It also tended to increase slightly as the reduction proceeded. The usual behavior was for the CO₂ rate to drop off as the reaction proceeded, while the CO rate remained more constant (albeit at a very low level). In some cases, when sulfate was depleted, there would be a brief rise and fall in CO.

This behavior is in general agreement with the predictions of thermodynamic equilibrium for this system. The reaction equilibrium governing CO/CO₂ distribution is

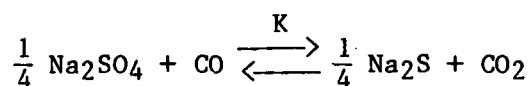


The governing equilibrium equation is

$$K = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \left(\frac{a_{\text{Na}_2\text{S}}}{a_{\text{Na}_2\text{SO}_4}} \right)^{1/4} \quad (4-13)$$

where P_{CO_2} and P_{CO} are partial pressures of CO₂ and CO, respectively, and $a_{\text{Na}_2\text{S}}$ and $a_{\text{Na}_2\text{SO}_4}$ are activities of sulfide and sulfate, respectively. The relevant equilibrium data calculated from data in the JANAF Tables (16) are summarized in Table 4-4.

Table 4-4. Equilibrium CO/CO₂ distribution.



Temperature, °K	1000	1200	1400
Temperature, °F	1340	1700	2060
K	29.4	12.9	7.08

The ratio of CO_2 to CO in the off gas would equal the ratio of partial pressures. Lacking information on activity coefficients for sulfide and sulfate in molten carbonate, the activities can be set equal to concentrations. For sulfide, the concentration is proportional to the reduction efficiency, while the sulfate concentration is proportional to one minus the reduction efficiency. Thus

$$\frac{\text{CO}_2}{\text{CO}} = K \left(\frac{1-r}{r} \right)^{1/4} \quad (4-14)$$

where r = reduction efficiency.

This states that the CO_2/CO ratio is a function of temperature (K is a function of temperature) and the degree of reduction. The temperature dependence of K is evident in Table 4-4.

The reduction efficiency term is a weakly varying function because of the $1/4$ power. Values are summarized below

$\left(\frac{1-r}{r} \right)^{1/4}$					
$\frac{1.00}{0.5}$	$\frac{0.707}{0.8}$	$\frac{0.577}{0.9}$	$\frac{0.479}{0.95}$	$\frac{0.378}{0.98}$	

The equilibrium considerations predict that the CO_2/CO ratio will decrease with increasing temperature and with increasing degree of reduction. This is in agreement with the general form of the data. Note that the measured CO_2/CO ratios on the order of 10 to 1 are about what is expected from equilibria in the temperature range of the experiments.

OXIDATION RATES

As was mentioned earlier, oxidation of char carbon can occur through a sulfate-sulfide cycle as well as by direct oxidation with air. In order to

demonstrate the dominance of the sulfate-sulfide cycle, oxidation rates in each of the following systems must be obtained and interpreted.

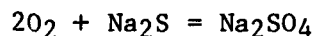
1. Sulfide oxidation in molten carbonate
2. Carbon oxidation in sulfur-free molten carbonate
3. Carbon oxidation by air in molten carbonate containing sulfur.

Experimental System

The same laboratory system which was used for carbon-sulfate rate determinations was used for the oxidation studies. The system was shown in Fig. 4-3. For oxidation experiments, the purge gas was an O₂-N₂ mixture, and the O₂ content of the off gas was measured as well as CO and CO₂. Details of the experimental system, procedures and data are given in Ref. (24).

Sulfide Oxidation

The oxidation of sulfide is described by the reaction;



Sulfide oxidation in molten carbonate is an inherently fast reaction. In experiments (24) in which air was bubbled thru molten carbonate containing sulfide, the oxygen was consumed as fast as it was supplied until very low sulfide concentrations were reached. A typical result is shown in Fig. 4-5. The break occurs at about 0.1 mole/liter, which corresponds to a reduction efficiency of 2% in a typical smelt.

These results indicate that sulfide oxidation would be oxygen mass transfer controlled under almost any circumstances. Control would shift to inherent chemical kinetics only when the sulfide is essentially depleted.

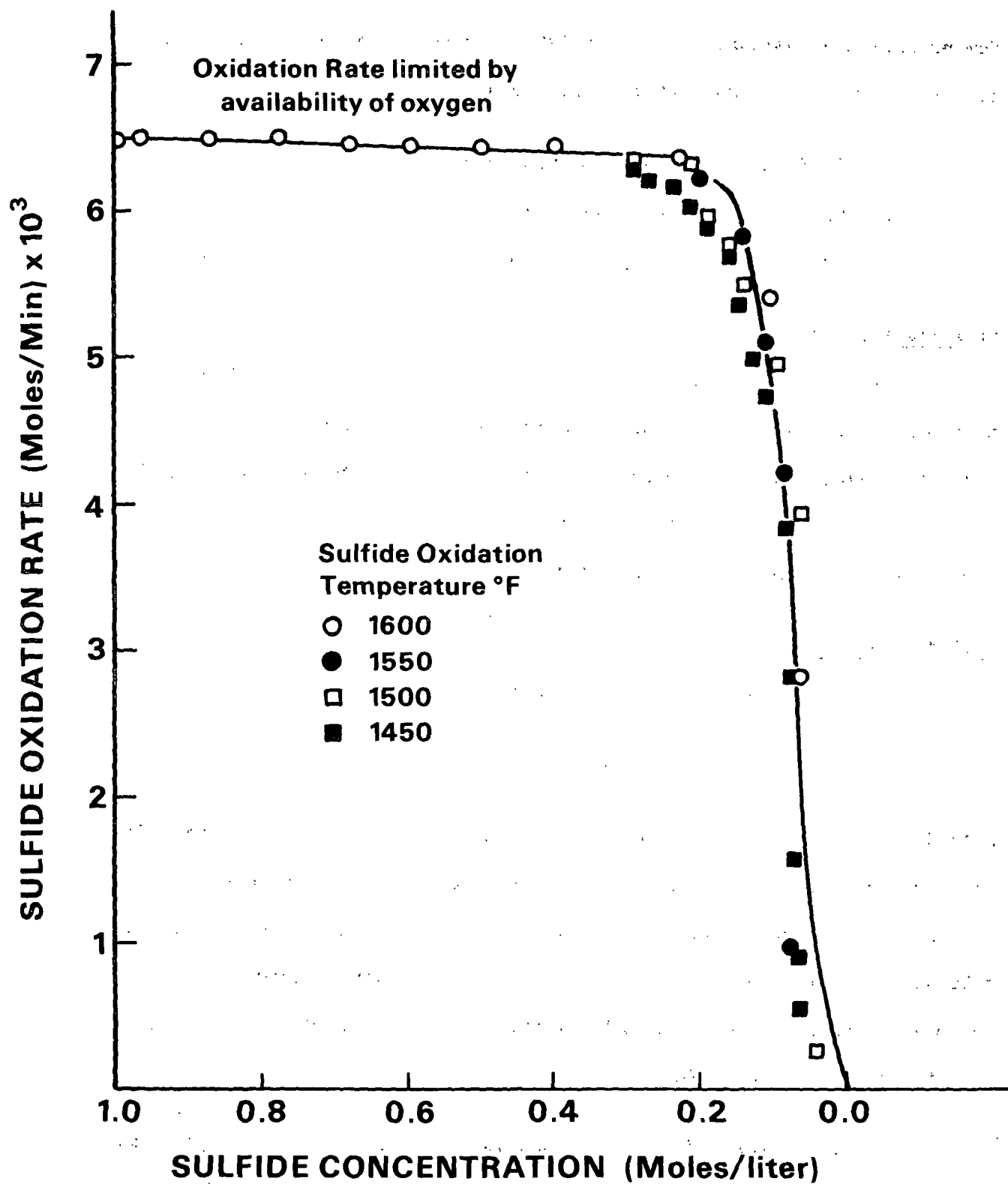


Figure 4-5. Sulfide oxidation rates.

Direct Carbon Oxidation

Direct carbon oxidation refers to the reaction between carbon and oxygen in the presence of large quantities of inorganic salt (sodium carbonate). In order to avoid interferences due to parallel reactions with sulfate and/or sulfide, this reaction must be studied in sulfur-free systems.

Experimental measurements of carbon oxidation rates in molten carbonate were obtained for two forms of carbon: pulverized graphite and the soda char. The reaction rate was first order in carbon content, independent of oxygen partial pressure, and increased with increasing temperature. The rate data could be described by the equation,

$$\frac{d[C]}{dt} = -k_o[C] e^{-\Delta E_o/RT} \quad (4-15)$$

where k_o is the direct oxidation rate constant and ΔE_o is the activation energy. As before, Eq. (4-15) can be expressed in terms of the temperature difference from a 1200°K (1700°F) reference temperature.

$$\frac{d[C]}{dt} = -k_o' [C] e^{+k_o'' \left(\frac{\Delta T}{1+\Delta T/T_R} \right)} \quad (4-16)$$

Values for the rate parameters are summarized in Table 4-5.

Table 4-5. Direct oxidation rate parameters.

Carbon Type	k_o , sec ⁻¹	ΔE_o cal/mol	k_o' , sec ⁻¹	k_o'' , °C ⁻¹
Pulverized graphite	123	27,900	1.02×10^{-3}	9.75×10^{-3}
Soda char	172	26,400	2.67×10^{-3}	9.22×10^{-3}

Because the rate is first order in carbon, carbon burnup follows a simple exponential decay. The half-life of the carbon at 1700°F is 680 sec for pulverized graphite and 260 sec for soda char. The temperature dependence is such that the rate increases by about a factor of 2.5 for a 100°C rise for pulverized graphite and about 2.35 for soda char. Direct carbon oxidation is a relatively slow reaction.

Graphite oxidation in molten carbonate has also been studied by Dunks et al. (25,26). They used a larger particle size, spectroscopic grade of carbon and got a similar, but somewhat more complex, kinetic expression. They state that the effect of sodium carbonate is to lower the ignition temperature or onset of weight loss of carbon by 150-175°C, thus acting as a rather efficient catalyst for the oxidation. This implies that direct carbon oxidation below the melting point is an even slower reaction than the reaction rates measured in this study.

In all of our experiments with direct carbon oxidation, the product gas was almost entirely CO₂. Similar results were found by Dunks et al. (25).

Carbon Oxidation with Sulfur Present

Experimental carbon burnup data with sulfur present were obtained by bubbling air thru a carbonate melt containing carbon and some sulfate. Because of the exothermic nature of the oxidation reactions, temperature control was not as straightforward as for reduction reactions, and this interfered somewhat with the data. This problem was more prevalent when relatively large amounts of sulfate were used.

Three different forms of carbon were used in these experiments: kraft char, soda char, and pulverized graphite. The most striking result was obtained with the kraft char (which has a small amount of sulfur in it). When the kraft

char was burned with air in a carbonate melt, the rate data were fit to the expression

$$\frac{d[C]}{dt} = -k_{KC}[C] e^{-\Delta E_{KC}/RT} \quad (4-17)$$

where $k_{KC} = 3,910 \text{ sec}^{-1}$

$\Delta E_{KC} = 30,170 \text{ cal/mol}$

This can be transformed as usual for a 1200°K reference temperature to

$$\frac{-d[C]}{dt} = 0.0125 [C] e^{+0.0105\left(\frac{\Delta T}{1+\Delta T/T_R}\right)} \quad (4-18)$$

(t in sec, ΔT in °C)

Eq. (4-18) is an experimentally-based rate equation for kraft char burnup when bubbling an O_2 - N_2 mixture through molten carbonate containing kraft char.

Earlier we developed an expression [Eq. (4-9)] for the rate of carbon burnup by carbon-sulfate reaction, R_C .

$$R_C = \frac{4k_1'}{(2-f)} \left\{ \frac{[SO_4]}{k_2 + [SO_4]} \right\} [C] e^{+k_3 \left(\frac{\Delta T}{1+\Delta T/T_R} \right)} \quad (4-9)$$

For the kraft char, $k_1' = 6.3 \times 10^{-3} \text{ sec}^{-1}$ and $k_3 = 0.0102^\circ\text{C}^{-1}$ ($T_R = 1200^\circ\text{K}$ and the sulfate term can be taken = 1). These values were obtained for carbon reacting with sulfate with no oxygen present in the purge gas.

$$\therefore R_C = \frac{-d[C]}{dt} = \frac{2.52 \times 10^{-2}}{(2-f)} [C] e^{+0.0102\left\{\frac{\Delta T}{1+\Delta T/T_R}\right\}} \quad (4-19)$$

If we compare Eq. (4-18) with Eq. (4-19) we see that they are practically identical for $f = 0$. A value of $f = 0$ corresponds to only CO_2 produced, which was essentially the experience in these experiments.

The fact that the rate expression for kraft char oxidation with air is the same as the rate expression for kraft char-sulfate reactions is very strong evidence that the kraft char burned via the sulfate-sulfide cycle in these experiments.

Only limited data were obtained on soda char, but it also appears to burn via the sulfate-sulfide cycle. Figure 4-6 shows the measured carbon burnup rate during one experiment on the air oxidation of soda char with sulfur present. Figure 4-6 also shows the predicted carbon burnup rates for sulfate oxidation of soda char [from Eq. (4-9) with $f = 0$] and for direct air oxidation of soda char without sulfur present [from Eq. (4-16)]. There is good agreement between the measured burning rate and that predicted for the sulfate-soda char reaction.

Somewhat different behavior was experienced with the pulverized graphite. The carbon burnup rate during air oxidation with sulfur present was about equal to the sum of the individual burnup rates (carbon-sulfate and direct carbon oxidation). This indicates that the sulfate-sulfide cycle and direct oxidation are occurring simultaneously in this case.

The apparent difference between the behavior of soda char and pulverized graphite can be rationalized. For soda char, the carbon-sulfate rate was about one order of magnitude greater than the direct carbon oxidation rate and any additive effect would be very difficult to detect. For the pulverized graphite, the two individual rates were of the same order, and the additive nature of burnup was evident.

Significance

All of the oxidation data obtained support the idea that the sulfate-sulfide cycle is dominant in char burning. The very rapid inherent kinetics of

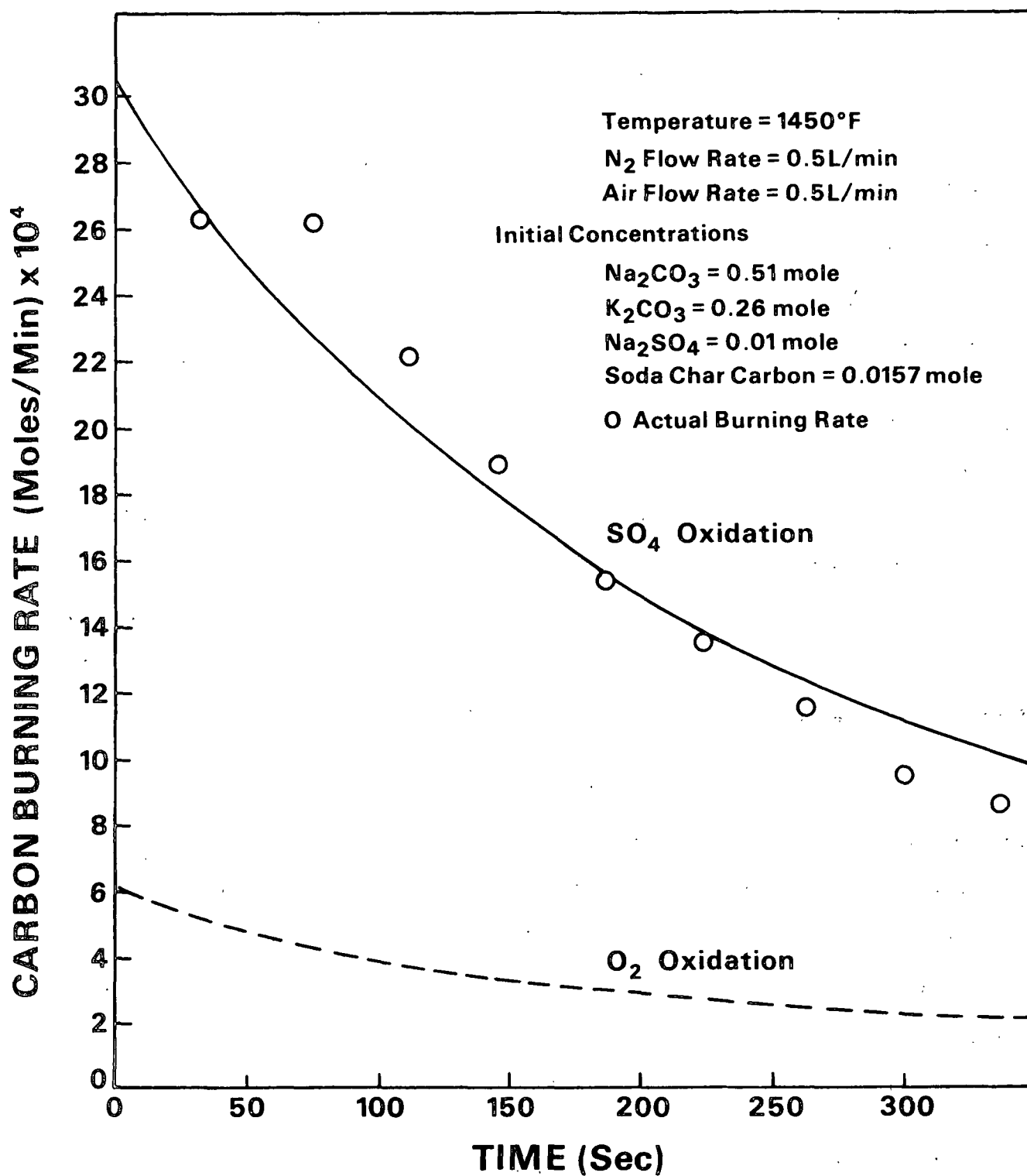


Figure 4-6. Soda char burning curves.

sulfide oxidation in molten carbonate is a key element. In effect, sulfide gets "first call" on any oxygen that arrives.

The experimental system that was used in these oxidation studies was one that tended to put the rate limiting step on the carbon reaction side. Sufficient oxygen was available to rapidly reoxidize any sulfide formed so that essentially all of the sulfur in the system was present as sulfate. This explains the excellent agreement between carbon burnup rates and carbon-sulfate reaction rates.

Parallel oxidation behavior (overall burning rate is the sum of carbon-sulfate and direct carbon oxidation) will only be observed in systems with no limitations on oxygen access. In such systems the sulfur is present as sulfate, and excess oxygen is capable of dissolving in carbonate and reacting directly with carbon. If any sulfide is present it will "scavenge" the oxygen because of the inherently rapid sulfide oxidation kinetics. Thus only carbon-sulfate reactions can burn carbon in O_2 mass transfer limited burns.

The oxidation results also support the idea that carbon gasification by reaction with CO_2 can be neglected during char burning. There is no reason to suspect that reactions between CO_2 and char carbon would be any faster than the direct O_2 -char carbon reactions. Since direct carbon oxidation rates for char were considerably lower than char-sulfate rates, CO_2 -C rates would also be much lower. Both direct carbon oxidation and CO_2 -char reactions can be neglected when the sulfate-sulfide cycle is operative.

THEORY OF CHAR BURNING

We are now in a position to pick up with the quantitative analysis of char burning via the sulfate-sulfide cycle at the point where it was left off.

At that point carbon and sulfide balances had led to two general equations (4-1 and 4-2) that described how the carbon content of the char and the sulfur oxidation state (expressed as a reduction efficiency) changed during char burning.

These equations are:

$$R_C + R_{CO_2} = \frac{-d[C]}{dt} \quad (4-1)$$

and

$$\frac{(2-f)}{4} R_C - \frac{R_O}{2} = s \frac{dr}{dt} \quad (4-2)$$

where R_C = rate of carbon burnup by C-Na₂SO₄ reactions

R_{CO_2} = rate of carbon burnup by CO₂-C reactions

R_O = rate of oxygen consumption by Na₂S-O₂

$[C]$ = carbon concentration, moles/mole Na₂

f = molar CO/(CO₂ + CO) ratio

r = "reduction efficiency" Na₂S/(Na₂S + Na₂SO₄)

s = moles S/mole Na₂

In subsequent sections it was shown that

$$R_C = \frac{4k_1'}{(2-f)} \left\{ \frac{[SO_4]}{k_2 + [SO_4]} \right\} [C] e^{+k_3 \left(\frac{\Delta T}{1+\Delta T/T_R} \right)} \quad (4-9)$$

with numerical values of the rate constants found for a kraft char, a soda char, and pulverized graphite.

It was also shown that the rate of reaction between O₂ and Na₂S was intrinsically very fast, so that either R_O was limited by O₂ mass transfer considerations or by sulfide depletion. (In the latter case the effective sulfide concentration would be zero and R_O would take on whatever value it needed to match the rate of formation of sulfide.)

For the present, R_{CO_2} will be neglected. Any effects of secondary CO_2 -C reactions can be handled through the factor, f , that specifies the CO/CO_2 ratio.

Before considering the general case of char burning, it is helpful to examine two limiting cases which bound the general case. The two limiting cases are

1. Unlimited oxygen access
2. Oxygen limited burning

Unlimited Oxygen Access

In this case sufficient O_2 is available to contact the char and immediately react with any sulfide. There is no rate limitation to the oxygen supply and thus the sulfide concentration in the char is negligibly small. (This condition was closely approached in the oxidation experiments in the laboratory smelt pool reactor.) In this limiting case $r = 0$ and $dr/dt = 0$. Then Eq. (4-1) becomes

$$\frac{-d[C]}{dt} = \frac{4k_1'}{(2-f)} \left\{ \frac{[SO_4]}{k_2 + [SO_4]} \right\} [C] e^{+k_3 \left(\frac{\Delta T}{1+\Delta T/T_R} \right)} \quad (4-20)$$

As was discussed earlier when the char-sulfate rate data were considered, the sulfate containing term in Eq. (4-20) is close to unity until very high reduction efficiencies are obtained. In the limiting case being considered here, the reduction efficiency is zero, and the sulfate term can be taken as equal to one. Then Eq. (4-20) becomes

$$\frac{d[C]}{dt} = \frac{-4k_1'}{(2-f)} [C] e^{+k_3 \left(\frac{\Delta T}{1+\Delta T/T_R} \right)} \quad (4-21)$$

At a constant temperature, the char carbon content will decay exponentially. The fractional rate of carbon depletion depends only on temperature. This is exactly the behavior that was found in the oxidation experiments discussed previously.

For the case of unlimited oxygen access, Eq. (4-2) becomes,

$$R_0 = \frac{(2-f)}{2} R_C = 2 k_1' [C] e^{+k_3 \frac{\Delta T}{(1+\Delta T/T_R)}} \quad (4-22)$$

The oxygen pick up rate just matches what is needed to burn off the carbon. The sulfur remains fully oxidized as the burning proceeds.

Oxygen Limited Burning

The other limiting case is that in which the rate of the entire cycle is totally controlled by the rate of oxygen supply (O_2 mass transfer rate). The reduction efficiency will be at a limiting value very close to 100%. Again $dr/dt \approx 0$, and Eq. (4-2) becomes

$$R_C = \frac{2}{(2-f)} R_0 = \frac{-d[C]}{dt} \quad (4-23)$$

In this case, the rate of carbon burnup is completely controlled by the value of R_0 . For example, if the oxygen supply is mass transfer limited we might have

$$R_0 = k_{O_2} A P_{O_2} \quad (4-24)$$

where k_{O_2} = oxygen mass transfer coefficient, moles O_2 /area time atm

A = contact area between oxygen supply and char, area/mole Na_2

P_{O_2} = oxygen partial pressure, atm

Equation (4-1) then takes on the form

$$R_O = k_{O_2} A P_{O_2} = 2 k_1' \left\{ \frac{[SO_4]}{k_2 + [SO_4]} \right\} [C] e^{+k_3 \frac{\Delta T}{(1+\Delta T/T_R)}} \quad (4-25)$$

This equality must hold as the burning proceeds ([C] will decrease as burning proceeds). At a given temperature, the equality in Eq. (4-25) can only be maintained if the sulfate-containing term adjusts itself. Equation (4-25) can be rewritten as

$$\left\{ \frac{[SO_4]}{k_2 + [SO_4]} \right\} = \frac{k_{O_2} A P_{O_2}}{2 k_1' [C]} e^{-k_3 \frac{\Delta T}{(1+\Delta T/T_R)}} \quad (4-26)$$

Since the characteristics of the carbon-sulfate reaction are such that $\left\{ \frac{[SO_4]}{k_2 + [SO_4]} \right\}$ does not deviate much from one until very high reduction efficiencies are reached, Eq. (4-26) guarantees a high reduction efficiency during char burning as long as sufficient carbon is present. [Note, if the right hand side of Eq. (4-26) takes on a value greater than 1, this limiting case cannot exist.]

The two basic characteristics of oxygen limited burning are evident in Eq. (4-23) and (4-26). They are

1. Carbon depletion is a linear function of time if the oxygen mass transfer rate is constant.
2. The reduction efficiency is very high as burning proceeds.

General Case

The same basic equations apply to the general case, except that they must be solved simultaneously. Using the values for the rate constants for the kraft char, and assuming $f = 0$, we get

$$\frac{-d[C]}{dt} = 1.26 \times 10^{-2} \left\{ \frac{(1-r)s}{0.0011 + (1-r)s} \right\} [C] e^{+0.0102\Delta T/(1+\Delta T/T_R)} \quad (4-27)$$

and

$$\frac{dr}{dt} = -\frac{1}{2s} \frac{d[C]}{dt} - \frac{R_0}{2s} \quad (4-28)$$

subject to the restriction that $0 \leq r \leq 1$

In deriving Eq. (4-27) and (4-28), use was made of the fact that $[SO_4]$ in moles/mole $Na_2 = s(1-r)$, and $k_2 = 0.022 \text{ mol/L} = \frac{0.022 \text{ mole/L}}{20 \text{ moles } Na_2/L} = 0.0011 \text{ mole/mole } Na_2$.

A generalized solution can be written for Eq. (4-27) defining $k''(T) = 1.26 \times 10^{-2} e^{+0.0102 \Delta T/(1+\Delta T/T_R)}$ and $f(r) = \frac{(1-r)s}{0.0011 + (1-r)s}$.

The solution is

$$[C] = [C]_0 e^{-\int_0^t k''(T)f(r)dt'} \quad (4-29)$$

where $[C]_0$ is the initial carbon concentration.

Equation (4-28) can be solved directly by integration.

$$r - r_0 = \int_0^t \left(\frac{dr}{dt'} \right) dt' = -\frac{1}{2s} \int_0^t \frac{d[C]}{dt'} dt' - \frac{1}{2s} \int_0^t R_0 dt'$$

where r_0 = initial reduction

Thus for a constant value of R_0 ,

$$r = r_0 + \frac{1}{2s} \{ [C]_0 - [C] \} - \frac{R_0}{2s} t \quad (4-30)$$

It is most convenient to have temperature constant. In this case $k''(T)$ is a constant and comes out of the integral in Eq. (4-29). Then Eq. (4-29) states that the carbon will decay along an exponential curve, except for the effect of $f(r)$. The function, $f(r)$, has a value close to one until r begins to

approach one, at which point $f(r)$ begins to drop rapidly. Marked deviations from exponential decay occur at very high reductions. Equation (4-30) is a simple, linear algebraic equation which is an oxygen balance over the duration of the burn.

Equations (4-29) and (4-30) can be solved numerically. The resultant curves show how the carbon content $[C]$ and the state of reduction vary with time as char burns. These are very useful in demonstrating the essential features of the char burning process.

Figure 4-7 shows two cases at a temperature of 1700°F . The values of the parameters are

$$[C]_0 = 3 \text{ moles/mole Na}_2$$

$$r_0 = 0.5$$

$$s = 1/3 \text{ mole S/mole Na}_2$$

$$T = 1200^{\circ}\text{K} = 1700^{\circ}\text{F}$$

$$R_0 = 0.01 \text{ and } 0.05 \text{ mole O}_2/\text{mole Na}_2, \text{ sec.}$$

These two values of R_0 span the range between oxygen limited burning and unlimited oxygen access.

The case with $R_0 = 0.01$ is one where the burning rate is limited by the rate of oxygen supply. There are three distinct periods in the burning curve. In the initial period the sulfate initially present in the char is reduced and the reduction rises quite rapidly to very high values (99+%). During this period the carbon content falls rapidly along an exponential curve. The second period begins when the limit on reduction efficiency is reached. Reduction remains very close to 100% during this period, and the carbon burnup rate slows

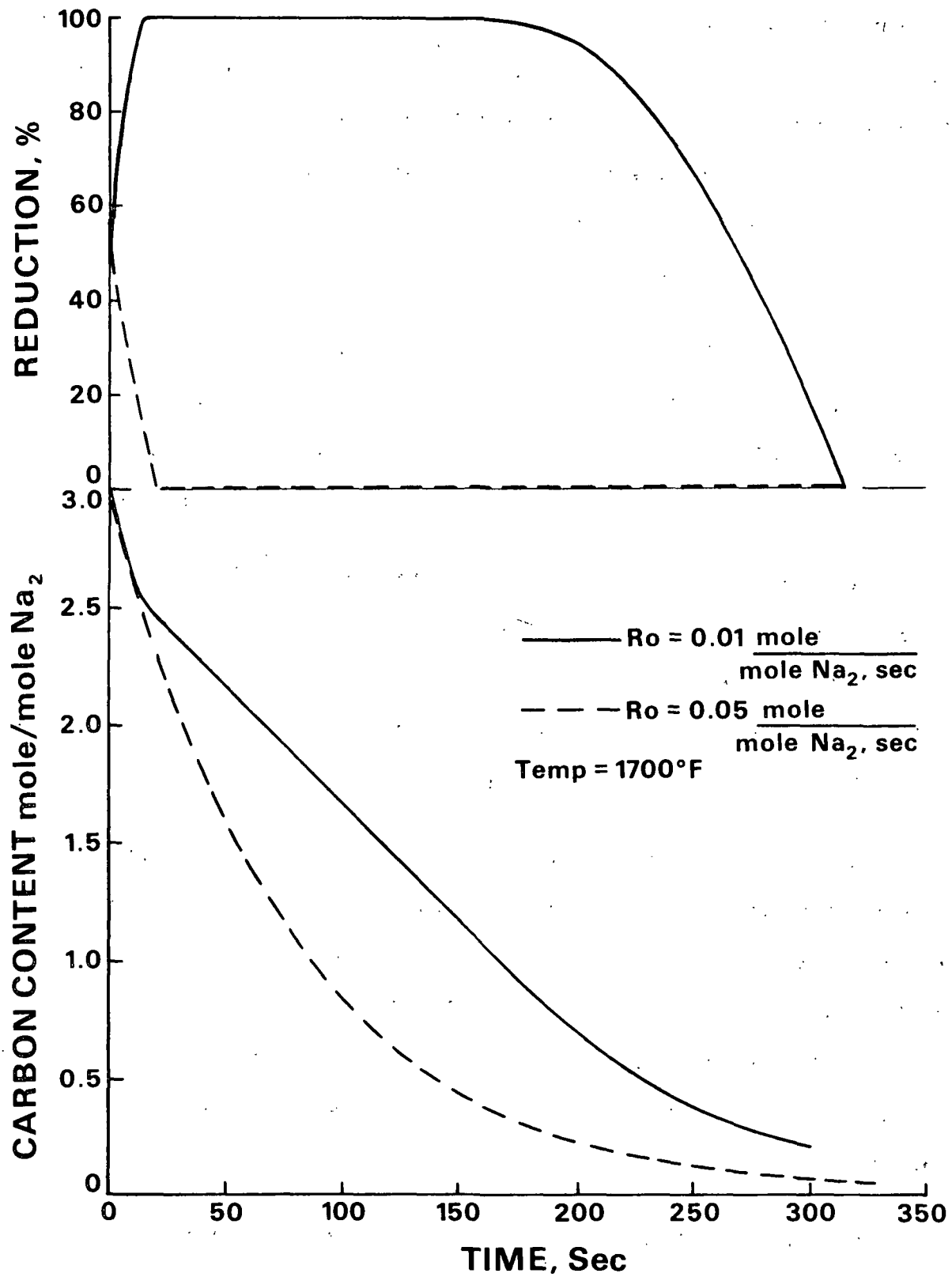


Figure 4-7. Calculated burning curves at 1700°F.

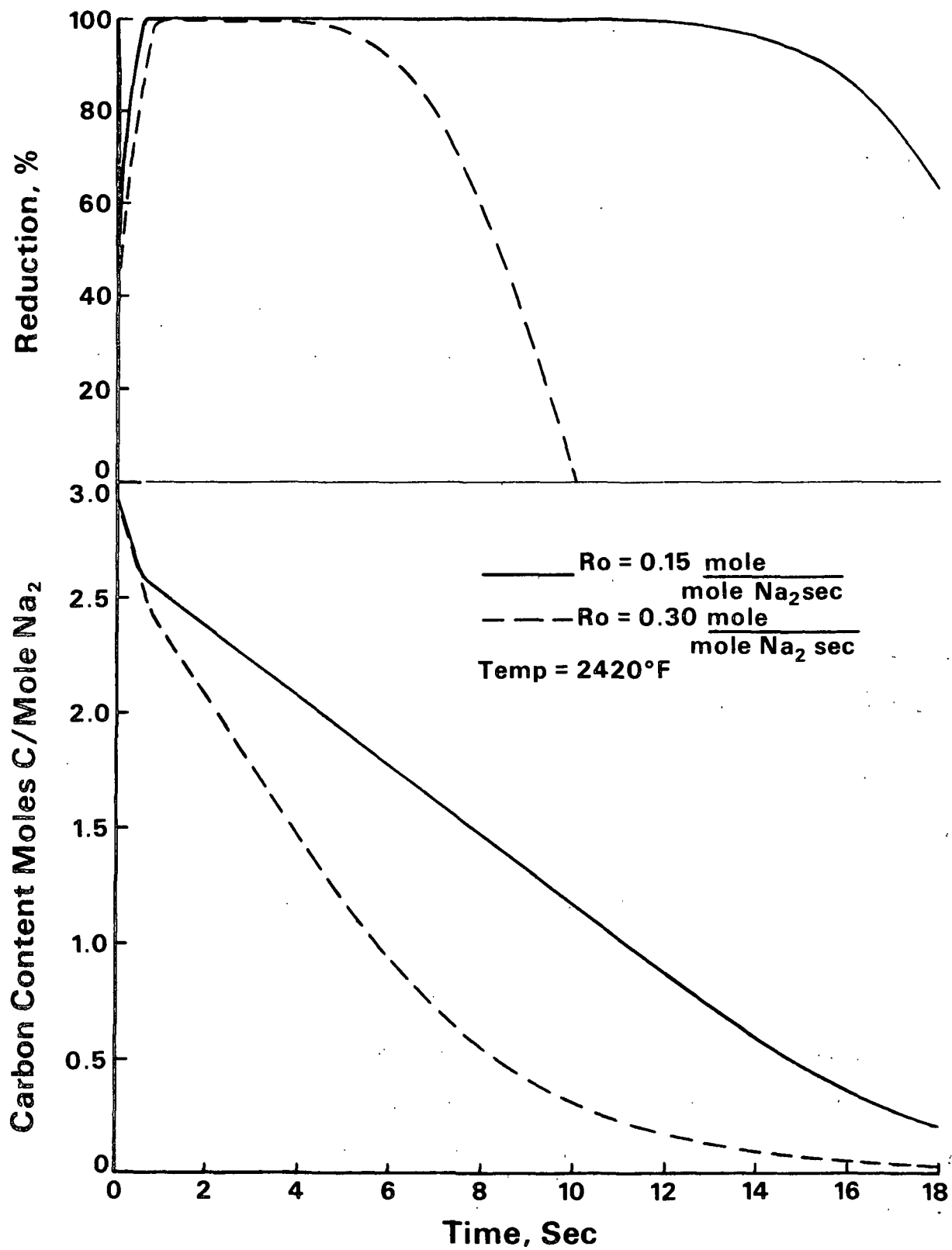
down to match the rate of oxygen supply. The third period begins when the carbon content has dropped to the point that the carbon burnup rate cannot match the oxygen supply rate. At this point sulfide reoxidation to sulfate begins and the reduction efficiency drops with increasing rapidity. During this period the carbon burnup rate reverts to an exponential decay. The time scale of the process is on the order of 5 minutes (300 sec).

The case with $R_0 = 0.05$ is one of excess oxygen supply. Oxygen is supplied at a faster rate than carbon can consume it, even at the initial carbon concentration. The sulfide is rapidly oxidized to sulfate until no sulfide remains. The carbon follows an exponential decay through the entire burning process.

Figure 4-8 shows two cases at a temperature of 2420°F ($\Delta T = 300^\circ\text{C}$). Values of the parameters $[C]_0$, r_0 , and s are the same as in the previous two cases (at 1700°F). Because of the much faster burnup rates possible at 2420°F , much higher oxygen transfer rates can be sustained. Two oxygen transfer rates, 0.15 and 0.30 mole/mole Na_2S ,sec are shown.

The most obvious difference in behavior at the higher temperature is the much shorter time scale of the event (about 20 sec). Both cases shown have the characteristic of an initial period of rapid reduction, an oxygen supply controlled carbon burnup period at very high reduction efficiency, and a period in which simultaneous sulfide reoxidation and carbon burnup occurs. This third period sets in faster, and with more carbon remaining, when the oxygen supply rate is higher.

These calculated burnup curves clearly illustrate one of the key features of the sulfate-sulfide cycle: it is entirely possible to have essentially complete reduction simultaneously with char carbon burnup in an oxygen-

Figure 4-8. Calculated burning curves at 2420°F .

containing atmosphere. All that is necessary is for the oxygen supply rate to be the rate-limiting step in the burning process.

Application to a Char Particle

Everything in the preceding discussion of the theory of char burning applies equally to a char particle (a finite amount of char burning as a discrete entity). Making the same assumptions about char composition as before, four parameters are needed to define char composition as burning proceeds.

N = total moles of Na_2 in the particle (assumed constant)

s = moles sulfur/moles Na_2 (assumed constant)

r = state of reduction = $\text{Na}_2\text{S}/(\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4)$

$[C]$ = carbon concentration, moles C/mole Na_2

Only r and $[C]$ change as burning proceeds, and this is described by Eq. (4-29) and (4-30).

The mass of a char particle, M , during burning is directly related to these four parameters.

$$M = 106(1-s)N + 142 Ns(1-r) + 78 Nsr + 12 N[C] \quad (4-31)$$

or

$$M = N\{106 + 36s - 64 sr + 12 [C]\} \quad (4-32)$$

Equation (4-32) can be used to develop mass vs. time curves for the two cases at 2420°F shown in Fig. 4-8. The value of N is chosen so that $M = 1$ at the initial conditions ($[C] = 3$ and $r = 0.5$). The mass-time curves are shown in Fig. 4-9. These curves show four distinct zones.

1. An initial rapid drop as the sulfate originally present in the char is reduced

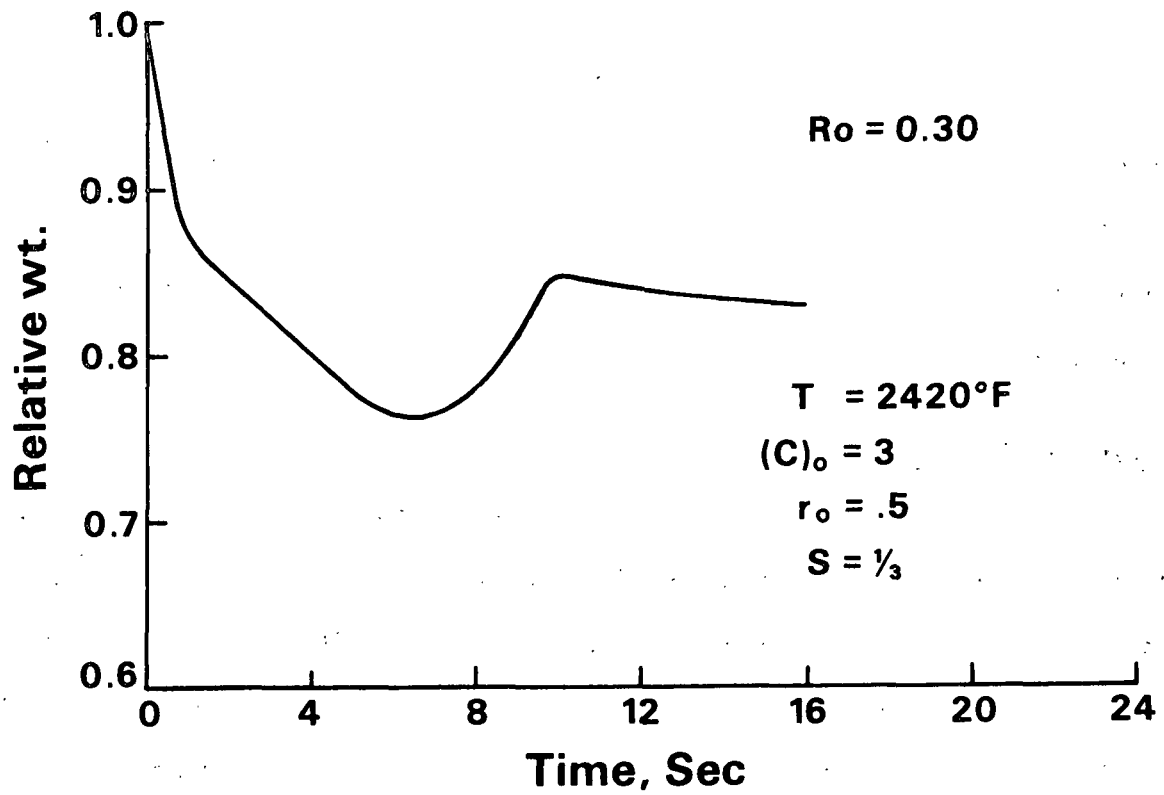
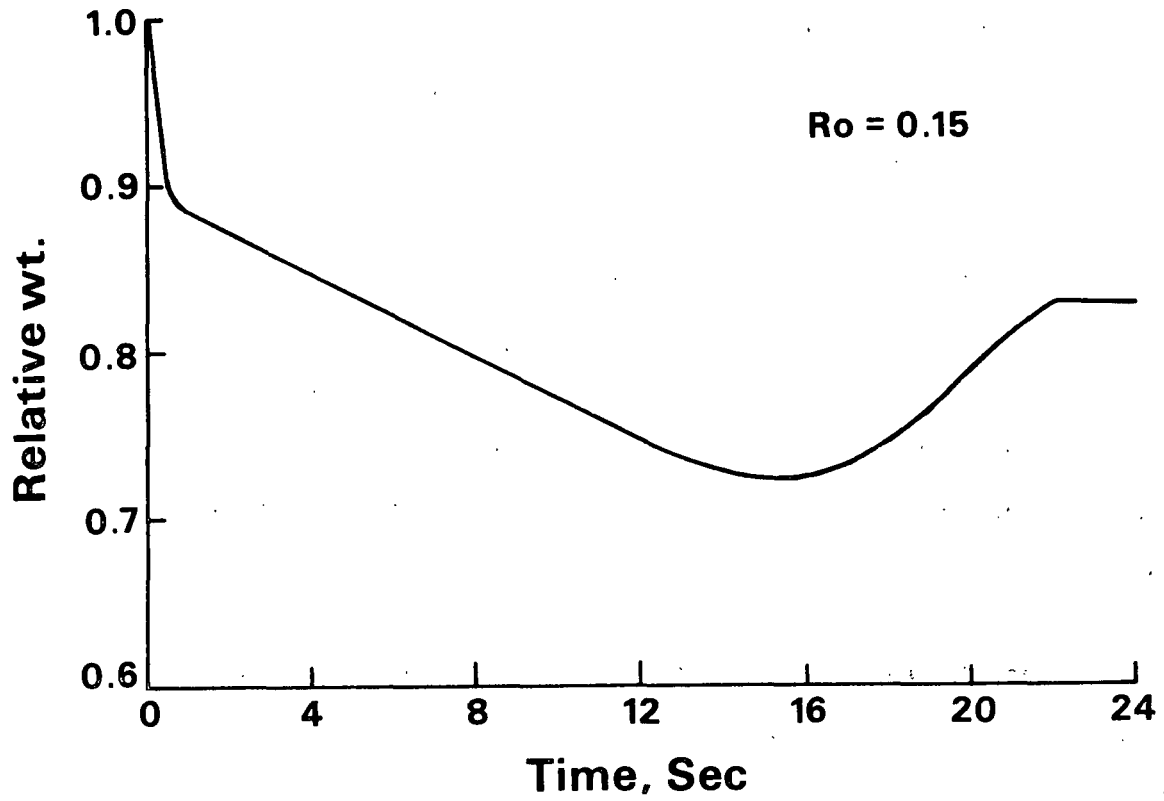


Figure 4-9. Calculated mass vs. time burning curves at 2420°F .

2. A constant rate of drop off as carbon is burned off under oxygen limited conditions (at a fixed, very high, state of reduction)
3. A period of weight gain as sulfide is reoxidized to sulfate
4. A final falling rate period, of exponential decay, as the final carbon is burnt out in a fully oxidized melt

It is assumed that both the oxygen supply rate and the temperature remain constant throughout the burn. Neither of these are likely to occur over the entire burning process.

If R_0 is governed by oxygen mass transfer rate, the factors that control it are mainly external to the burning char particle. If we represent R_0 by Eq. (4-24),

$$R_0 = k_{O_2} A P_{O_2}$$

R_0 depends on a mass transfer coefficient k_{O_2} (which will be a function of gas flow, gas properties, and system geometry), oxygen partial pressure, and the contact area per unit mole of Na_2 . The only particle features that would influence R_0 are its external geometry.

Temperature Effects

Char burning rates are very sensitive to temperature. The kraft char used in this study had a temperature dependency such that rates tended to double for a 130°F rise and increase by a factor of 10 for a 500°F rise. The soda char burning rate increased by 2 for a 95°F rise and by a factor of 10 for a 350°F rise. These are probably representative of the range of temperature sensitivities most chars would experience.

Since burning rates are strongly temperature dependent, the actual burning curves would be affected significantly by temperature changes occurring during burning. Because there are significant heat of reaction effects associated with char burning, such temperature changes would be expected. The carbon-sulfate reaction by itself is endothermic, while sulfide oxidation and carbon burnup (at a fixed reduction state) are exothermic.

Heat of reaction effects would tend to straighten out the mass burning curves (as shown in Fig. 4-9) to some extent. The initial rapid drop is due to net reduction occurring. Since this is endothermic, temperatures would tend to be lowered, thus decreasing rates in this period. The oxygen-limited burning rate period would occur under exothermic conditions but at a constant rate, so that a stable temperature level should be reached in that period. In the period where sulfide reoxidation is occurring, the reaction is highly exothermic. This will tend to increase temperature which will increase the rate of carbon-sulfate reactions. This will increase the carbon depletion rate and lower the net rate at which reduction falls off.

It is not possible to incorporate the coupling between temperature, heats of reaction, and burning rates into the quantitative model at the present. Heat transfer considerations are very complex. The dominant heat transfer mode is expected to be radiation, but convective heat transfer can also be important, especially at the lower range of burning temperatures.

CHAR PARTICLE BURNING

The work, discussed previously, showed that char burned via the sulfate-sulfide cycle if sulfur was present. However, these data were obtained with a small amount of carbon suspended in a large amount of molten smelt. Thus

the preceding experiments omit one important aspect of char burning - that char burning takes place as a heterogeneous reaction on the "surface" of a solidlike char particle. This aspect must be addressed before drawing firm conclusions about the char burning process.

In this section we will consider the question of burning geometry, briefly describe an experimental system for carrying out burning experiments on char particles, present the results of char particle burns, and interpret the results in terms of the theory of the sulfate-sulfide cycle.

Burning Geometry

Two aspects of the geometry of char burning are important: the geometry of the char particle itself and the geometry of air-char contact. The former is critical to the development of char models and for describing the smelting process. The latter is critical in determining the O_2 mass transfer rate.

The important elements of char geometry are the macroscopic size, shape, and surface area, and the porosity (density) of the char. This is primarily determined by processes occurring before char burning, especially pyrolysis. Swelling of the particle during pyrolysis is a critical factor in determining char particle shape and porosity.

The structural elements of a particle must be defined in order to treat smelting and the metamorphosis of the particle into a stream of smelt. It appears that carbon provides the structural matrix so that a solidlike structure can persist indefinitely at temperatures above the inorganic melting point. Coalescence and formation of free flowing smelt occur when the carbon content had been reduced to the point where it no longer supports a structural matrix.

Surface tension causes the structure to contract into a smelt drop. In larger, denser particles, smelt drops can "sweat" out of the burning char.

Geometrical considerations are also important in determining the O_2 mass transfer rate from combustion air to the char surface. These influence local Reynold's numbers and boundary layer thicknesses which determine the resistance to mass transfer. Possible air-char geometries include air jets impinging on char surfaces, char particles in stagnant air, and char particles in convective air streams.

The O_2 mass transfer rate, R_O , depends on the air-char contact area, A , in area per unit mole Na_2 . This contact area can be written as

$$A = \left(\frac{46}{W_{Na}} \right) \frac{\text{mass particle}}{\text{mole } Na_2} \times \left(\frac{6F}{D} \right) \frac{\text{area particle}}{\text{volume particle}} \times \frac{1}{\rho} \frac{\text{volume particle}}{\text{mass particle}}$$

or

$$A = \frac{276}{W_{Na}} \frac{F}{D\rho} \quad (4-33)$$

where

A = air-char contact area, area/mole Na_2

W_{Na} = wt. fraction Na in char particle

D = particle diameter, length

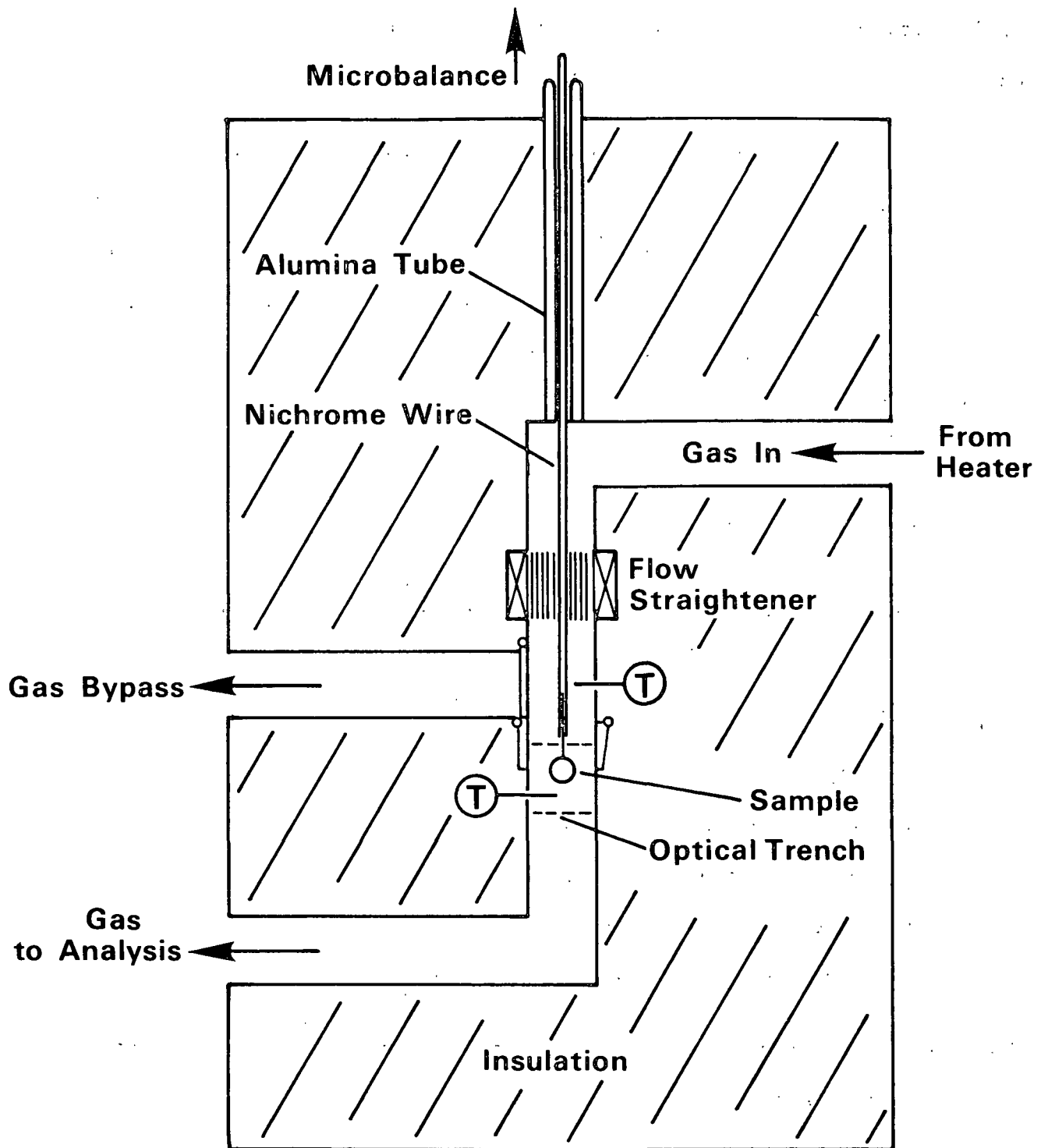
ρ = char particle density, mass/vol

F = shape factor for deviations from spherical

The contact area is greatest for small diameter particles and for swollen, high porosity, low density char.

Single Particle Burning System

The experiments on the burning of single particle of char were carried out on a specially designed apparatus referred to herein as the single particle



Note: All gas passages are 2" x 2"

Figure 4-10. Schematic of single particle reactor.

reactor (SPR). This reactor is designed to provide a direct measurement of mass changes as a char particle reacts. The particle is suspended from a sensitive microbalance and is continuously exposed to a convective gas stream of controlled temperature and composition. The composition of the gases leaving the reaction zone can be monitored. A viewport allows visual observation and photography of the burning particle.

A schematic diagram of the SPR is shown in Fig. 4-10. The particle is suspended from the microbalance in the area of the viewport. Typical particles contain about 0.1-0.2 g of black liquor solids or char and are about 1/4 inch in diameter. Swollen char particles have dimensions on the order of 1/2 to 1 inch. Preheated gas (N_2 , air, etc.) passes through a flow straightener and then downward over the reacting particle. Gas flowing in this direction helps keep fume and other combustion products out of the microbalance. A bypass arrangement and dampers are used to stabilize gas flow and temperature before the gas is passed over the particle. Available instrumentation on the off-gas allows measurement of CO , CO_2 , O_2 , $H_2O(v)$ and Na fume as a function of time. Photographs of the experimental system are shown in Fig. 4-11.

A sequence of pictures illustrating the burning of a char particle is shown in Fig. 4-12. (Formation of char particles by pyrolysis was shown in Fig. 3-1 earlier in this report.) A pellet of dried liquor solids pressed into a pill is first hung on the microbalance and exposed to hot nitrogen gas at $800^\circ C$ ($1470^\circ F$). Pyrolysis produces the swollen char particle which is subsequently burned. Burning is initiated when hot air is admitted past the particle. Burning begins on the leading edge where the air strikes the particle and proceeds rapidly down the particle. Molten smelt beads up and tends to remain with the particle or become attached to the support wires. On completion of burning

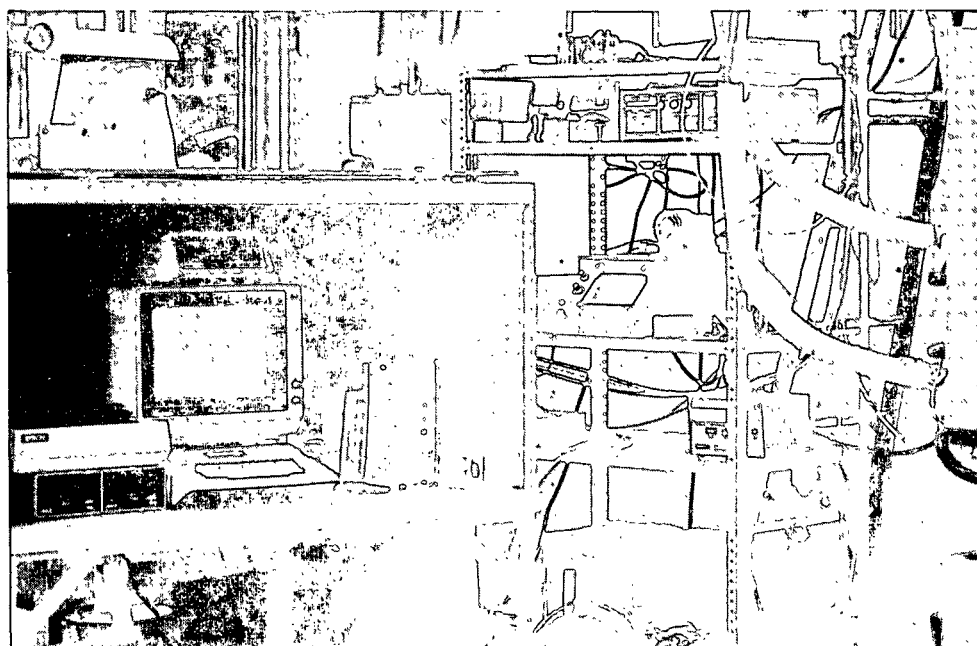


Figure 4-11. Photographs of single particle reactor.

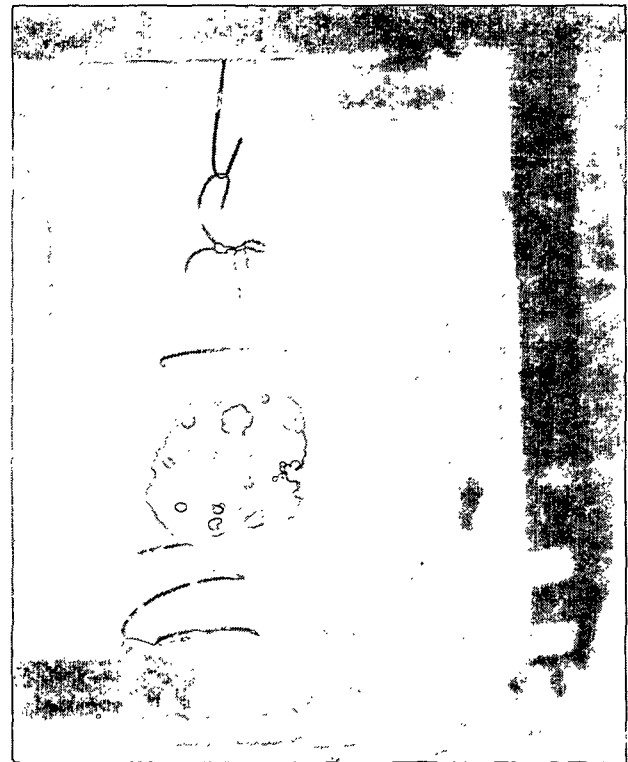
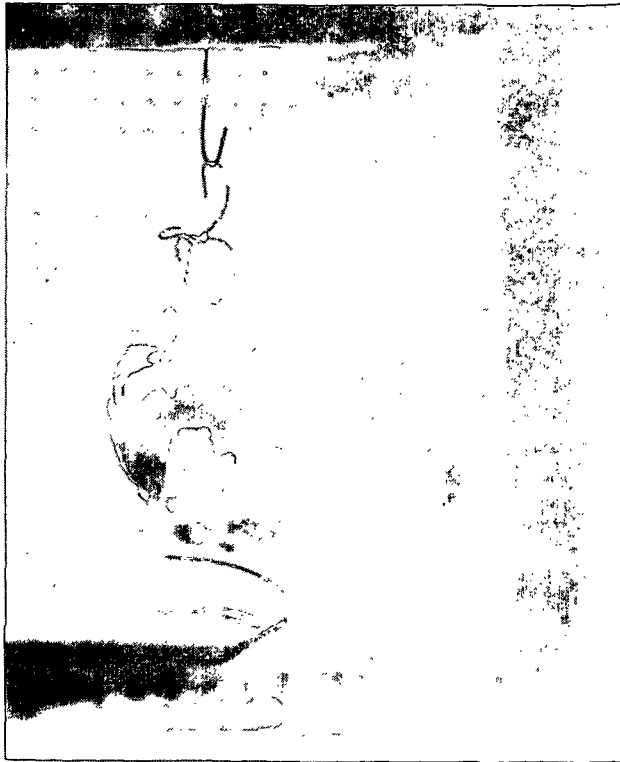
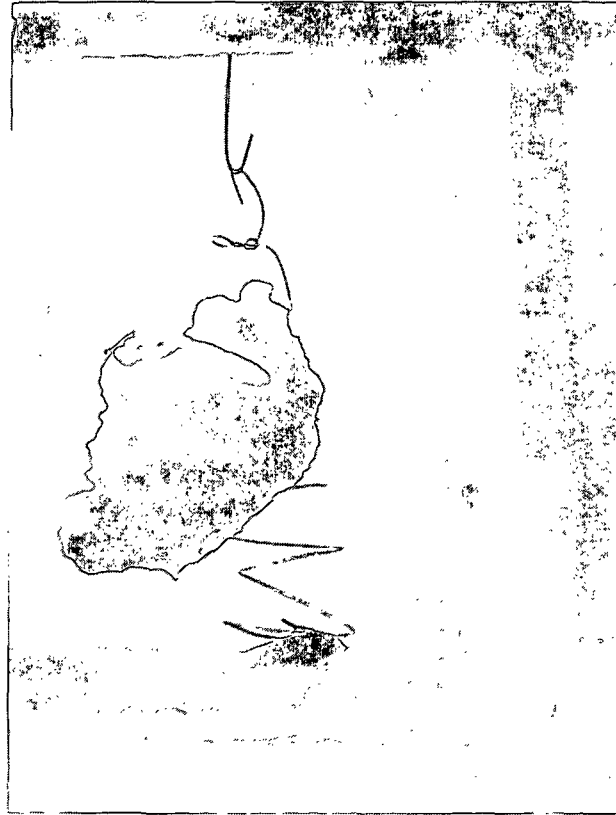


Figure 4-12. Picture sequence showing char burning.

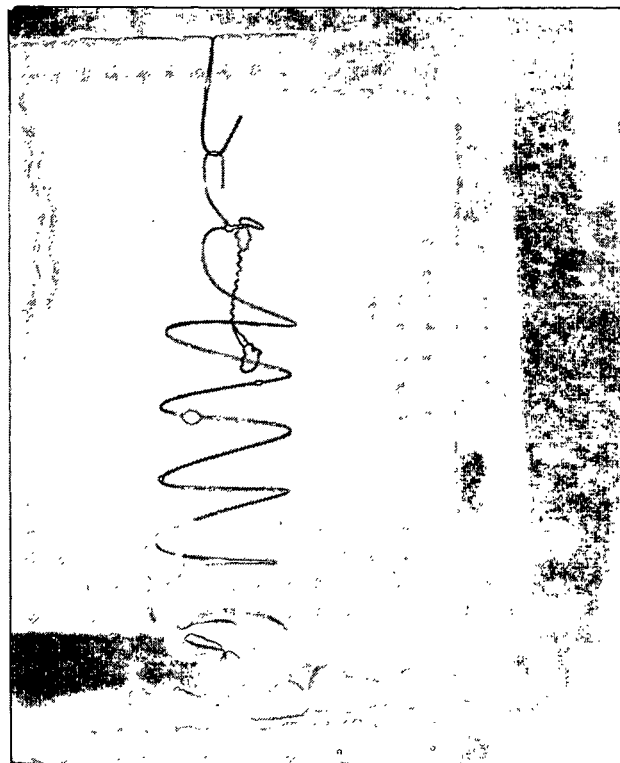
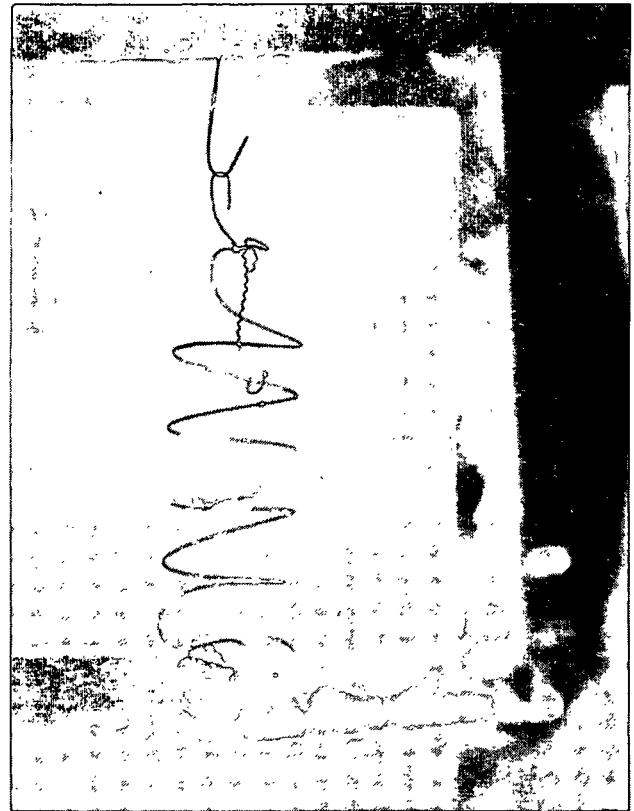
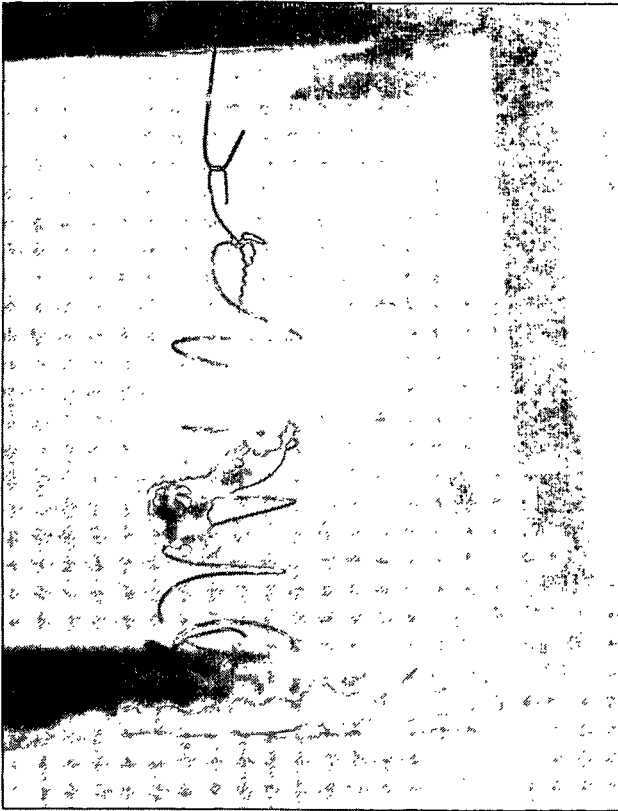


Figure 4-12 (Contd.). Picture sequence showing char burning.

Burning Rate Curves

The prime measurement of burning rate in the char particle experiments was the particle weight as a function of time. A large number of experimental burns were carried out. A typical result for kraft char burning in air (21% O₂) is shown in Fig. 4-13. There is a period of a reasonably linear decline in weight followed by a weight gain at the end. These correspond to the periods of oxygen-limited burning followed by sulfide reoxidation discussed in the previous section. The slow rate at the beginning is due to ignition lag and the time to establish high temperature conditions. For kraft char burning in air, burn times were normally 10 to 20 seconds. The major gas product was CO₂ with little CO. The total amount of air passing the particle in the course of a burn was well in excess of that needed for complete burning of the particle.

A typical weight vs. time curve for kraft char burning in 10% O₂ (90% N₂) is shown in Fig. 4-14. The general shape of the curve is similar to that for kraft char burning in air. However, the constant rate period is much longer in the 10% O₂ case. Total burn times ranged from 25 to 30 seconds. Again there is a weight gain at the end due to sulfide reoxidation. The behavior in this case is also in close agreement with theory. Oxygen limited burning rates would be expected to be proportional to the oxygen concentration.

A typical weight vs. time curve for burning a soda char particle in air is shown in Fig. 4-15. The times for all weight changes for soda char are about the same as for kraft char, 10 to 20 seconds. However, this is a bit misleading, because some residual carbon remained at the end of the burn. A partial lattice of carbon would not burn out. This is probably due to a coupling between low rates, low heat production, and temperature. In contrast to the kraft char, no

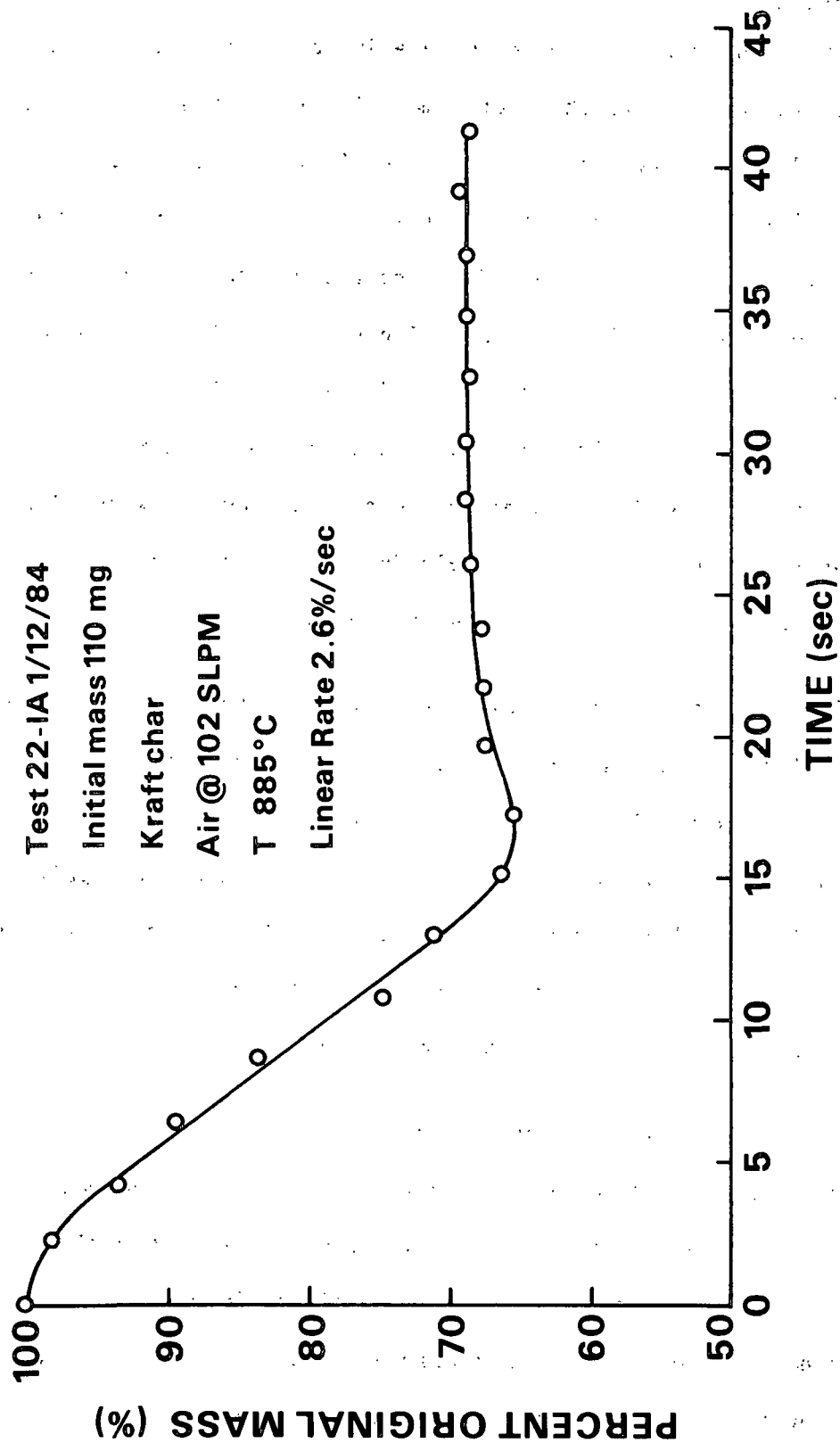
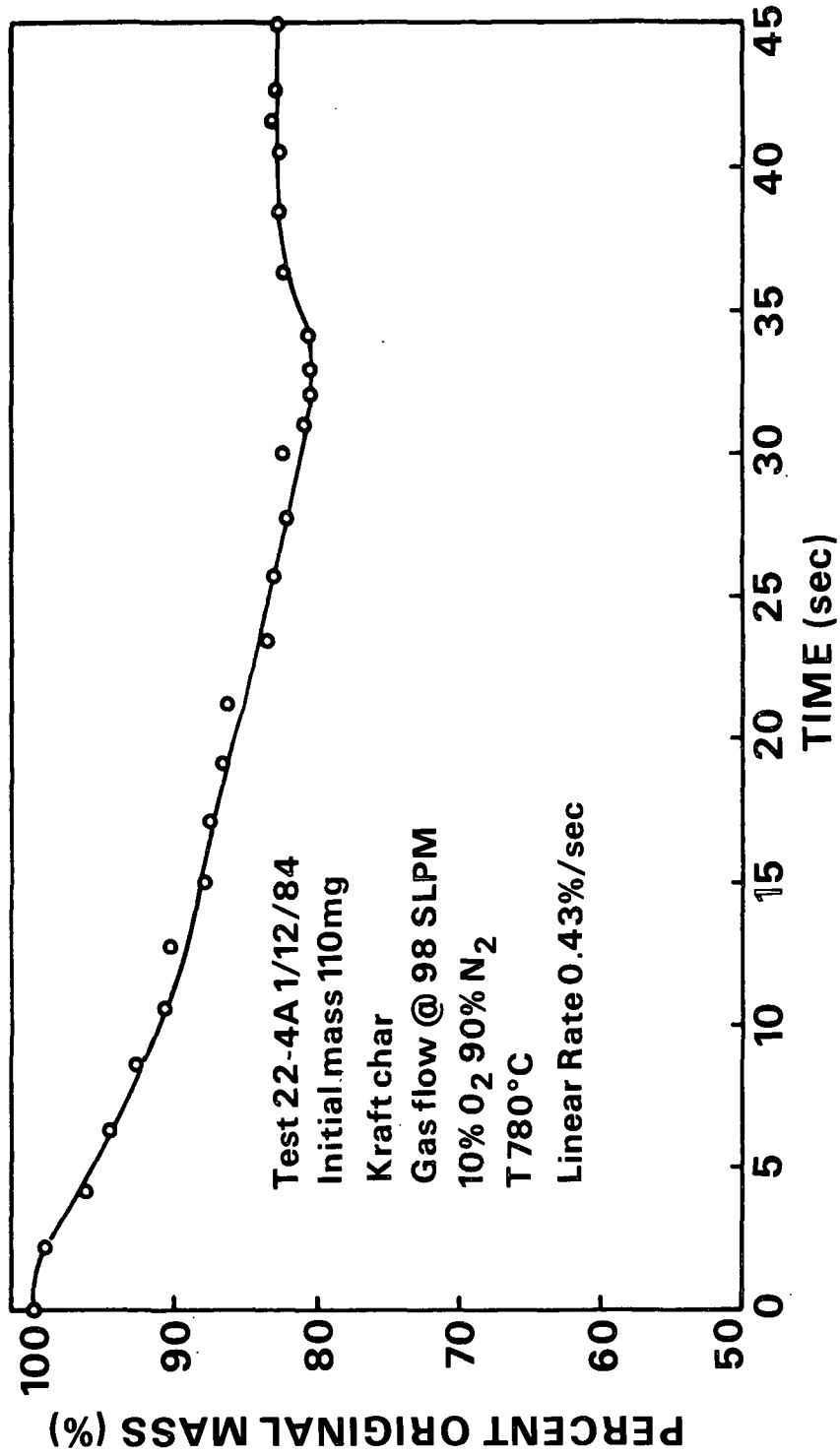


Figure 4-13. Kraft char particle burning in air.



Kraft char burning (10% O₂, 90% N₂) weight vs. time

Figure 4-14. Kraft char particle burning in 10% O₂.

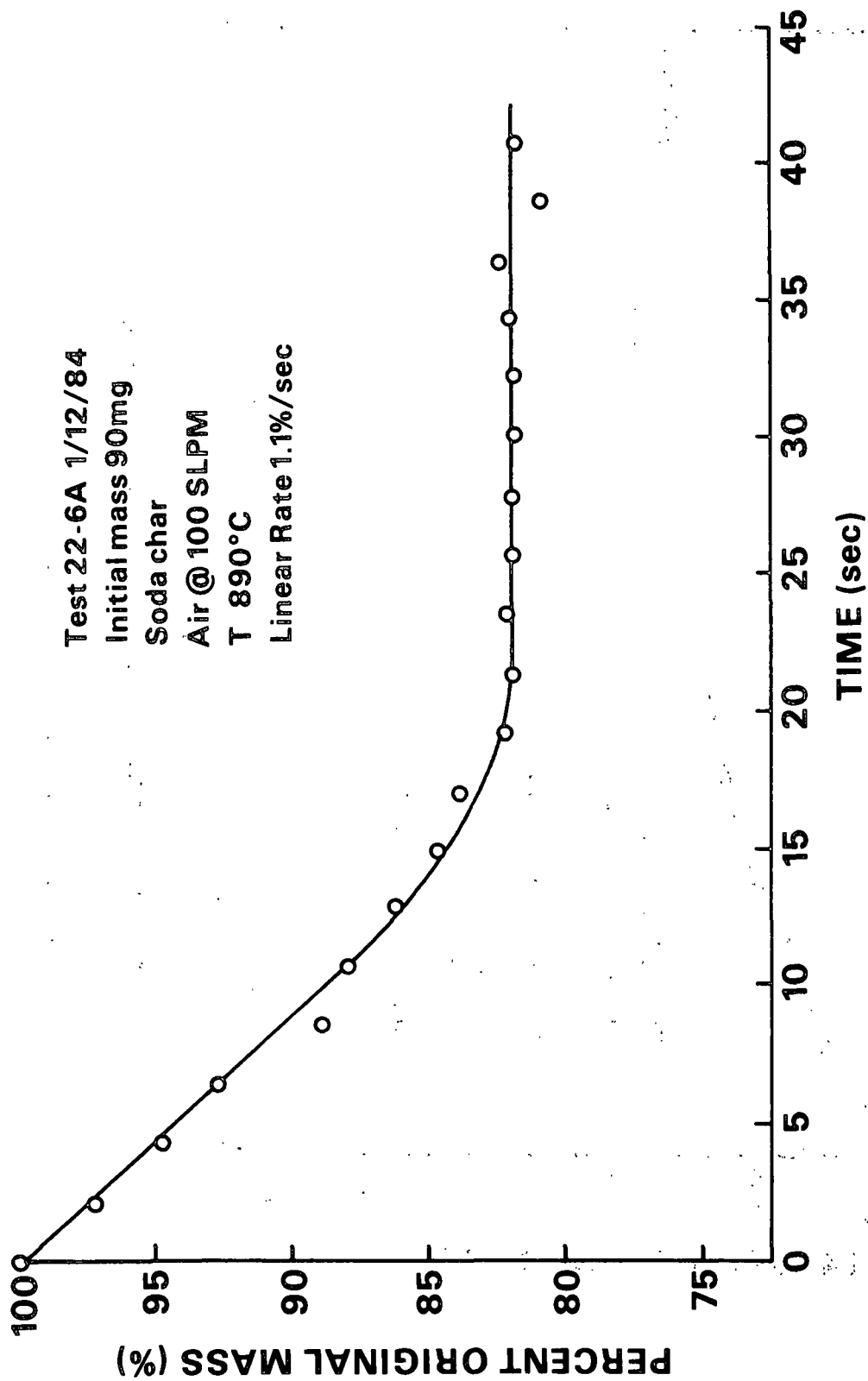


Figure 4-15. Soda char particle burning in air.

weight gain was observed at the end of the burnout with soda char. This confirms that the weight gain at the end of char burns is due to sulfide oxidation.

Addition of Na_2SO_4 to the soda char (15% based on the initial black liquor solids) resulted in a weight gain at the end of the burn and eliminated the residual carbon matrix at the end of the burn. In other words, addition of sulfate to the soda char before the burn caused the system to behave like a kraft char.

Interpretation

All of these results on the SPR are consistent with the predictions of the theory of the sulfate-sulfide cycle and with the fundamental work on reduction and oxidation.

The linearity of the weight vs. time curves and the similar "total burn times" between kraft char and soda char are what would be expected for an O_2 mass transfer controlled process. The variables influencing the mass transfer rate lie mainly outside the particles and hence are not changed as burning proceeds. Visual evidence also confirms a mass transfer controlled burn. The reaction initiates at the leading edge of the particle where the air impacts the particle, and burning then proceeds down along the particle as the top portion burns away. Burning remains most intense at the top of the particle.

The weight gain at the end shows that sulfur is present in a reduced state as burning proceeds. This is in accordance with predictions from the analysis of the sulfate/sulfide cycle. The sulfur remains in a reduced state until the carbon becomes depleted, and then the reduced sulfur oxidizes. The weight gain at the end of the oxidations of kraft char and soda char with sulfate, (and

the absence of a weight gain with soda char) can only be interpreted as being due to the reoxidation of sulfide.

The entire particle appears to heat up rapidly once burning initiates. This seems to be a case of radiation enhanced conduction through the porous char particle.

The concentration of O_2 in the convective gas stream flowing past the particle had a pronounced effect on kraft char burning. The burning rate was reduced at lower O_2 concentrations. For 10% O_2 (90% Na_2), the time for complete burnout ranged from 25 to 30 seconds. When burning was carried out with only 2% O_2 , the rate was very slow and burn times exceeded 60 seconds. For a mass transfer controlled process, one would expect the burning rate to tend to be related to the O_2 concentration and that seems to be what is observed in these experiments.

Once pyrolysis is complete, char undergoes no further reactions in N_2 up to at least $850^\circ C$. No detectable weight loss or release of CO_2/CO occurred under these conditions. The physical character of the char remained intact. No melting was evident. Even a char produced by pyrolyzing kraft BL solids + 15% $NaCl$ showed no signs of melting under these conditioning.

CONCLUSIONS

1. Char burns in oxygen-containing gases via the sulfate-sulfide cycle. Char carbon reacts with sulfate, producing carbon dioxide (and monoxide) and sulfide. Oxygen reacts with sulfide and reforms sulfate. The net result is a cycle that oxidizes carbon. The sulfur reduction state during the process is determined by the relative rates of the carbon-sulfate and oxygen-sulfide steps.

2. It is entirely possible to burn off char carbon in air while still maintaining very high degrees of sulfur reduction. A necessary criterion for achieving high reduction efficiencies during char burning is for oxygen mass transfer to be the overall rate limiting step in the process.
3. The carbon-sulfate reaction rate is a strong function of temperature, is a linear function of carbon content, and is practically independent of sulfate concentration until very high reduction efficiencies are obtained. The particular features of this rate behavior allow high reduction efficiencies simultaneously with char burning in air.
4. Sulfide reoxidation will always occur when oxygen contacts smelt or char which is deficient in carbon.
5. Rates of char burning via the sulfate-sulfide cycle can be treated quantitatively. All that is required is the rate equation for the carbon-sulfate reaction [Eq. (4-9)] and an expression for the rate of oxygen supply to the reacting surface (obtainable from ordinary mass transfer considerations).
6. The determination of char burning rates is greatly complicated by the temperature sensitivity of the reaction rates and the close coupling between reaction rates, heats of reaction, and temperature. Hence heat transfer considerations are vitally important in determining actual burnup rates.
7. The factors that govern the CO/CO_2 ratio in char burning are not completely understood. The laboratory data suggest that CO_2 is the major product, and that the relative amounts are in reasonable agreement with equilibrium above a sulfate-sulfide mixture.

8. One source of CO may be a secondary reaction between CO_2 and carbon. Experimental evidence for this reaction was obtained with the SPR. However, the reaction rates were very slow. The slow rates in the SPR could have been due to low reaction temperatures, since the endothermic heat of reaction would tend to keep the char surface below the gas temperature. We do not presently know how fast CO_2 -C reactions can go at temperature levels of interest in the char bed.

FUME FORMATION

BACKGROUND

Definition of Fume

Fume is a name given to small-sized (normally submicron) particulate present in the combustion gases. Fume is formed by condensation of inorganic sodium and potassium salts from the vapor state. The vaporization process is believed to occur primarily during char burning. Vaporization is the most critical aspect of the fume forming process, because it determines the amount of fume formed. Condensation appears to take place rapidly and spontaneously when the proper gas conditions are reached. Control of fume ultimately rests with control of the inorganic vaporization process.

Scanning electron microscope pictures of fume particles generated in the laboratory from a commercial smelt are shown in Fig. 5-1. These particles are very similar in appearance to fume samples taken from operating recovery furnaces (27). The particles are smooth spheres with varying degrees of agglomeration. Particle diameters are in the range 0.2 to 0.5 μm . No cracks, fissures, or dendritic structures are observed. These characteristics appear to be typical of most of the fume found in the recovery boiler. Under some conditions, elaborate dendritic crystal structures were found in laboratory experiments. These also have been found in furnaces, but seem to be less common. The exact nature of the fume structure is determined by processes during and after its condensation from the gas phase.

Fume particles are primarily sodium salts, normally sodium sulfate and sodium carbonate. In a kraft recovery boiler the fume is usually 90% or more Na_2SO_4 and 10% or less Na_2CO_3 . Fume will also contain potassium and chlorine if

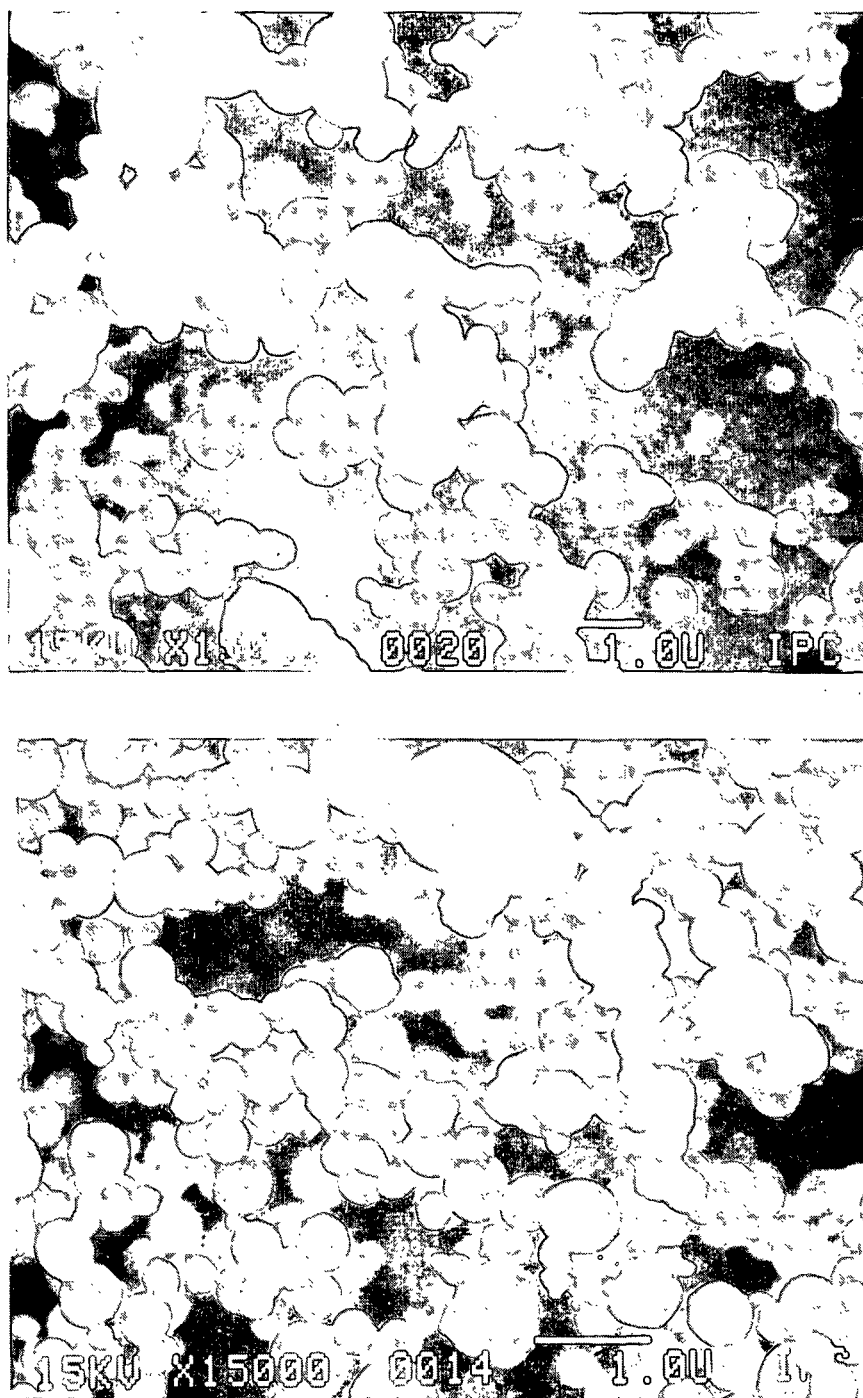


Figure 5-1. Scanning electron microscope pictures of fume particles generated from commercial melts. Part A - Sulfide oxidation via dry air. Part B - Sulfide oxidation via moist air. Part C - Sulfide oxidation via dry air with carbon present.

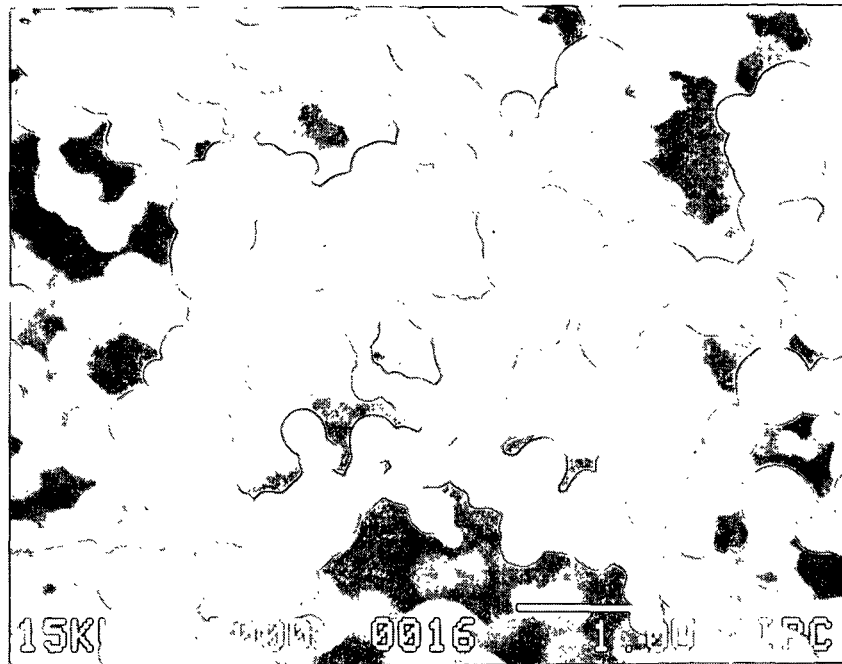


Figure 5-1 (Contd.). Scanning electron microscope pictures of fume particles generated from commercial melts. Part A - Sulfide oxidation via dry air. Part B - Sulfide oxidation via moist air. Part C - Sulfide oxidation via dry air with carbon present.

those elements are present in the liquor being fired. Because potassium compounds and sodium chloride are more volatile than the normal sodium salts, the fume will tend to be enriched in those elements. The composition of the fume as it reaches the precipitator is a result of many reactions that take place between volatilization and the fume leaving the furnace. The composition of the volatile substance is not necessarily the same as the final fume product.

Volatiles

This section deals primarily with Na_2SO_4 and Na_2CO_3 fumes, since they constitute the bulk of the fume. There are three volatile sodium species that have been generally recognized in the literature as sources of fume in recovery boilers:

Sodium vapor - Na(g) and $\text{Na}_2\text{(g)}$, b.p. = 1621°F

Sodium hydroxide vapor - NaOH(g) , b.p. = 2421°F

Sodium chloride vapor - NaCl(g) and $\text{Na}_2\text{Cl}_2\text{(g)}$, b.p. = 2575°F

Sodium vapor is, by far, the most volatile of these species as indicated by its much lower boiling point. All three have significant vapor pressures in the temperature range of interest. Reeve (28) indicates vapor pressures of about 3 mm Hg for NaCl and 15 mm Hg for NaOH at 1700°F.

The major fume products themselves, Na_2SO_4 and Na_2CO_3 , are much less volatile. There is conflicting data in the literature on the vapor pressure of Na_2SO_4 (29-31). The best estimate appears to be about 10^{-7} atm (0.1 ppm) at 1700°F and about 5×10^{-6} atm (5 ppm) at 2060°F. The major factor in vaporization of Na_2SO_4 is decomposition of the molecule (32). Sodium carbonate also decomposes rather than vaporizing (33). The reaction is $\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2$. Na_2O is reported to have a decomposition temperature of 3542°F.

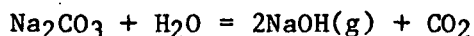
The JANAF Tables (16) list sodium monoxide gas, NaO(g) , as another gaseous sodium species. The free energy of formation of sodium monoxide is slightly positive and reaches a minimum of + 1.981 kcal/mol at a temperature of 1200°K (1700°F). No condensed phases are listed for NaO and no vapor pressure information is available. It does appear, however, to be a possible volatile sodium compound.

Existing Knowledge

Existing concepts of how fume is formed in the recovery furnace are derived from thermodynamic equilibrium analyses of furnace reactions. Bauer and Dorland (34) and others have constructed equilibrium diagrams giving the partial pressures of chemical species as a function of furnace conditions (temperature

and extent of reducing environment). These diagrams show that sodium vapor pressures become appreciable at high temperature (1700 to 2000°F) reducing conditions. The higher the temperature and the stronger the reducing condition, the higher the vapor pressure of sodium. Thus fume has been considered to arise from the formation of elemental sodium (by carbon reduction of sodium carbonate: $\text{Na}_2\text{CO}_3 + 2\text{C} = 2\text{Na} + 3\text{CO}$) and its subsequent vaporization.

Later Warnqvist (35) carried out an equilibrium analysis of fume formation in which sodium hydroxide vapor was included among the allowable species. He concluded that sodium hydroxide vaporization was significant and was the primary factor responsible for sodium salt emissions in a high temperature oxidizing atmosphere. This suggests that reactions such as



are important in fume formation.

Thus the present concept is that fume comes from sodium vapor and sodium hydroxide vapor (and sodium chloride vapor when chlorine is a furnace elemental input). Thermodynamic equilibrium analyses have been deemed adequate for treating fuming. They predict the general order of magnitude of the amount of fume formed and indicate that the amount of fume formed is expected to increase with increasing temperature.

APPROACH

Our original intention was to approach the study of fuming in the same manner that was used for the char burning reactions. We started with the assumption that fume came from sodium vapor and sodium hydroxide vapor. We wanted to set up specific chemical reactions for generating those vapors and

determine the rate equations for those reactions. However, what we found was that the most intense fuming was generated under conditions that were not easily explainable in terms of sodium vapor or sodium hydroxide vapor production. At this point our program shifted toward a phenomenological approach which focussed on identifying the major variables influencing fume formation and trying to explain this behavior chemically.

Experimental

The experimental system which was used in the fuming work is shown in Fig. 5-2. This system is similar to, but larger than, the system used in the carbon-sulfate rate experiments. (The melt inventory is about 30 times larger in the fuming experimental system.) A metered gas stream was bubbled through the melt in a temperature controlled environment and the off-gas from the reactor was discharged into the atmosphere inside a large hood. A black background was provided and the discharging stream was photographed. The range of fume intensities observed is shown in Fig. 5-3. These are arbitrarily ranked in terms of a "fume intensity rating" (FIR) as shown in the figure. In some experiments the gas being discharged was filtered and a weight rate of fuming determined.

Fuming rates were also measured during char burning experiments on the single particle reactor. A portion of the off-gas from the SPR was introduced into the air supply of the burner on a flame photometer. This provided a measurement of the sodium salt content in the gas stream.

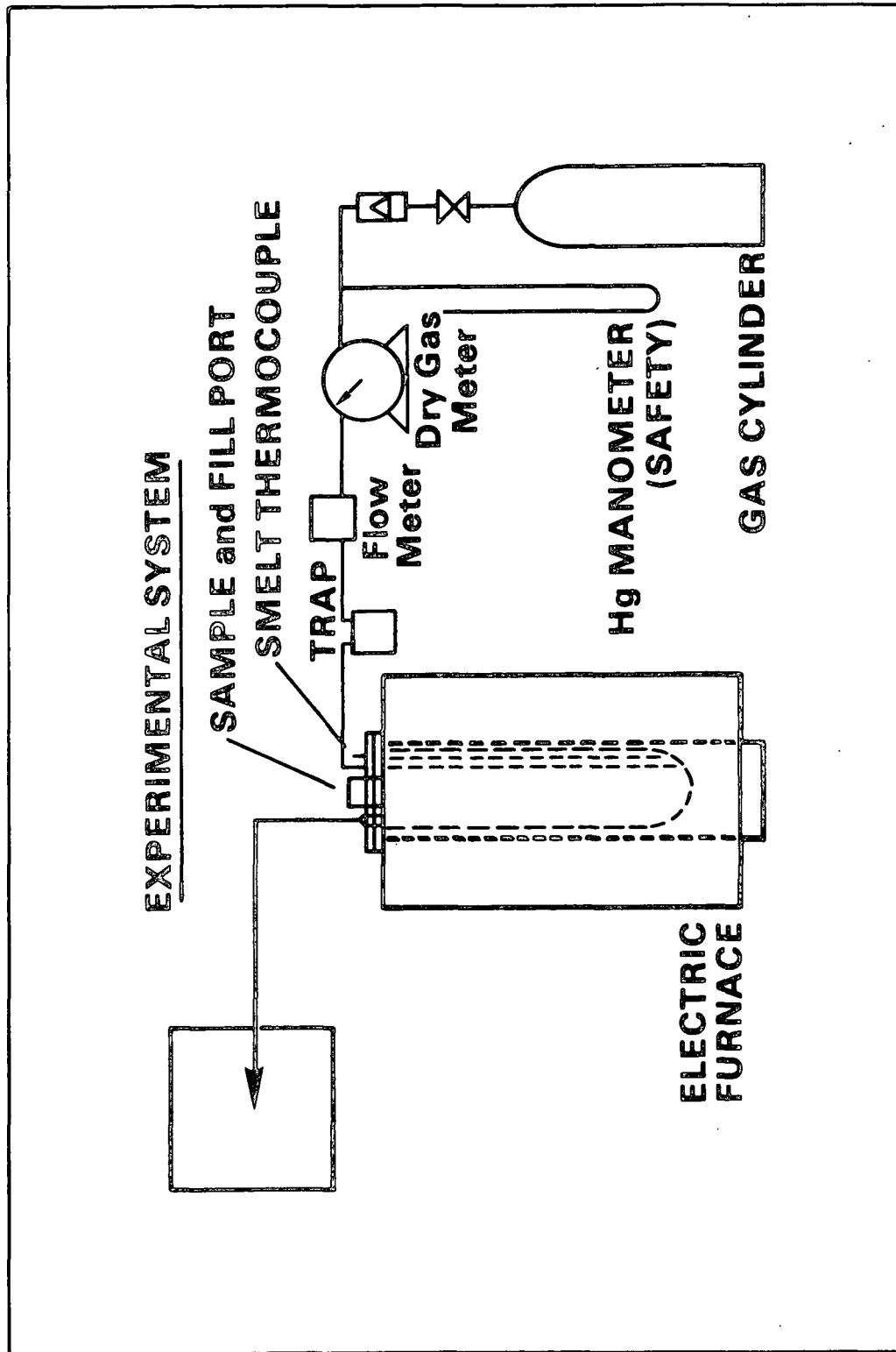


Figure 5-2. Experimental system for fume studies.

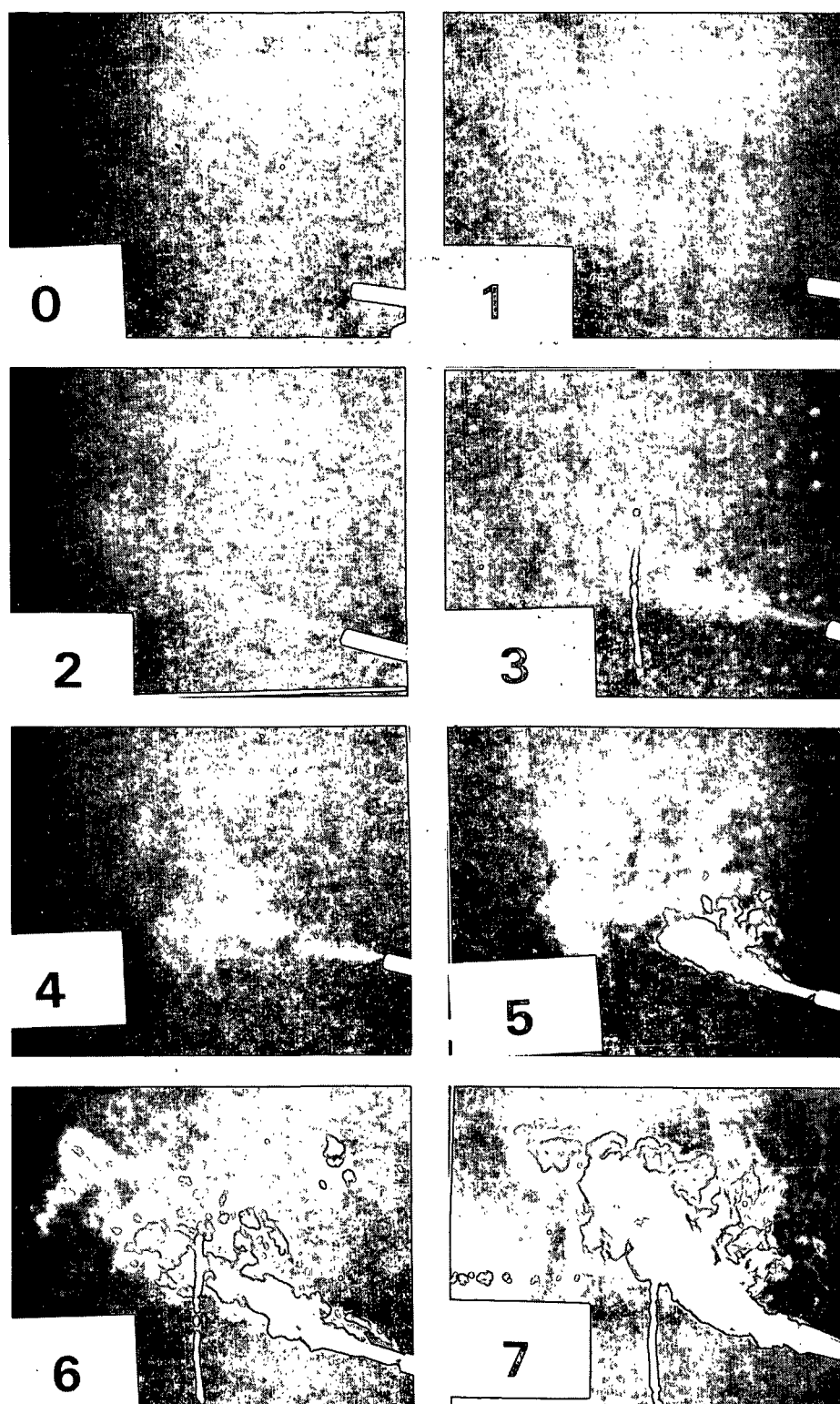


Figure 5-3. Range of fume intensities observed. Ranking numbers are the fume intensity rating.

OXIDATIVE FUMING

Definition and Significance

The greatest amounts of fume, by far, were produced when Na_2S was air oxidized to Na_2SO_4 in molten carbonate. The fume which was produced was almost entirely Na_2CO_3 . This fuming process, which seems very different from the generally recognized fuming processes, has been given the name oxidative fuming.

Oxidative fuming appears to be the most significant source of fume. Oxidation of Na_2S to Na_2SO_4 in molten carbonate typically generated fumes with an FIR of 7 or 6. In contrast, the highest FIR for reductive fuming (fuming in a strong reducing environment under conditions favorable for producing sodium vapor) was 4. This corresponds to about a one order-of-magnitude difference in the weight rate of fume formation.

Oxidative fuming was totally unexpected at the start of this work. The expected volatiles, sodium vapor or sodium hydroxide vapor, would be formed under reducing conditions or neutral conditions. Nothing connected to the oxidation of sulfide to sulfate would obviously lead to volatile sodium compounds. Because oxidative fuming was both unexpected and the source of the greatest amount of fume, it received the most attention in the program.

Results

Experiments were designed to characterize the oxidative fuming process and to determine the variables which had a significant effect on fuming rate. Rate equations were not developed. Details of the experimental fuming work are given in Ref. (36), which will be issued separately.

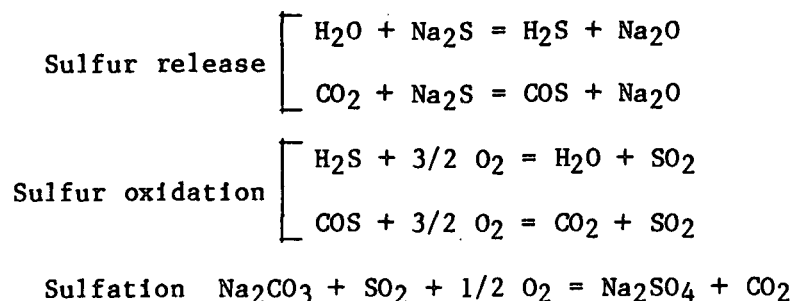
One requirement for oxidative fuming was to have a reduced form of sulfur present as well as oxygen. This combination always gave fume. Blowing air through a carbonate melt, both with and without carbon present, but without any sulfur in the system, did not generate fume. Similarly, fuming stopped abruptly when all of the reduced sulfur was oxidized to sulfate.

The fume particles produced by oxidative fuming have physical characteristics that closely resemble fume particles from recovery furnaces. The SEM photograph shown in Fig. 5-1 is of a fume sample produced in the laboratory by oxidative fuming. This photomicrograph is typical of all of the oxidative fumes produced.

The fume which was produced when sulfide was oxidized to sulfate in molten carbonate, with no other substances present, consisted of 94 to 96% Na_2CO_3 with the remainder Na_2SO_4 . Typical experiments were carried out with a molar ratio of $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}$ in the melt of 25/1. However, the low concentration of sulfur in the melt was not the reason for the high fraction of Na_2CO_3 in the fume. In one experiment in which the $\text{Na}_2\text{S}/\text{Na}_2\text{CO}_3$ ratio in the melt was 0.55 (in the commercial range), the fume particles were still 92% Na_2CO_3 . Only when carbonate was excluded from the system by using a sulfate melt (a small amount was reduced to sulfide with CO before oxidation), was the fume substantially all Na_2SO_4 .

The addition of SO_2 to the gas phase above the melt in the reactor produced a fume with a composition of 98% Na_2SO_4 and 2% Na_2CO_3 . This demonstrated that a carbonate based fume will react avidly with SO_2 to produce Na_2SO_4 . This agrees with the concept that the sulfate fumes found in recovery furnace gases are the result of sulfation of carbonate fumes within the furnace rather than from direct release of Na_2SO_4 from the bed.

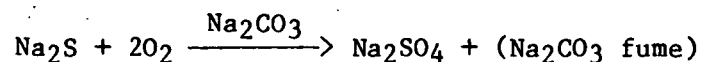
The sulfate content in oxidative fume was greater when water vapor was present in the oxidizing air or when carbon (carbon rods) was present in the melt. Typically the fume would contain about 30% Na_2SO_4 and 70% Na_2CO_3 under these conditions. It is believed that these additional substances lead to some sulfur release from the melt separate from sodium, and the released sulfur is oxidized to SO_2 which then sulfates the fume. Possible reactions include:



Certain substances were able to partially suppress oxidative fuming. These included H_2O vapor or CO_2 in the oxidizing air and carbon in the melt. Typically they would reduce the FIR by one to two units. It should be noted that the effect of carbon may be the same as the effect of CO_2 , since some sulfate would always be present when sulfide was oxidized and the reaction between sulfate and carbon produces CO_2 .

Oxidative fuming increases with increasing temperature, but the effect is not a strong one. Initial screening experiments showed that 900°C vs. 980°C had minimal effect on fuming. Later experiments did show an effect of temperature, particularly at the low temperature end. Oxidative fuming essentially ceased below 820°C (1500°F). Recent, more quantitative, experiments indicate that the fuming rate increases by about a factor of two for a 200°F increase in temperature.

The overall behavior that was observed can be summarized as follows:



The oxidation of sulfide in a sodium carbonate melt results in sulfate in the melt and sodium carbonate fume. As has been mentioned before, sulfide oxidation is a very rapid reaction whose overall rate is controlled by oxygen supply to the sulfide. Essentially all the oxygen was depleted from the incoming air stream in these experiments. Fuming ceases when inlet air stops or the sulfide is completely oxidized.

The major variables influencing oxidative fuming are summarized in Table 5-1.

Table 5-1. Major variables influencing oxidative fuming.

Essentials: Oxygen in gas stream

Reduced sulfur (e.g., Na_2S) in melt

Increased by: Higher temperature - doubles/200°F

Decreased by: Carbon dioxide in gas stream

Water vapor in gas stream

Carbon in melt

Char Burns

Oxidative fuming was also observed during char burns on the SPR. Two distinct modes of particulate generation were observed. One mode was the volatilization and condensation process which generated the submicron fume particles observed in the other reactor. This showed up visually as a pinkish-orange corona around the burning particle. The second mode was the violent ejection of tiny smelt droplets during intense burning. The visual appearance of this latter process was much like a Roman candle.

Measurements were made of the sodium fume concentration in the discharge gas from the SPR along with measurements of CO_2 and CO . The results for a kraft char burn are shown in Fig. 5-4. There is intense fuming during kraft char burning. The Na curve correlates with visual observations of a pinkish corona and with violent ejection of tiny smelt droplets, much like a Roman candle, during the burn. The major gaseous product is CO_2 with only small amounts of CO emitted (the air is in large excess in these experiments).

The comparable curves for a soda char burn are shown in Fig. 5-5. An important aspect of the soda char burn was the minimal to negligible amount of fume formed. (The sodium scales are the same in Fig. 5-4 and 5-5.) The burn was rapid, but calm. There was no Roman candle effect and no corona. The main gaseous product was CO_2 , although some CO was present about midburn. Addition of Na_2SO_4 to the soda char (15% based on the initial black liquor solids) did result in fuming during the burn. Addition of sulfate to the soda char caused the system to behave like a kraft char.

For kraft char burned in 10% O_2 (90% N_2), the time for complete burnout ranged from 25 to 30 seconds and fuming was greatly reduced. Total fume generated was only about 10% of that produced when burning with air. The Roman candle effect was eliminated.

When kraft char burning was carried out with only 2% O_2 , the rate was very slow and burn times exceeded 60 seconds. Fuming was essentially eliminated.

Fuming was intense when sulfur was present during char burning and was practically negligible when sulfur was absent. This is consistent with the previous finding that fume is generated most intensely when sulfide is oxidized to sulfate. The presence of relatively large amounts of carbon in the char did not suppress fuming.

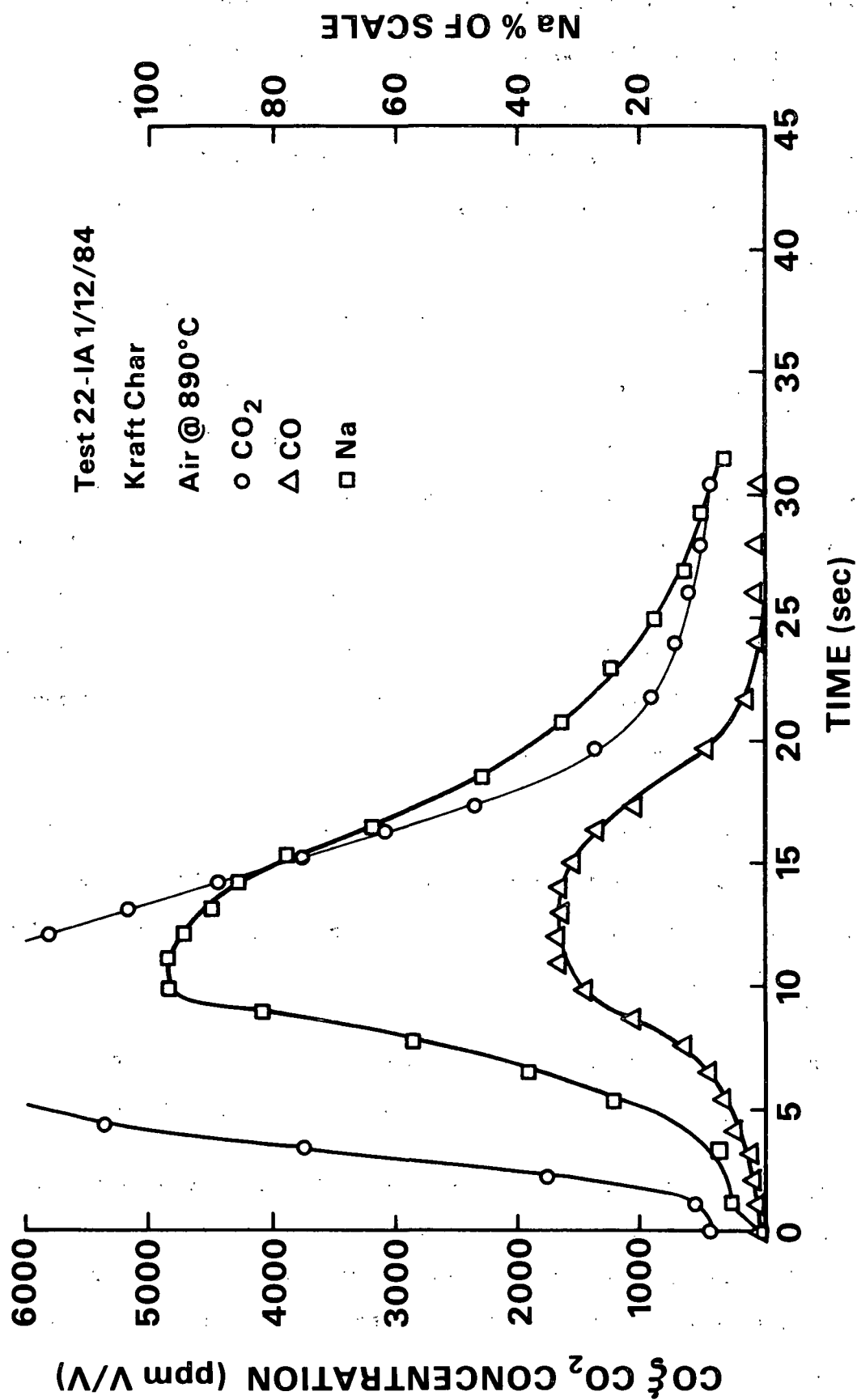


Figure 5-4. Fuming during a kraft char burn.

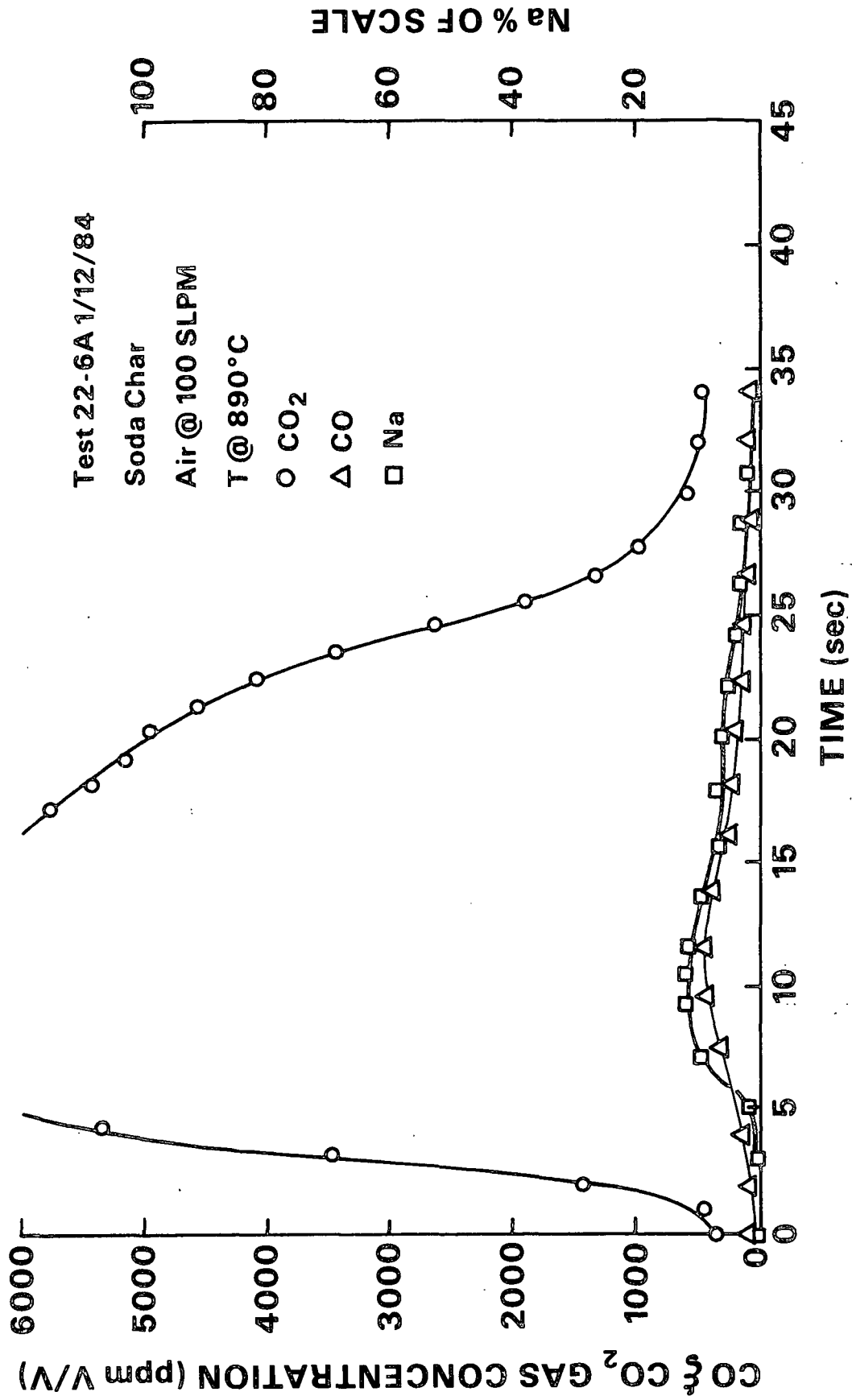


Figure 5-5. Fuming during a soda char burn.

The addition of 10% CO₂ to the air stream used for kraft char burning did not cause a reduction in fume intensity. None of the variables that partially suppressed fuming in the smelt pool experiments appeared to suppress fume during char burns.

There did appear to be a correlation between the intensity of char burning and the fuming rate. Slowing down the burning (e.g., by reducing the O₂ content of the combustion air) lowered fuming. This is most probably a temperature effect. Char burning is not isothermal. Increased burning rates will increase temperature and this in turn would increase fuming.

Chemistry of Oxidative Fuming

The chemistry of oxidative fuming is not well understood, and this makes it difficult to interpret data and extrapolate the results to new conditions (e.g., inside the furnace). Three explanations of the oxidative fuming phenomena have been considered:

1. Formation of a volatile intermediate species in the course of oxidation of sulfide to sulfate
2. Lowering of the gas side resistance to sodium vaporization by reaction of sodium vapor and oxygen
3. Thermal decomposition and volatilization due to locally high interfacial temperatures resulting from the oxidation

Since the fume produced when sulfide is air oxidized to sulfate in molten carbonate is essentially sulfur free, the volatile sodium species must also be sulfur free. The fundamental problem in describing the chemistry of oxidative fuming is to define the volatile sodium species. Both sodium vapor (Na) and sodium hydroxide vapor (NaOH) are sulfur-free volatile sodium species.

It is logical to begin by considering why or why not these can be used to explain oxidative fuming.

Sodium exists in the melt primarily as sodium ion (Na^+). Metallic sodium (Na) is in a reduced state compared to sodium ion. If metallic sodium is to form and volatilize, some reducing agent must reduce sodium ion to sodium. The difficulty with sodium vapor as the volatile in oxidative fuming is the problem of explaining how sodium ion can be reduced to sodium during an oxidative process.

The sodium in sodium hydroxide is in the same oxidation state as it is in sodium ion. The formation of the hydroxide can be considered to occur by



Thus the choice of NaOH as the volatile eliminates the problem of explaining how sodium ion is reduced during an oxidative process. The problem with NaOH vapor is that we could never find any evidence for it experimentally. Conditions that should have led to NaOH formation, such as the presence of water vapor in the purge gas, tended to suppress fuming under both oxidative and reductive conditions. In many experiments NaOH pellets were deliberately added to the melt. In general, this had no significant impact on fuming. The addition of one mole of NaOH (40 g) to a carbonate melt did not result in any detectable fuming. We are forced to conclude that the release of volatile NaOH is not a significant source of fume.

The difficulties in explaining oxidative fuming in terms of sodium vapor or sodium hydroxide vapor led to the postulate of a volatile intermediate species. The most attractive candidate for this intermediate is sodium monoxide

involved along the path leading to fume. Both CO_2 and H_2O can react with the oxide ion to form carbonate and hydroxide ion. This will shift all of the equilibria involving the oxide and lower the concentrations of peroxide and superoxide in the melt.

Thus the volatile intermediate hypothesis (with NaO as the candidate intermediate) provides one explanation for oxidative fuming. It is not the only possible explanation.

The second hypothesis provides an explanation of oxidative fuming in terms of sodium vapor as the volatile species. It draws heavily on the experience with a similar type of fuming problem in the iron and steel industry (38,39). Fume formation is considered to be a vaporization-oxidation process involving the counterdiffusion of oxygen and sodium vapor in the gaseous boundary layer. These interact to form sodium oxide fume (Na_2O) in the gas close to the smelt-gas interface. (Na_2O can subsequently react with CO_2 to form Na_2CO_3 .) As a result of the gas phase sodium-oxygen reaction, the diffusion layer for sodium vapor decreases, resulting in increased vaporization rates. Cameron (40) reports that this hypothesis agrees with much experimental data on oxidative fuming. Sulfide is apparently a strong enough reducing agent that some metallic sodium is present in the melt which can then vaporize when gas-side conditions are correct. There are two attractive features of this second hypothesis:

1. It involves a known volatile, sodium vapor.
2. It has successfully explained fuming during oxidation of molten metals.

The third explanation, that oxidative fuming is simply a manifestation of high interfacial temperature due to the exothermic oxidation reaction, is unlikely for the following reasons:

1. A thermocouple located at the discharge of the air tube in the melt never detected a significant temperature rise when air was bubbled through the melt.
2. The fuming rate was not very sensitive to the oxygen content of the purge gas while the heat released, and hence any temperature increase would tend to be directly proportional to the oxygen content.
3. No fume was generated when a mixture of O_2 , CO and N_2 was passed through molten carbonate. The O_2 and CO reacted in the gas phase to generate heat which would have raised interfacial temperature, but this did not cause fume.

REDUCTIVE FUMING

Reductive fuming is the term used to describe fuming under nonoxidizing conditions. Experimental conditions for reductive fuming included purging the melts with nitrogen gas. Reducing agents (e.g., carbon) could be added to the melts. Reducing gases (e.g., carbon monoxide) were sometimes used.

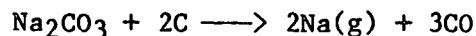
Results

Reductive fuming was noticeably less intense than oxidative fuming. The maximum FIR during reductive fuming was about 4, compared to 7 for oxidative fuming. Fuming was most intense at the strongest reducing conditions (carbon in carbonate). Addition of CO_2 to the purge gas tended to reduce fuming. Presence of sulfur compounds or sodium hydroxide in the melt either decreased fuming or

had no effect. Sulfate tended to suppress fuming. The observed temperature dependence of reductive fuming was much greater than that for oxidative fuming.

Chemistry

Reductive fuming is caused by the release of volatile sodium compounds under reducing conditions. It is due to the formation of elemental sodium in the melt, which then vaporizes. Experiments in which the CO/CO₂ ratio in the off-gas was monitored showed negligible CO₂ during strong reductive fuming. This means the reaction involved is



$$\Delta H_{1700^\circ\text{F}} = +222.6 \text{ kcal/mole}$$

$$\Delta F_{1700^\circ\text{F}} = +35.1 \text{ kcal/mole}$$

The reaction is strongly endothermic and the equilibrium is unfavorable (positive free energy). Because of the endothermic nature of the reaction, the equilibrium becomes more favorable at higher temperatures. As expected, experiments showed lower fuming intensities at lower temperatures. Reductive fuming was negligible at temperatures below $\approx 1550^\circ\text{F}$. Equilibrium considerations also predict that CO should suppress reductive fuming. This was confirmed experimentally.

Reductive fuming requires a strong reducing environment. The presence of oxidizing agents tends to suppress reductive fuming. In one test in which N₂ was bubbled through a carbonate melt (no sulfur) with carbon present, fuming was dramatically reduced when 10% CO₂ was added to the N₂. In sulfate reduction rate experiments it became evident that significant sodium formation did not take place until sulfate was depleted. In some of the early sulfate reduction rate tests small sodium fires or hydrogen pops occurred when the downstream piping was washed out after a run. It was rapidly learned that these could be

prevented by terminating reduction runs before all the sulfate had reacted. This suggests that reductive fuming could only be important where sulfate reduction is complete.

The strongly endothermic nature of the sodium producing reaction along with the temperature dependence of the equilibrium means that the reaction is self limiting unless heat is supplied from an external source. In this respect it is similar to sulfate reduction but with two major differences.

1. The endothermic heat of reaction is much greater
(+3780 Btu/lb Na_2CO_3)
2. Sulfate reduction does not require strong reducing conditions, so that simultaneous oxidation, generating heat, is permissible.

Thus the endotherm is much more restrictive for sodium formation.

As was mentioned earlier, sodium hydroxide vapor is not a significant source of fume. Addition of sizable quantities of NaOH to the melts either reduced fuming or had no effect. It never resulted in an increase in fume.

FUME SUMMARY

Major Findings

The major findings of the fume work can be summarized as follows:

1. Fume is produced when sulfide is oxidized to sulfate in molten carbonate. This fume is sodium carbonate. The process is called oxidative fuming.

2. Oxidative fuming is the most significant source of fume in a kraft system.
3. Oxidative fume is suppressed to some extent when CO_2 , C, or H_2O vapor are present.
4. Reductive fuming is the production of sodium vapor. It requires very strong reducing conditions and an external source of heat. It is suppressed strongly when sulfate or CO_2 are present.
5. Sodium hydroxide vapor is not a significant source of fume in kraft recovery operations.
6. Carbon and water vapor can gasify some of the sulfide in the smelt. After oxidation to SO_2 , this can readily react with the carbonate and convert it to sulfate.
7. The main source of fume during char burning is oxidative fume associated with the oxidation of sulfide to sulfate in the sulfate-sulfide cycle.
8. Fuming rate increases as the intensity of char burning increases. This is due to the effect of burning rate on temperature and to the ejection of smelt droplets during high intensity burns.

Further Work

Although oxidative fuming is a very significant source of fume, it is not well understood. This makes it difficult to extrapolate the results of laboratory tests to furnace conditions. Work is continuing to resolve the uncertainties concerning oxidative fuming, conclusively determine the volatile sodium species, and develop predictive rate equations.

6. OPERATIONAL IMPLICATIONS

APPLICATION TO FURNACE

The overall goal of this project was an understanding of the char burning process that could be used to analyze recovery furnace operation and identify means for improving performance. The preceding sections have dealt with the fundamental processes that occur during char burning. In this section we will attempt to apply the knowledge gained to the recovery furnace.

Char Beds and Char Burning

As was discussed in Chapter 2, char burning and burning in the char bed of the recovery furnace are not identical. Char burning (a process) is the last stage in the black liquor burning process. Where it takes place in the furnace is dependent on operating conditions. Some char burning always occurs on the bed but it may also occur as the particle falls to the bed or as it is swept upward with the combustion gases. Bed burning, on the other hand, includes all of the processes occurring in and on the bed in the furnace. These include char burning, but may also involve volatile burning and even drying. In an individual small liquor particle the processes tend to occur sequentially. Within the furnace, large numbers of particles are involved at various stages in the burning process. This tends to blur the distinctions between the process steps.

The relationship between pyrolysis conditions and char composition and properties was beyond the scope of this project. The relationship between process conditions and the extent that pyrolysis had proceeded at any given time was also excluded. This means that the prediction of the composition and heating value of the partially burnt liquor landing on the bed is also beyond

the scope of this project. This restriction has its greatest impact on char bed material and energy balance calculations. We cannot directly answer the question "how much air is actually taken up by the bed and how much heat is released there"? We can, however, look at what would happen if bed burning was the same as char burning and compare that with experience.

Char burning is the final step leading to the separation of inorganic pulping chemicals from the organic in the black liquor. The inorganic is released as molten smelt when the char carbon burns away. Since the bed is the most innocuous place to form molten smelt and remove it from the furnace, this is the location where char burning should occur (particularly the last stage of char burning). It appears to be a reasonable first approximation to identify bed burning with char burning. There is no doubt that knowledge of char burning is directly applicable to interpreting bed behavior.

Overall View

The results of this work can be used to provide an overall view of how black liquor burns in a recovery furnace. The two most significant findings in this respect are

1. Kraft char burns via a sulfate-sulfide cycle. This permits reduction to occur simultaneously with carbon burnup, even through sizable quantities of oxygen reach the char.
2. Char burning is an exothermic reaction. Heat release on the burning char bed can provide the heat needed to maintain the bed temperatures required by the temperature-sensitive reaction rates.

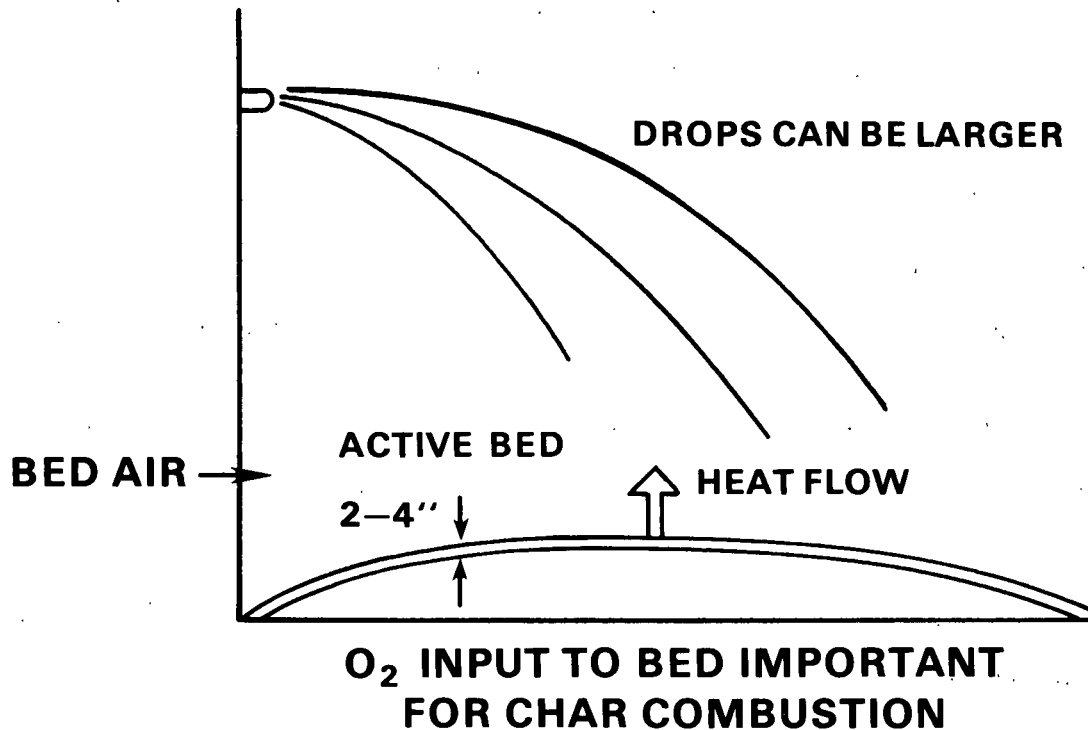
It is not necessary to maintain an oxygen deficient atmosphere above the char bed in order to achieve satisfactory reduction efficiencies. Adequate reduction can be obtained as long as bed temperatures are high enough and there is an excess of carbon in the bed. The chemically active region of the bed is that portion where the char has access to oxygen from the combustion air. Char reactions in the absence of oxygen tend to be self limiting, since they are endothermic and the reaction rates decrease rapidly as temperature decreases.

The view of burning in the lower part of the furnace resulting from this work is summarized in Fig. 6-1. This may be contrasted with the view coming from the ADL furnace model which is illustrated in Fig. 6-2. The major difference between these concepts is in the amount of combustion (and reduction) that takes place on the bed.

In our view a substantial fraction (up to 50%) of the total combustion occurs on the bed, (along with a demand for a corresponding amount of the total air to be supplied to the bed). The capability to burn large amounts of combustibles on the bed permits operations with coarse sprays (which minimizes entrainment). All that is required to achieve this is an adequate supply of combustion air to the bed and sufficiently high bed temperatures.

The ADL view sees very little combustion occurring in the bed because of very limited air access. This view requires that most of the combustion must take place in flight. For this to occur, liquor sprays must be fine and the burning becomes very sensitive to spray parameters. Although it is possible to operate recovery boilers along these lines, it is not preferred. Fine spray firing aggravates boiler plugging and can lead to combustion instability.

NEW LOWER FURNACE MODEL



ACTIVE BED: Major part of combustion occurs on bed.

Almost all reduction occurs in thin layer on the bed.

BURNING CYCLE: $\text{Na}_2\text{SO}_4 + 2\text{C} = \text{Na}_2\text{S} + 2\text{CO}_2$
(Exothermic) $\text{Na}_2\text{S} + 2\text{O}_2 = \text{Na}_2\text{SO}_4$

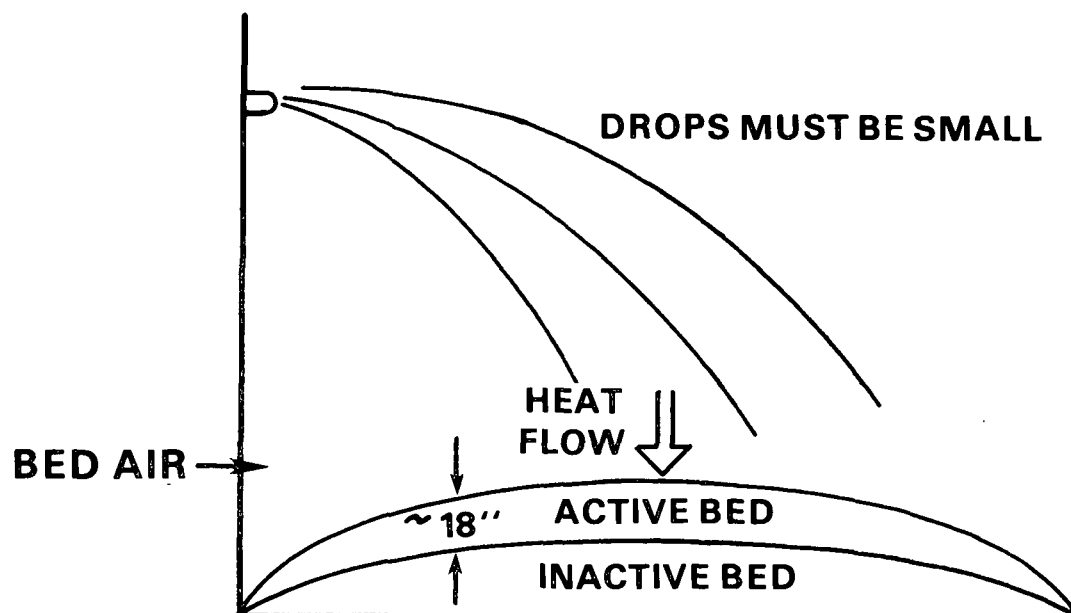
Faster than $\text{C} + \text{O}_2 = \text{CO}_2$

Requires less than 1 minute to go to 95% reduction.

Thermal conduction effects not important.

Figure 6-1. New lower furnace model.

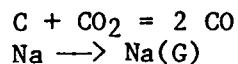
ADL LOWER FURNACE MODEL



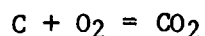
**MOST CHAR COMBUSTION OCCURS IN GAS PHASE
BED SURFACE LIMITED IN O₂ SUPPLY**

AT BED SURFACE:

Strongly endothermic
reactions

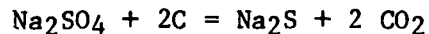


Too Slow to provide
significant heat



Reactions at bed surface cool bed significantly —>
Reduction strongly dependent on heat transfer within
the bed.

IN ACTIVE BED:



- Requires 90 minute residence time to go to 90% red.

Figure 6-2. ADL lower furnace model.

The advantage of the new view is that it provides a rationale for maximizing combustion on the bed. Air must be supplied directly to the bed in proportion to the distribution of combustible over the bed. Temperature is the other key variable. Increased burning rates are obtainable by increasing bed temperature. Since the temperature is self-generated by the combustion exotherm, the effective heating value of the material reaching the bed is very important. Complete dryness of the material landing on the bed would be very important. So would the extent of pyrolysis and prior char burning.

SPECIFIC OPERATING OBJECTIVES

Burning Rates

Typically, design firing rates correspond to about 2 to 2.5 lb dry solids per ft² of floor area per minute. It is of interest to compare these design firing rates with the char burning rates observed in this work. For a liquor with a sodium content of 20% by weight on the solids, a firing rate of 2.5 lb dry solids/ft² min corresponds to 0.5 lb Na/ft² min or $0.5/46 = 0.0109$ mole Na₂/ft² min. Thus it is reasonable to assume a sodium flux to the bed of 0.01 mole Na₂/ft² min. If the carbon content is 3 moles C/mole Na₂, the carbon flux is 0.03 mole C/ft² min.

A steady-state material balance over a reacting layer of thickness, h , gives

$$N_N \{ [C]_1 - [C]_0 \} = h \rho_N R_C \quad (6-1)$$

where N_N = molar sodium flux to bed, moles Na₂/ft² min

$[C]$ = carbon concentration, moles C/mole Na₂

h = thickness of reacting zone, ft

ρ_N = molar density of char, moles Na₂/ft³

R_C = carbon burnup rate, moles C/mole Na₂ min.

The molar density of char is approximately given by $\rho_N = 1.5 (1 - \phi)$ moles Na_2/ft^3 , where ϕ = void fraction of the char. Equation (6-1) can be solved to give the average carbon burnup rate in the reacting layer.

$$R_C = \frac{0.01 \{ [C]_1 - [C]_0 \}}{h \times 1.5 (1 - \phi)} \cdot \frac{\text{moles C}}{\text{mole Na}_2 \text{ min}} \quad (6-2)$$

Let $\phi = 0.8$, $h = 1/3$ (4-inch thick zone), $[C]_1 = 3$, $[C]_0 = 0$
then $R_C = 0.3$ mole C/mole Na_2 , min.

Note that R_C is inversely proportional to the assumed thickness of the reacting layer (e.g., if the zone is 2 inches thick, $R_C = 0.6$, etc.).

According to the sulfate-sulfide cycle theory, the maximum rate of carbon burnup is given by the carbon-sulfate rate equation in the sulfate independent region. (It will always be less than this value in the oxygen supply limited region). The relevant rate equation for the kraft char used in this study is

$$R_C = \frac{-d[C]}{dt} = \frac{1.5}{(2-f)} e^{0.0102 \Delta T / (1 + \Delta T / 1200)} [C] \frac{\text{moles C}}{\text{mole Na}_2, \text{ min}} \quad (6-3)$$

For $f = 0$ (all CO_2) and 1700°F ($\Delta T = 0$),

$$R_C = 0.75 [C] \frac{\text{moles C}}{\text{mole Na}_2 \text{ min}}$$

(Note that this is a conservative expression for the maximum burning rate.

Increasing CO production or higher temperature would increase the value of R_C .)

The value of carbon concentration, $[C]$, to use in Eq. (6-3) is some appropriate average in the reacting layer. This requires a "model" of the reaction zone. For example, if the reacting zone is treated as a perfectly back-mixed reactor, the appropriate value would be the concentration in the smelt

leaving the zone ($[\bar{C}] = [C]_0$). However, a back-mixed model does not seem realistic. A much better model is to treat the char as moving through the zone in plug flow. In this case the appropriate average is the log mean of the incoming and discharge concentrations. (For 95% carbon burnup, ($[\bar{C}] = 0.32 [C]_i$, and for 99% carbon burnup, $[\bar{C}] = 0.21 [C]_i$). It is of interest to compare these values with the measured carbon content of bed samples obtained by ADL (11) and Borg et al. (12). They found carbon contents in char of about 5% by weight. This would correspond to $[\bar{C}]$ of about 0.4 mole/mole Na_2 or about 13% of $[C]_i$.

The value of $[\bar{C}]$ which satisfies the steady-state mass balance on the bed [Eq. (6-2)] for the assumed conditions discussed above is found from

$$R_c = 0.3 \frac{\text{moles C}}{\text{mole Na}_2, \text{ min}} = 0.75 \text{ min}^{-1} [\bar{C}]$$

or

$$[\bar{C}] = 0.4 \frac{\text{moles C}}{\text{moles Na}_2} = 0.133 [C]_i$$

This is equivalent to about 5% carbon by weight in the char and is in agreement with those measured values of samples taken from burning beds (11,12). This means that burning rate equations developed in the course of this study are directly applicable to burning in char beds.

This calculation indicates that an average carbon content as low as 13% of the initial value is sufficient to meet the carbon burnup rate required at these conditions. Since this value is well below that needed to give 99% carbon burnup in a plug flow model, and is similar to that in samples removed from operating furnaces (which would provide a lower estimate of the char carbon content, since any burning during and after sampling would lower the carbon

content), there should be no problem in reaching such an average value. This means that a four-inch-thick reaction zone at 1700°F is more than sufficient to handle the entire char burning load at typical design firing rates.

There is an inverse relationship between temperature and the necessary thickness of the reaction zone. If the reaction zone thickness were halved, the required carbon burnup rate would be doubled. On the other hand, the burning rate can be doubled by increasing temperature 100 to 125°F. Thus a 4-inch-thick zone at 1700°F is equivalent to a 2-inch-thick zone at 1825°F.

The thickness of the reaction zone for char burning is determined by the depth of air penetration into the bed. For a porous, open bed, a reaction zone of 4 inches does not appear unreasonable. For a closed up, nonporous bed, an oxygen-accessible zone of this size is more difficult to imagine. The required carbon burnup rate is inversely proportional to the zone thickness. On the other hand it is also inversely proportional to the solid fraction (1 - void fraction). These two factors tend to compensate for each other to some extent so that the required burning rate is not overly sensitive to the voidage.

The fact that a four-inch-thick reaction zone at 1700°F is capable of handling the entire char burning load at design firing rates suggests there is ample opportunity to increase bed burning rates and hence total liquor solids throughput. To determine the conditions needed to achieve this, we need to go back to the sulfate-sulfide cycle for char burning. The theory states that a prerequisite for obtaining high reduction efficiencies simultaneously with char burning is for the rate limiting step to be oxygen mass transfer to the char. This is the regime in which the bed must operate. Since the carbon actually burns by reacting with sulfate, higher intrinsic carbon-sulfate reaction rates

allow higher oxygen mass transfer rates while retaining oxygen transfer as the rate-limiting step. Higher intrinsic carbon-sulfate rates, in turn, are obtained at higher temperatures.

Thus there are two keys to increasing bed burning rates.

1. The oxygen supply rate to the bed must be increased. The burning rate cannot exceed the oxygen supply rate.
2. The bed must be maintained at a sufficiently high temperature to allow carbon-sulfate reaction rates to keep pace with the air supply rate.

The oxygen supply rate can be increased by increasing the O_2 content of the air reaching the bed and increasing the relative velocity of the air past the char. Bed temperature levels can be increased by keeping the evaporative heat sink away from the bed and by carrying more fuel value into the bed.

Bed Temperature

The temperature in the reaction zone where char burning is occurring is a very important parameter. The rate of the carbon-sulfate reaction, which is the reaction by which char carbon is burned, increases strongly with increasing temperature. Higher carbon-sulfate rates, in turn, allow higher air supply rates to the burning char and hence higher overall burning rates without loss of reduction efficiency. Based on the data obtained in this study, we expect the burning rate to double for about a 100-125°F increase in reaction zone temperature.

The relevant temperature is that which exists in the reaction zone where active char burning is occurring. Since char burning requires reaction

with oxygen gas, the reaction zone is that layer (probably only a few inches thick) on the surface of the bed which is accessible to oxygen. Clearly there is no such thing as a bed temperature. A wide variation in temperature exists across the surface of the bed and with depth into the bed. The most appropriate single parameter would be the bed surface temperature averaged over the entire bed surface. However, a single temperature is inadequate to describe bed burning. Some indication of the spread in temperature from place to place is also needed. Since potential burning rates are exponentially dependent on temperature, it might be useful to use an exponentially weighted temperature average (somewhat analogous to the H-factor used in pulping) to characterize the state of burning of the char bed.

The smelt discharge temperature is not an appropriate measure of the reaction zone temperature. The temperature at which the smelt leaves the unit can be considerably different from the reaction zone temperature because of processes occurring after the molten smelt leaves the reaction zone. Smelt is cooled by endothermic reactions occurring in the interior of the bed and by heat transfer to the floor and lower walls. Smelt temperature is increased by the exothermic reoxidation of sulfide to sulfate. Reoxidation has considerable potential for raising smelt temperature. If all of the heat of reaction goes into raising smelt temperature, a 5% loss of reduction efficiency by reoxidation can raise the temperature by 200°F. These processes do occur in furnaces. Smelt discharge temperature is often more closely related to the amount of reoxidation that has occurred than it is to surface temperature.

Radiation-type temperature measuring devices (e.g., pyrometers) have the potential to provide a reasonable measurement of average bed surface temperature, provided they overcome two problems.

1. They must see and respond to the bed surface temperature and not radiation from surrounding combustion gases and entrained particles.
2. They must see a reasonably wide area of the bed. Several sensors, located in different positions, could be used to provide the necessary coverage.

Bed surface temperature (reaction zone temperature) is established by a heat balance that includes heats of reactions, heat exchange with the surrounding gases, and heat transfer to the interior of the bed. This is a local phenomenon and depends on local reaction rates and heat exchange rates. Increased bed surface temperatures are obtained by increasing exothermic reaction rates (char burning), decreasing endothermic processes (such as drying) or by radiating more heat from the gases above. Char burning is an oxygen supply limited process. Thus increased burning rates require increasing the rate of oxygen (air) supply to the bed surface. This must be matched by a corresponding increase in the local supply of burnable material in order to sustain a bed. Increasing burning rates in this manner will increase bed temperature. All drying should occur before the material lands on the bed to eliminate evaporative heat sinks that would lower bed temperature. Increasing bed temperatures by intensifying combustion in the gases above the bed and radiating heat to the bed is a less desirable method. If auxiliary fuel is used to do this, the heat content of the auxiliary fuel is a load on the heat absorption capability of the unit which reduces the amount of heat that can be absorbed from burning liquor (and thus reduces the amount of liquor that can be burned). If firing conditions are adjusted to intensify combustion in the gas space above the bed, it will inevitably result in increased solids entrainment and boiler fouling and plugging.

It is fair to ask, if bed temperature is such an important parameter, what is the optimum temperature? To a first approximation, the higher the temperature the better. Nothing connected with the sulfate-sulfide cycle itself is adversely affected by increased temperature. There are two factors that do tend to put an upper limit on desired bed temperature. These are

1. Excessive burning rates could exceed the rate of supply of material to be burned and result in bed burndown.
2. Increasing temperature increases the amount of fume formation and thus the particulate load to the heat traps and electrostatic precipitator.

The first of these problems can be counteracted by increasing the supply of material to the bed, and this is normally a desirable operating objective. The second factor is more complex. Fume particles can react with oxidized sulfur gases formed by combustion and convert them to sodium sulfate. Thus a certain amount of fume is desirable because it improves overall sulfur retention, reduces SO_2 emissions, and results in a less-sticky dust in the generating bank, economizer, and precipitator. Fume becomes a detriment when it reaches levels where it fouls heat transfer surface and plugs gas passages and thus limits throughput. It is not at all clear just what the upper limit on bed temperature is. We believe it is realistic to consider that it is at least 2000°F.

Bed Stability

Char beds are dynamic in nature. Fresh material is continually supplied to the bed from the liquor sprayed into the furnace. Material is removed from the bed by burning off the char carbon and smelting out the inorganic. If the bed is to be stable, the rates of addition and removal must be in balance.

The amount, composition, and distribution of the material arriving on the bed is dependent on the amount of drying, pyrolysis, burning, and physical entrainment that takes place before the material reaches the bed, as well as the rate of liquor introduction. The rate of removal of bed material depends on chemical reaction rates (char burning rates). These rates must be kept in reasonable balance if the size, shape, mass, and composition of the bed are to remain reasonably constant. Either or both of these rates can be manipulated to achieve this balance.

One commonly used operating strategy is to manipulate the rate of supply of material to the bed to match bed burning rates. This is achieved, primarily, by adjusting the liquor spray size. Finer sprays result in less combustibles reaching the bed and coarser sprays carry more combustible to the bed. The spray size is adjusted in response to visual observation of bed size and shape. Feedback of information on whether the bed is growing or decaying is essential to this strategy, since the process is not inherently stable. Operating in this mode can stabilize bed size, but it does not necessarily stabilize the burning rate or the chemical processes occurring in the bed. Frequently, this approach leads to fine spray firing with a minimum of bed burning, because that condition requires less operator attention. Fine spray firing has several detrimental effects including increased carryover and fouling, poorer reduction, and a potential for rapid onset of blackout.

A more optimal strategy is to create conditions that allow the burning rate to match the rate of arrival of bed material. The two parameters that govern the char burning rate are the rate of air supply to the bed and the bed temperature. The necessary temperature can be self-generated by the exothermic char burning reaction, provided there is sufficient fuel value present and the

incoming material is essentially dry (no heat sinks). Thus the air supply can control the burning rate and the bed inventory. This makes it possible to achieve self-stabilizing conditions through the proper spacial distribution of air. The basic requirement is to introduce the air into the lower furnace in such a way that an increase in bed size increases air-bed contact and hence air supply to the bed. This will increase bed burning rates and reduce the rate of bed growth leading to a stable size.

Self-stabilizing beds are most easily obtained with an air supply system in which there are at least two levels of air supply in the lower furnace (primary-secondary or primary-high primary). A zone of high air flow is maintained some distance above the hearth with the upper air ports. If the bed is below this zone, burning rates will be low and the bed will grow. As the bed penetrates the upper air zone the burning rate is increased until it matches the rate of char supply. This concept is illustrated in Fig. 6-3.

Operation with a self-stabilizing bed is less dependent on the need for continuous observation of bed shape or size. Visual (or other) observation would still be valuable for fine tuning, but it would not need to be part of the feedback loop.

Reduction Efficiency

Overall smelt reduction efficiency is another variable important in kraft recovery boiler operation. Good practice would require maintaining reduction efficiencies greater than 90%, and preferably about 95%.

Reduction of oxidized sulfur compounds to sulfide in the furnace occurs primarily through the carbon-sulfate reaction. The two main variables influencing the reduction rates are the amount of carbon present and the temperature.

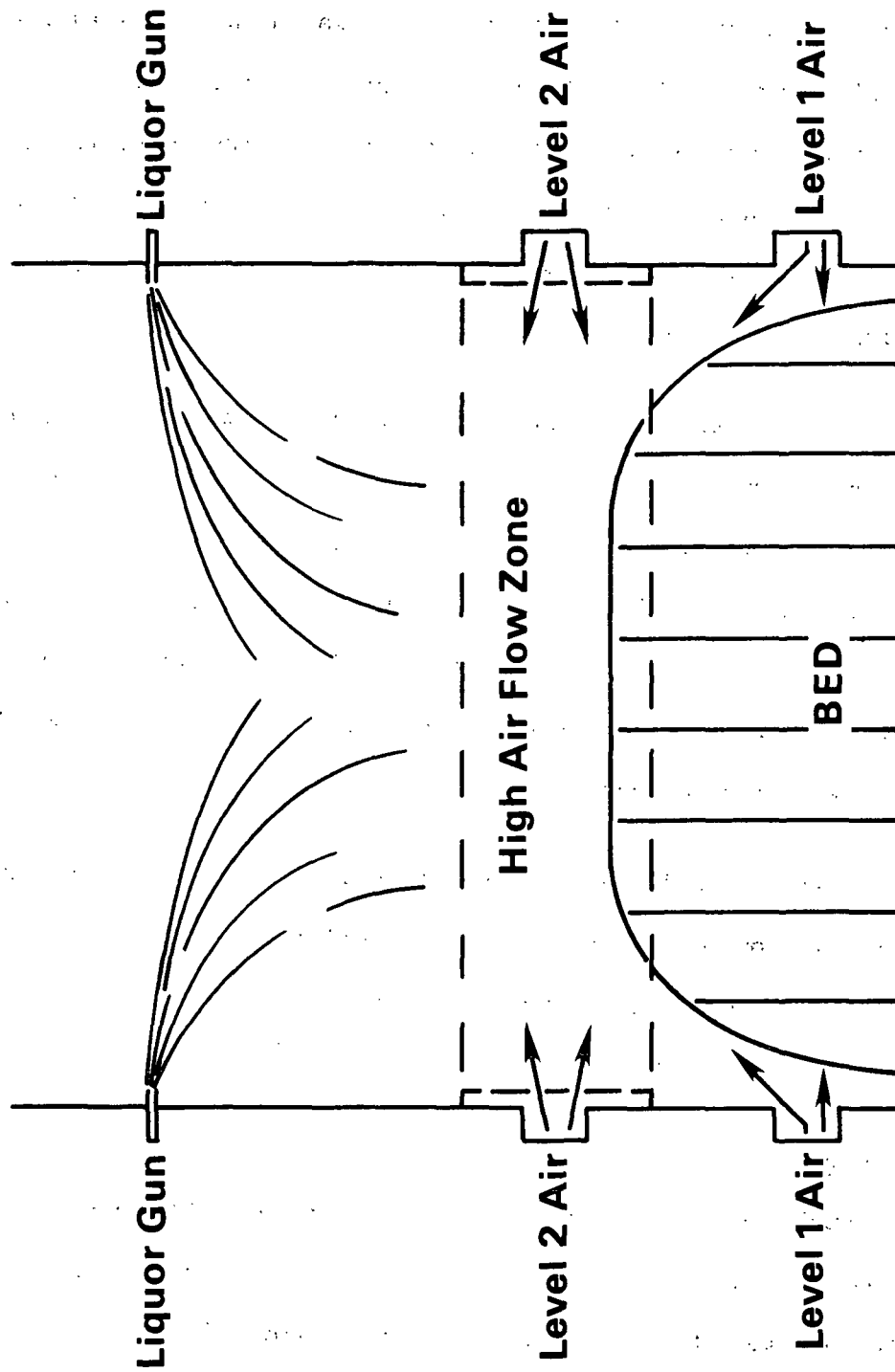


Figure 6-3. Air levels and bed stability.

The pyrolysis reactions which precede char burning provide char carbon in quantities well in excess of those needed for sulfate reduction. Thus the main parameter influencing reduction rates in the furnace is temperature.

As was shown in this study, the carbon-sulfate reaction is one-half of the sulfate-sulfide cycle by which kraft char burns. Thus reduction occurs as a normal part of the char burning process. Vigorous char burning with the rate limiting step on the oxygen supply side is all that is needed for reduction to occur. No special steps need be taken. It is not necessary to have a reducing gas environment to get good reduction, nor is it necessary (or even desirable) to starve the lower furnace for air. Those operating conditions which provide for vigorous burning of black liquor solids on the bed are exactly those which provide for high reduction efficiency.

Reduction is not limited to the char bed. Reduction also takes place in liquor particles burning in suspension. Sulfate reduction is an intrinsic part of char burning and takes place wherever char burning occurs, on the char bed or in flight. Reduction efficiencies normally approach 100% in the burning char particle at some point in the burning process. They begin to drop away from 100% as the carbon content of the burning char becomes depleted. The key to sustaining high reduction efficiencies is to get the reduced smelt away from the oxidizing air before the carbon content has become so depleted that substantial sulfide reoxidation takes place.

The conditions favorable for sustaining high reduction efficiencies are met with a proper, porous char bed. The bed provides a route by which reduced smelt can make its way to the spouts without being oxidized. As char burning proceeds in a particle in the thin reaction zone on the surface of the bed, a

point is reached when the carbon content of that particle has become too low to sustain a solid structure and the particle coalesces into a smelt drop containing some suspended char carbon. If the burning particle is large and dense, the molten smelt freed by burning out the carbon saturates the particle and begins to ooze out as smelt drops. In either event smelt drops are formed as carbon is burned away. If the burning temperature is high, the released smelt will be highly reduced. These reduced smelt drops leave the reaction zone and permeate through or across the surface of the bed until they reach the hearth and ultimately run out the spouts. Thus a char bed helps reduction efficiency by providing a path by which reduced smelt can move out of the air contact zone and by shielding reduced smelt from the primary air supply as the smelt moves to (and out) the spouts.

As mentioned, some reduction can also take place in flight if char burning takes place in flight. In the extreme, the complete burning process can occur in flight resulting in a smelt droplet. If this droplet is large enough, it will fall to the bed. If a good deal of suspension burning is occurring, it could result in a "rain" of smelt falling on the bed. The state of reduction of this "rain" will depend on the amount of oxygen the drops encounter as carbon becomes depleted and they fall to the bed. This would impact significantly on carbon-sulfate ratios in the material landing on the bed, and under some conditions could result in low overall reduction efficiencies (< 85%). In general, in-flight burning is a less desirable means of achieving good reduction.

Limited reduction can take place in the interior of the char bed. This provides some back-up to restore very high reduction efficiencies to smelt which left the active zone less than fully reduced, or to smelt raining down on the

bed from above. The carbon needed for "inside bed" reduction can only come from two sources.

1. The entrained char carbon carried with the molten smelt
2. Carbon already present within the bed from incomplete combustion during a bed-building phase

This latter source cannot be sustained on a steady-state basis because the carbon within the bed would eventually be depleted.

There is a limit to "inside-bed" reduction. The reduction reaction is endothermic and will lower the temperature inside the bed. Lowered temperatures, in turn, lower the reduction reaction rate. Thus "inside-bed" reduction is a self limiting process because the local temperature will drop to a point where reaction rates will be negligible. For a typical smelt, a 5% gain in reduction efficiency within the bed will drop the temperature about 60°F. It thus appears that an upper bound to the amount of reduction occurring inside the bed is that corresponding to a 25% gain in reduction efficiency.

All of the factors involved in obtaining high reduction efficiency in a kraft furnace are illustrated in Fig. 6-4. These include reduction in the active burning zone on the bed, in-flight reduction, "inside-bed" reduction, and smelt reoxidation. The optimum method for achieving good reduction is vigorous char burning on the surface of the char bed, along with an adequately sized bed to shield the smelt from the primary air.

Unburned Carbon in Smelt

Unburned carbon in the smelt leaving the furnace is a loss of potential fuel value, a load on the green liquor clarifier and dregs handling system, and

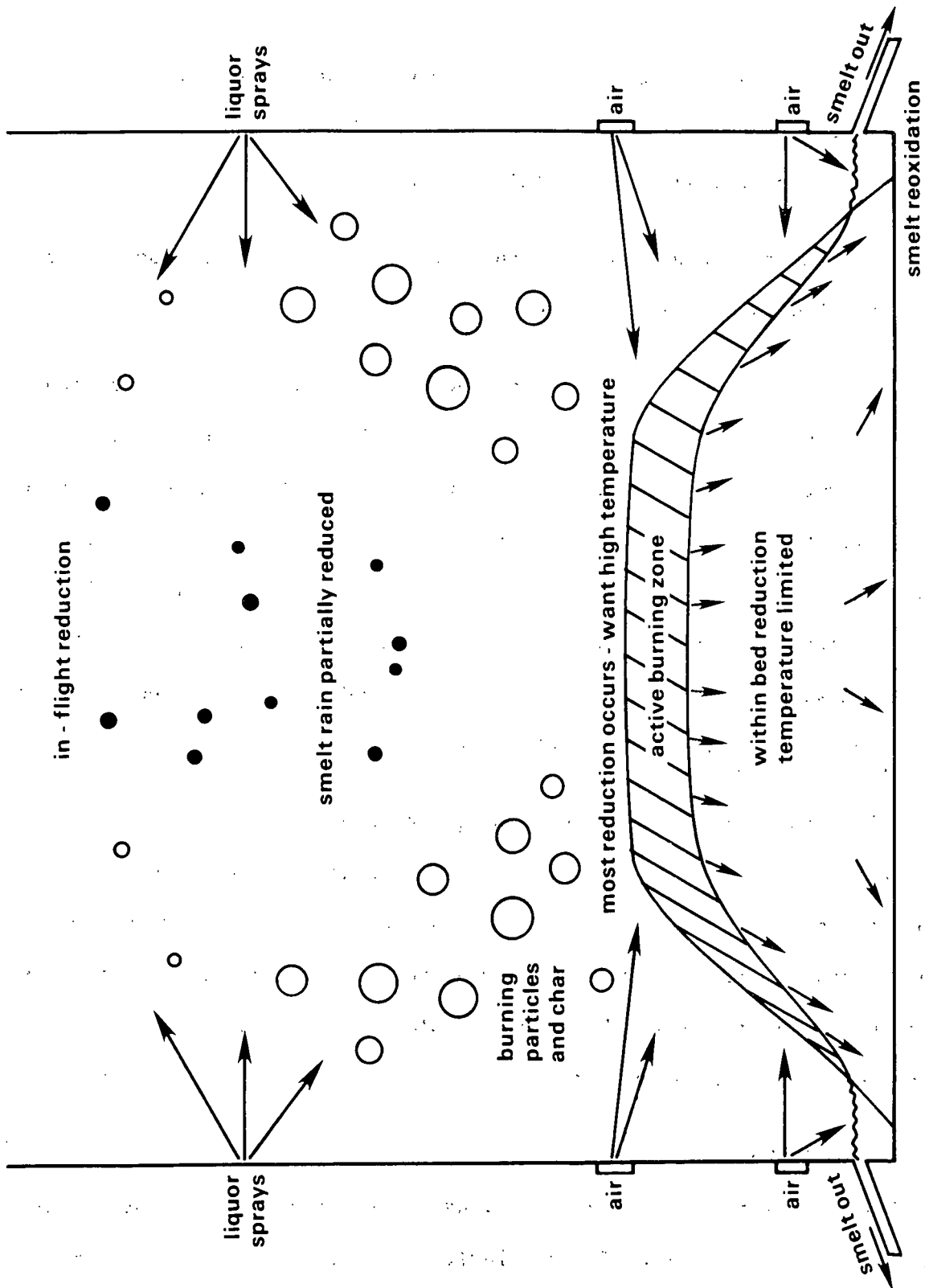


Figure 6-4. Factors involved in reduction efficiency.

may act to catalyze sulfide oxidation in the dissolving tank and in the green liquor system. It is desirable to minimize unburned carbon in smelt.

Unburned carbon in smelt can come from two sources: very small char carbon particles entrained in the smelt when the char particle structure collapses and large chunks of char which are swept up by the moving smelt stream and carried out the spouts. The former have some value, since they are quite reactive and help control smelt reoxidation. The larger char particles that are swept out carry no such benefit.

The conditions which generate a hot active burning zone help to minimize entrained char carbon because they increase carbon burnup rates. Hot smelt is much more reactive toward entrained carbon. It is also much more free flowing and thus able to move to the spouts without carrying a lot of char with it. Thus the first prescription for reducing the amount of unburned carbon in smelt is to increase the bed temperature by intensifying bed burning.

Since some carryout of macroscopic char particles is inevitable because the flowing smelt exerts viscous drag and can readily buoy up char, it is also desirable to minimize the amount of char falling to the hearth in the close vicinity of the spouts. This suggests modifying spray patterns to cut down on the amount sprayed near the spouts.

Fume Control

At the present time it is not possible to make definitive statements on how to control fume in the kraft furnace. Oxidative fuming is clearly a very significant source of fume, but it is not well understood. This makes it difficult to extrapolate the results of laboratory tests for furnace conditions.

In addition, our laboratory work has cast considerable doubt on the significance of some of the fuming processes previously thought to have been important in the furnace.

Based on the work discussed in Chapter 5, only two sources of fume production seem reasonable in the furnace (this excludes consideration of chlorides, a separate issue). These are oxidative fume produced as a side reaction during the sulfate-sulfide cycle in char burning or during smelt reoxidation, and elemental sodium formation (and volatilization) inside the bed in sulfate depleted areas. Sodium hydroxide vaporization does not appear to be significant.

Control of fuming suggests some criteria for deciding how much fume is desirable. There are both good and bad effects of fume produced in the kraft furnace. The bad effects are fairly obvious. Fume is a source of particulate in the furnace gases. This particulate can cause slagging in the superheater and front of the generating bank as well as contribute to dust loads in the generating bank and economizer (requiring more sootblowing) and the electrostatic precipitator. The relative extent that fuming and physically entrained burning particles contribute to slagging and fouling is still subject to debate and study. Clearly, however, fume production does have costs associated with it for keeping heat transfer surface clean and for cleaning the combustion gases. However, fume production is also beneficial. The fume sodium carbonate particles can react with SO_2 and O_2 in the furnace, converting the sulfur gases to sulfate. In effect the fume acts as a "getter" for SO_2 . This not only improves sulfur retention for the kraft process and cuts down on SO_2 emissions to the atmosphere, but also eliminates sticky ash deposits within the boiler and

precipitator, and cuts down on corrosion problems. The best current guideline as to the "correct" amount of fume is that the precipitator dust should contain about 10% Na_2CO_3 (the remainder being Na_2SO_4).

We have only limited quantitative data on the oxidative fuming process. It is a temperature dependent phenomenon, with the rate doubling for about a 200°F increase in temperature. In experiments in which a $\text{N}_2\text{-O}_2$ gas was bubbled through smelt, the rate was only a weak function of the oxidation rate. On the other hand, when char particles were burned, fuming rate was a strong function of the burning intensity (this could have been due to the much higher temperatures reached in intense burns).

Our best interpretation of fuming in the furnace, at the present time, is that fuming is a natural consequence of char burning, and that fume will be produced wherever char burning occurs. Thus the bed surface and burnout of entrained particles appear to be the main sources of fume. Increased char burning intensity will increase fuming rates. The temperature dependence of oxidative fuming is relatively weak. A 200°F increase in temperature is needed to double the fuming rate.

Reductive fuming (the formation of metallic sodium in the bed and its subsequent vaporization) can only occur in a strong reducing environment. Oxidizing agents (such as sulfate) inhibit sodium formation by preferentially reacting with the reducing agent (carbon). Thus reductive fuming would only be important in those regions of the furnace where sulfate was absent. The main place where this can occur is the interior of the char bed. However, sodium formation within the char bed is a self limiting reaction because it is a temperature dependent endothermic process. In this respect it is similar to

sulfate reduction, except the endothermic heat of reaction is much greater (+ 8710 Btu/lb Na_2). Sodium volatilization within the bed will cause the temperature within the bed to drop. Volatilization of 1% of the sodium would result in a temperature drop of 140°F. Thus it is unlikely that reductive fuming inside the bed could be responsible for converting more than about 2-3% of the incoming sodium salts to fume. Experience indicates that fuming rates are normally in the range of 10-15% of the incoming sodium.

The production of fume in the recovery furnace is illustrated in Fig. 6-5. This shows oxidative fuming occurring in the active char burning region of the bed and in entrained liquor drops burning in flight. It also shows reductive fuming occurring in the interior of the bed. Quantitative predictions of fuming rates are not presently available. Changes in firing practices to intensify combustion on the bed surface will increase fuming from the active burning zone. However, if this is achieved by minimizing the amount of droplets burning in flight, the overall results may be a decrease in fume production.

AIR/FUEL DISTRIBUTION

If the bed surface temperature is kept hot enough the chemical recovery functions in the furnace tend to take care of themselves. No other special actions need to be taken to achieve acceptable reduction, sulfur scavenging and low residual carbon in smelt. The main additional requirement is to introduce the liquor in such a way that entrainment is minimized.

Spray Size

One of the key variables in recovery boiler operation is the spray size distribution of the liquor introduced into the furnace. This more than any other single parameter determines the amount of sodium salts physically

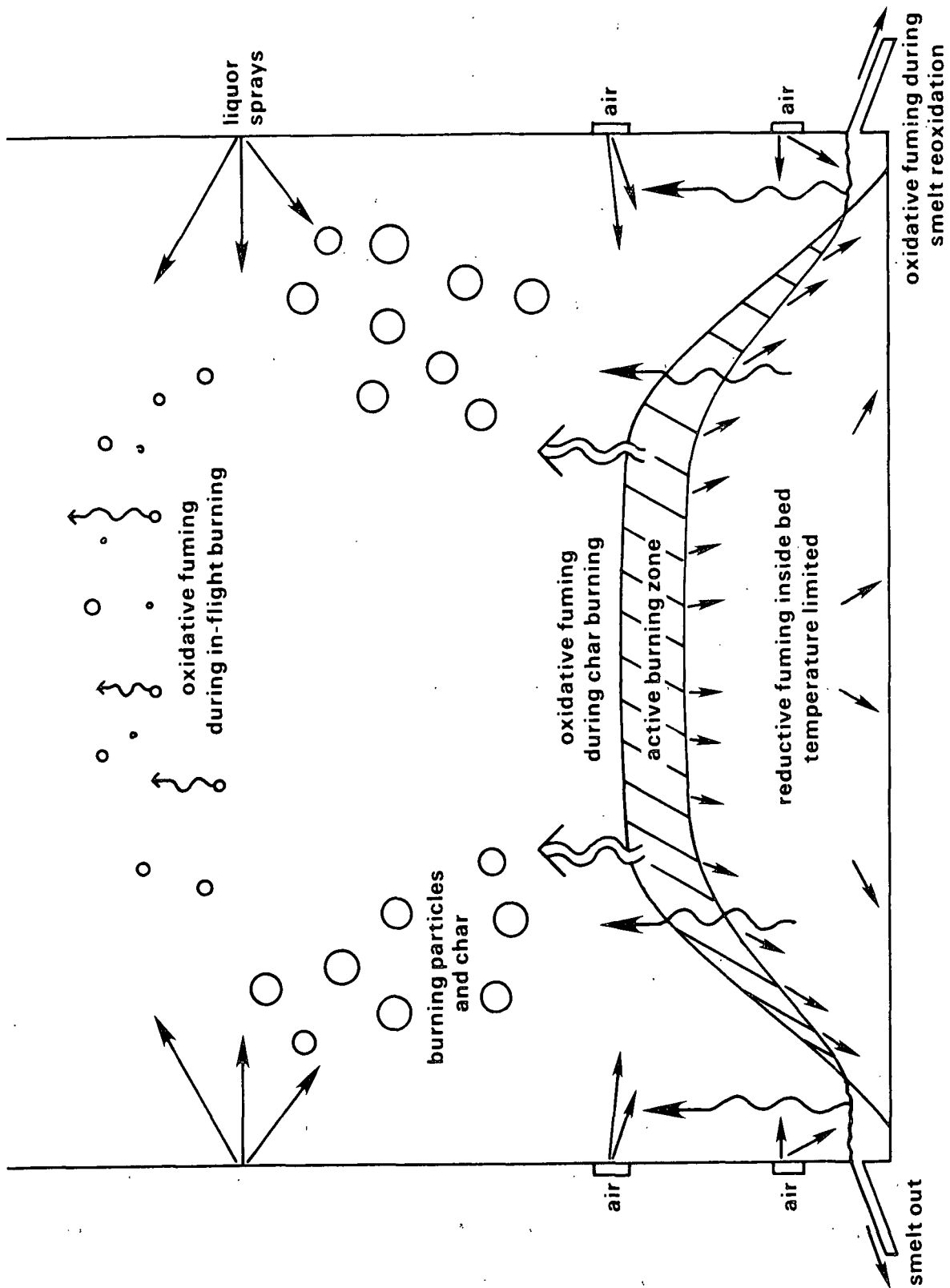


Figure 6-5. Fume production in the furnace..

entrained in the combustion gases, and the split in the fuel value between bed material and that which burns above the bed. Small drops dry and burn faster and are more easily entrained. Large drops are much more likely to reach the bed, and at a much earlier stage in the burning process.

Analyses of the trajectories of liquor particles in a furnace have been carried out by Merriam (41) and in a more refined manner by Shick (42). These show that the behavior of a particle is very sensitive to size as well as to the velocities and angles of injection and the gas flow patterns. The size region of about 1-2 mm seems to be critical. Smaller droplets are almost certain to be entrained, while larger ones are likely to reach the bed in a wet state.

It is beyond the scope of this study to consider the behavior of liquor drops before they land on the bed and predict the amount and fuel value of the material reaching the bed. Our intention here is to consider what the results of this study have to say about what should arrive on the bed, and what implications this has on liquor sprays.

One of the main conclusions of the study is that vigorous burning on the char bed with combustion air impinging directly on the bed is not only allowable but desirable. The goal should be to maximize the amount of combustion occurring on the bed. This means that we want to deliver the maximum amount of fuel value to the bed, and have a significant portion of the volatiles burning and all of the char burning take place there. Since high bed temperatures are desirable, we want to keep heat sinks, particularly wet liquor, out of the bed. Thus we would look for a spray size that would let drying take place in flight along with a small amount of volatiles burning. If bed combustion were very intense, even some partially dried liquor may be allowed.

The results of this work suggest that the challenge is not to "fine tune" the liquor spray size, but rather to create firing conditions that successfully allow intense burning with very coarse sprays. Adiabatic flame temperatures for kraft black liquors at 65% solids are on the order of 2500°F, so it appears that even wet liquor could be burned on the bed if the burning rate were fast enough.

Air/Fuel Coupling

The black liquor combustion process should be treated in the same manner as any other fuel. Each portion of black liquor fuel has a requirement for a certain amount of air (stoichiometric air requirement). The essence of good combustion control is to introduce the fuel (black liquor) and air into the furnace in such a manner that the air reaching a given location is proportional to the stoichiometric demand of the liquor at that location. This implies that the black liquor spray system and the air supply system must be coupled.

The coupling between liquor sprays and air supply must take place over the entire cross-section of the furnace. The distribution of air to the bed must match the distribution of the combustible content of the material landing on the bed. If most of the char is landing close to the walls, most of the air is needed near the walls. If the char is spread uniformly over the bed surface, the combustion air should also be distributed evenly over the bed. Imbalance between char supply and air supply will result in bed growth or decay in regions where the imbalance exists.

Air and fuel supply coupling is especially important in considering changes in firing practice to increase the amount of burning taking place on the bed. Liquor spray and air supply changes should take place in tandem. As

mentioned previously in this report, increased char burning rates require a higher bed temperature and an increase in oxygen (air) supply to the burning char. Since the burning process is exothermic, the temperature increase should be self-generated by the increased burning rates. Thus the key to increasing bed burning rates is to increase the air supply rate to the bed. This change in air supply rates cannot take place in isolation. More combustible material must arrive on the bed to match the increased rate, and hence the sprays must be adjusted to deliver more material to the hearth (by running them coarser, pointing them down, etc.). The ability to make such changes can be limited by the available hardware and by reluctance to deviate considerably from past practice.

Bed Air Supply

The purpose of air supply to the bed is to provide the stoichiometric amount of air needed to burn the combustible content of the material landing on the bed. Combustion air in the lower furnace also supplies oxygen to burn combustible gases and for in-flight burning in the bed region. Through the balance between air supply rates and the stoichiometric demand of the char landing on the bed, the bed size and shape can be controlled by controlling the air distribution. Since bed temperatures are dependent on the exothermic heat of reaction from bed burning, and burning rates are controlled by air supply rates, air supply also tends to determine bed temperature.

Combustion air to the lower furnace is introduced from the periphery through a series of air ports in the walls. There is considerable variation in the types of air supply systems in use and this has a profound effect on the air distribution in the lower furnace and the ability to control this distribution.

Some units have only a single level of bed air, others two or more. Most units that have two levels of bed air have a higher pressure supply to the upper level which gives higher injection velocities and hence better penetration into the furnace. Some units have variable area on the discharge side of the air ports, providing separate adjustment of the quantity of air introduced and its velocity. Most do not. The ability to modify the air distribution in the bed region can be severely limited by the available hardware. In some cases, retrofitting of air supply systems may be needed to implement desired changes in the air distribution.

The air distribution patterns in the lower furnace are also strongly influenced by the combustion gas circulation patterns and by the ongoing combustion process. There are large secondary flows present that can bring hot combustion gases down from higher in the furnace. The bed can self-generate part of its own air supply by setting up convection patterns. The bed can "breathe" like a coal or wood fire.

The type of air supply needed to maximize bed burning would appear to require two levels of air, with the upper level at a significantly higher pressure. The objective is to spray the liquor as uniformly as possible over the surface of the bed and match this with the air supply. The upper level of bed air would be relied on to carry most of the air. The lower level would be relied on mainly to push the bed away from the walls, keep the air ports open, and trim the edges of the bed.

Stationary Firing

Stationary firing is a technique that has been used to improve recovery boiler operation by maximizing burning in the lower furnace. The chief advocate

of stationary firing is Pantsar (43). The technique has been used successfully at quite a few mills in Finland and at several mills in the United States.

In stationary firing, the liquor guns are not oscillated but remain stationary. The best liquor droplet size control and spray pattern is obtained with a low velocity splash-plate nozzle. This gives relatively uniform, coarse particles which cover a reasonable area of the bed. A proper arrangement of nozzles around the furnace can provide fairly uniform coverage of the bed, a desirable goal. Of all the firing techniques in use today, this one appears to have the greatest potential for delivering the liquor solids to the bed in the proper form with a minimum of physical entrainment.

Implementation of stationary firing usually requires modification of the air supply to the lower furnace to match the new distribution of liquor solids. Proper air distribution is best achieved with a two level air system. In fact, the full advantages of stationary firing can only be achieved with a two level bed air system. The need for two levels of bed air has been recognized as being so important in Finland, where the stationary firing concept was developed, that many recovery boilers have been retrofitted to a two-level bed-air system.

The main benefits of stationary firing are increased lower furnace temperatures, which give higher reduction efficiencies and less sulfur release, and less slagging and fouling due to less entrained droplets and lower temperatures entering the furnace heat traps. The biggest potential problem with stationary firing is excessive bed growth or even black out if the air supply is not properly matched to the liquor solids falling on the bed or if wet liquor reaches the bed. A key to successful stationary firing is a consistent supply

of good quality, high solids liquor. Liquor solids should preferably be 65% or more. Stationary firing should not be attempted with low solids (e.g., 60% solids) liquor because of the danger of blacking out. However, with high solids liquor and a proper air supply system, stationary firing can significantly improve recovery boiler operations.

7. ACKNOWLEDGMENTS

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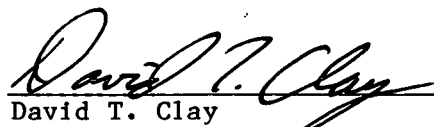
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