**IPST Technical Paper Series Number 516**


Sulfate Reduction and Carbon Removal During Kraft Char Burning

T.M. Grace, K.J. Wag, R.R. Horton, and W.J. Frederick

February 1994


Submitted to
Combustion and Flame

# Sulfate Reduction and Carbon Removal During Kraft Char Burning

Thomas M. Grace, Kaj J. Wag, Robert R. Horton, and Wm. James Frederick

## ABSTRACT

This paper describes an improved model of char burning during black liquor combustion that is capable of predicting net rates of sulfate reduction to sulfide as well as carbon burnup rates. Enhancements include a proper treatment of $CO_2$ and $H_2O$ gasification, reactions between oxygen and combustibles in the boundary layer, and integration of sulfate reduction and sulfide reoxidation into the char burning process. Simulations using the model show that for typical recovery boiler conditions, char burning behavior is independent of oxygen concentration up to the point of carbon depletion. Under these conditions, $H_2O$ and $CO_2$ gasification reactions are primarily responsible for carbon removal. The $H_2$ and CO coming from the gasifying particle consume oxygen in the boundary layer and help protect against sulfide reoxidation. After carbon depletion, sulfide reoxidation occurs at a rate determined by oxygen mass transfer. The process variables having the biggest effect on char burning behaviour are initial black liquor drop diameter and temperature. There is a direct tie between char burnout times and the amount of sulfate reduction. Increasing drop size increases char burnout times and the extent of reduction. Increasing temperature gives shorter char burnout times but higher reduction. At a given temperature, any variable that shortens the char burnout time will result in proportionately less reduction. There are some indications that the model underpredicts reduction rates. There remains a need for experimental data on sulfate reduction kinetics under typical char burning conditions.

## INTRODUCTION

Black liquor is a biomass fuel which is generated as a byproduct of the pulping of wood by the kraft process. It is a concentrated aqueous solution containing the spent inorganic pulping chemicals and organic substances dissolved from the wood. The inorganic (ash) content of the liquor is about half of the weight of the dissolved solids. Black liquor is burned in a recovery boiler to recover the the inorganics as a molten mixture of $Na_2CO_3$ and $Na_2S$, called smelt, and to generate steam. The $Na_2S$ is an active pulping chemical. It is produced in the recovery furnace by the reduction of $Na_2SO_4$ by reaction with carbon. This process is called reduction in the kraft pulp industry.

Black liquor is sprayed into the recovery furnace as coarse drops, 1-10 mm in diameter. The drops dry and burn in suspension. The inorganic and some partially burnt organic accumulates on the furnace hearth to form a char bed. Part of the burning takes place in suspension and part on the char bed.

Black liquor burning is usually considered to take place in four stages; drying, volatiles burning, char burning, and smelt reoxidation. Char burning is a very critical step. It is a relatively slow process and takes place when the liquor particle is in a highly swollen state, typically 50-90 $cm^3$/g char at the onset of char burning. Thus, the rate of char burning has a large effect on the trajectories followed by the burning black liquor particles in the furnace. Slow rates of char burning can cause increased physical carryover of particles out of the furnace into the convective heat transfer sections and this can cause boiler plugging. A substantial amount of sulfate reduction also occurs during char burning.

Many of the available models of char oxidation have focused on coal chars (1,2). The model presented by Bartok and Sarofim(2) represents the current state of global modeling for char oxidation. Their model accounts for film mass transfer and intraparticle diffusion as well as the intrinsic rate of oxidation of carbon. These authors suggest that, since the rates of carbon oxidation by steam and $CO_2$

2

are much lower than that of carbon with oxygen, often only the oxidation reaction with oxygen needs to be considered in heterogeneous combustion . Char oxidation models of the type described by Bartok and Sarofim have been implemented in many reactor models for both combustors and gasifiers.

Black liquor char combustion involves two features not seen in coal chars. These are the extremely high reactivity of the chars and the importance of reducing $Na_2SO_4$ to $Na_2S$. Black liquor char carbon is several orders of magnitude more reactive than other carbons because of the catalytic effect of sodium inherent in the char(3,4). Because of this higher reactivity, the rate of carbon oxidation with oxygen is film mass transfer controlled at temperatures above 1000°C for char particles of typical size (3-20mm). One effect of this is that the rates of carbon oxidation with oxygen and water vapor, at the same $O_2$ and $H_2O$ partial pressures, are similar for temperatures as low as 900°C for black liquor char particles . Since the black liquor is fired as an aqueous fuel, the concentration of $H_2O$ in the furnace gases is high, typically 15-20%. The rate of oxidation with $CO_2$ is slower but definitely significant at temperatures of 1000°C and higher. Thus, all three oxidants are important in black liquor char burning.

An accurate model of char burning must deal with three process items:

1.      conversion of char carbon to the gases CO and $CO_2$,

2.      the state of reduction of the sulfur in the burning particle, and

3.      the decrease in the size of the swollen char particle as the carbon is burned away.

None of the previous models of char burning have properly dealt with all of these issues. Models which have been used for black liquor drop trajectory calculations (5,6) have focused on carbon removal. Char burning was modeled as an oxygen  mass transfer limited process. Chemical kinetic limitations and gasification of carbon with $H_2O$ and $CO_2$  have not been handled in a rigorous manner. These models have not dealt with sulfate reduction.

The only self-consistent reduction model currently in existence is the sulfate-sulfide cycle model (7). This model assumes that all char carbon is gasified by reaction with sulfate to form sulfide. The sulfide is then reoxidized by reaction with oxygen to form sulfate. The degree of reduction of the sulfur is then determined by a balance between the competing rates of sulfate reduction and sulfide reoxidation. The sulfate-sulfide cycle model has been used to make quantitative predictions of reduction occurring during char burning in $N_2$ - $O_2$ mixtures (7). However, it was necessary to either assume very high reaction temperatures or arbitrarily increase the reaction rate constant in order to predict high amounts of reduction in typical char burning times.

This paper describes an improved model of char burning that is capable of predicting reduction changes as well as the rate of carbon removal. This model includes the following:

1. gasification of carbon by $H_2O$ and $CO_2$

2. direct carbon oxidation with $O_2$

3. reactions between $O_2$ and combustibles in the boundary layer which reduce the transfer of $O_2$ to the particle surface

4. simultaneous sulfate reduction with carbon and sulfide reoxidation with oxygen

5. reduction computed by a sulfur balance

6. a methodology allowing parallel volatiles burning and char burning

By treating both the char gasification and sulfur oxidation/reduction reactions simultaneously, the model allows a gradual transition between char carbon removal and net sulfide reoxidation as the char carbon is depleted. Thus, this new model is applicable to both the char burning and smelt reoxidation stages and, in fact, eliminates the need to make a distinction between them.

## DESCRIPTION OF CHAR BURNING MODEL

Char burning involves the reactions occurring in a smelt/char particle. Each particle is considered as a mini chemical reactor interacting with the surrounding gases. The smelt/char particle is considered to contain carbon and three inorganic compounds, $Na_2CO_3$, $Na_2S$, and $Na_2SO_4$. The model described herein does not include sodium vaporization reactions or sulfur release as $H_2S$, both of which can occur during char burning. Thus, the amount of sodium in the particle is assumed to remain constant and the total number of moles of inorganic compounds remains constant.

The chemical composition of the particle is completely specified by giving the initial values for moles of inorganic, I, and the sulfidity, S, and determining the moles of fixed carbon, C, and the reduction efficiency, E, as functions of time. Other characteristics of the burning particle, such as mass and swollen volume, can be calculated from these four quantities.

The following five reactions involving the constituents in the smelt/char are considered.

1. $C + O_2 \rightarrow CO_2$

2. $C + CO_2 \rightarrow 2\,CO$

3. $C + H_2O \rightarrow CO + H_2$

4. $C + (2\text{-}f)/4\ Na_2SO_4 \rightarrow (2\text{-}f)/4\ Na_2S + f\ CO + (1\text{-}f)\ CO_2$

5. $Na_2S + 2\,O_2 \rightarrow Na_2SO_4$

Reactions 1, 2, and 3 are heterogeneous reactions between furnace gases and char carbon. Reaction 4, the reduction reaction, is treated as a homogeneous reaction occurring in the condensed smelt/char phase. The variable stoichiometry indicated by the use of the parameter "f" is a reflection of the fact that both CO and $CO_2$ can be products of the sulfate-carbon reaction. Reaction 5, sulfide reoxidation, is treated as a heterogeneous reaction between gas phase oxygen and sulfide. Reactions 1 and 5 are assumed to be totally mass transfer controlled. Data supporting this assumption are contained in references (8) and (9). Reactions 2 and 3 are treated as controlled by external mass transfer,

intraparticle diffusion and chemical kinetics in series. Reaction 4 is assumed to be completely controlled by chemical kinetics.

Reduction reactions between sulfate and reducing gases such as $CO$ or $H_2$ are not included in this treatment. Experimental work (10) has shown that the rates of these reactions are several orders of magnitude less than those between carbon and sulfate.

In addition to reactions occuring with smelt/char components, there are also gaseous reactions occurring in the boundary layer adjacent to the smelt/char phase. These gaseous reactions are:

6. $\quad CO + 1/2\ O_2 \rightarrow CO_2$

7. $\quad H_2 + 1/2\ O_2 \rightarrow H_2O$

8. $\quad V + O_2 \rightarrow VO_2$
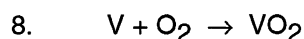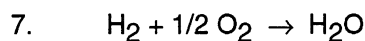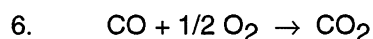
The CO and $H_2$ are produced by gasification of carbon by $CO_2$ and $H_2O$ and by the sulfate-carbon reaction. "V" represents a combustible volatile produced by pyrolysis. If volatile production by pyrolysis is completed, reaction 8 can be ignored. This reaction is included to permit a gradual transition between the volatiles burning and char burning stages. Another reason for including it in this model is to allow a similar treatment of char burning chemistry in particle burning and char bed burning, since some pyrolysis is certain to be occurring in the bed.

Grace (11) showed that, when water vapor was present, the rate of oxidation of carbon in black liquor char was consistent with complete oxidation of CO in the boundary layer, limited only by the availability of oxygen. These results were based on experimental studies with kraft char beds with surface dimensions 20 cm by 10 cm. They imply that the boundary layer reactions are very fast and go to completion. The modelling work of Mitchell et al. (12) showed that very little CO is consumed in the boundary layer surrounding small (less than 100 μm) char particles. The reason for the differences in these results is not clear, but could result from the large differences in boundary layer thicknesses. In our

model, the boundary layer reactions are assumed to be very fast and to go to completion. This means that either all of the oxygen will be depleted or all of the combustibles will be combusted in the boundary layer.

The net rate of mass transfer of $O_2$ to the particle surface is determined by calculating the $O_2$ mass transfer rate in the absence of gas phase reactions and then subtracting the rate of $O_2$ consumption in the boundary layer. The following considerations apply.

Each $CO_2$ that reacts in the particle produces 2 CO which then react with one $O_2$ in the boundary layer. Thus each $CO_2$ that reacts consumes one $O_2$ in the boundary layer.

Each $H_2O$ that reacts in the particle produces one $H_2$ and one CO which then react with one $O_2$ in the boundary layer. Thus each $H_2O$ that reacts consumes one $O_2$ in the boundary layer.

Each V that comes off will react with one $O_2$ in the boundary layer.

Each CO produced by sulfate reduction consumes $1/2$ $O_2$. The amount of $O_2$ consumed is then $2f/(2-f) \times R_{CS}$.

These considerations are valid as long as there is sufficient $O_2$ to consume all of the combustibles produced. If there is insufficient $O_2$, the net oxygen flux at the surface will be zero and there will be some net production of combustibles.

The net $O_2$ rate to the smelt/char particle is then:

$$R'_{O2} = \max \left( R_{O2} - R_{CO2} - R_{H2O} - R_V - 2f/(2-f) \times R_S , 0 \right) \tag{1}$$

The $O_2$ reaching the surface can react with either $Na_2S$ or C. The relative amount of oxygen reacting with each is specified by a partition parameter, p, the fraction of $O_2$ reaching the surface that reacts with C. The use of an arbitrary partition parameter is necessary because there are no kinetic data on carbon burnup and sulfide oxidation occurring in parallel.

The rate of carbon burnup is then given by

$$R_C = 4/(2-f) \times R_{SO4} + R_{CO2} + R_{H2O} + p \times R'_{O2} = - d[C]/dt \qquad (2)$$

If all oxygen is consumed in the boundary layer, $R'_{O2} = 0$.

The reduction efficiency in the particle is calculated from a sulfide balance. Sulfur is assumed to be present only as sulfide and sulfate. The reduction efficiency, E, is the fraction of the sulfur that is sulfide.

$$S \times I \times dE/dt = R_{SO4} - R_S = R_{SO4} - (1-p)/2 \times R'_{O2} \qquad 0 < E < 1 \qquad (3)$$

The rate of carbon consumption then becomes

$$R_C = max(R_{CO2} + R_{H2O} + 4/(2-f) \times S \times I \times dE/dt , R_{O2} - R_V + 2 \times S \times I \times dE/dt) \qquad (4)$$

If there is no change in the reduction state of the particle,

$$R_C = R_{O2} - R_V \text{ or } R_{CO2} + R_{H2O}, \text{ whichever is greater.} \qquad (5)$$

This is the same result as that which had been obtained earlier by Grace (11) in the treatment of bed burning when reduction state changes were neglected.

The key expressions for the char burning model are Equations 1,3, and 4. To solve them, rate equations for $R_{O2}$, $R_{CO2}$, $R_{H2O}$, $R_V$, and $R_{SO4}$ and values for the parameters "f" and "p" are needed.

The overall rates of consumption of $CO_2$ and $H_2O_{(v)}$ were calculated as:

$$1/R_i = 1/R_{mi} + 1/(\eta_i R_{ci}) \tag{6}$$

where rates of consumption of gas species i under film mass transfer limited conditions were calculated as:

$$R_{mi} = k_{gi} A_p C_i \tag{7}$$

The mass transfer coefficient was estimated from:

$$Sh = k_g \mathcal{S} / D_p = 2 + 0.6 Re^{0.8} Sc^{1/3} \tag{8}$$

and diffusion coefficients for the reacting gas species were estimated by the Chapman-Enskog equation using Neufeldt's correlation to estimate the diffusion collision integral (13).

The rates under chemical kinetic controlled conditions were calculated from the rate equations of Li and van Heiningen (3,4) for black liquor char:

$$R_{c,CO2} = 6.3 \times 10^{10} [C] P_{CO2}/(P_{CO2} + 3.4 P_{CO}) \exp(-30070/T) \tag{9}$$

$$R_{c,H2O} = 2.56 \times 10^9 [C] P_{H2O}/(P_{H2O} + 1.42 P_{H2}) \exp(-25300/T) \tag{10}$$

The rate limiting effect of interparticle diffusion was accounted for with a Thiele modulus-based effectiveness factor:

$$\eta_i = \tanh(M_{Ti})/M_{Ti} \qquad (11)$$

where:

$$M_{Ti} = D/6 \, (k_i/\mathcal{D}_i)^{1/2} \qquad (12)$$

and

$$k_i = R_{ci}/(V_p C_i) \qquad (13)$$

The overall rate of consumption of $O_2$ was assumed to be limited by the rate of film mass transfer and was calculated from Equation 7.

The reduction rate equation was taken from Cameron and Grace (14), whose data were obtained under conditions where there was a continuous smelt phase containing a small concentration of suspended carbon particles. This would be expected to be applicable toward the end of the char burning stage as the carbon becomes depleted. Its applicability to the earlier stages when the inorganic is imbedded in a carbon matrix may be questioned. However, these are the only quantitative sulfate reduction kinetic data available for use at temperatures above 780°C.

$$R_{SO4} = 1310 \, [SO4]/\{0.0011 \, ([C] + I) + [SO4]\} \, [C] \, e^{-14700/T} = S \, I \, (1-E) \qquad (14)$$

The parameter "f" is the fraction of CO in the gas produced by the sulfate reduction reaction. Cameron's data (14) indicates that $CO_2$ is the major product of this reaction, and that f is probably less than 0.1. We choose to leave it in as a parameter at this point to allow sensitivity studies to be done.

There are no data available on which to base an estimate of the partition parameter "p". It was set equal to the mole fraction carbon in the particle, i.e. $p = C/(C + I)$. This approach has the advantage that all of the $O_2$ will react with sulfide as the carbon becomes depleted.

## SENSITIVITY TESTS OF MODEL

The model was used for a series of simulations to illustrate the effect of process variables on char burning. A base case set of model parameters was chosen to reflect typical conditions in a recovery boiler. They are:

Initial Drop Diameter = 4.0 mm
Temperature = 1300°K
$O_2$ = 5%
$H_2O$ = 15%
$CO_2$ = 10%
$H_2$ = 2%
CO = 2%.

The initial char particle diameter was assumed to be three times the initial black liquor drop diameter for all of the simulations. The sulfate reduction reaction was assumed to produce only $CO_2$.

The gas mass transfer coefficients depend on the Reynolds number, Re, which is proportional to the product of the particle diameter and the relative velocity of the gas past the particle. Black liquor drops swell greatly during pyrolysis and then contract as the carbon is burnt away during char burning. The changing diameter, particle density and relative velocity must be accounted for in determining Re.

In a complete computational fluid dynamics based recovery furnace model the trajectories of individual particles are calculated as they respond to fluid drag and gravity. Reynolds number calculations are an inherent part of such models. For this paper, Re was estimated by assuming that, during char burning, the particles are entrained in the gas and the relative velocity will be close to the terminal velocity of the particle. Typically, Re decreases by about 15-20% as char burning proceeds, since decreasing diameter and increasing terminal velocity offset each other. Thus an assumption of constant Re during

11

char burning is reasonable. Using a diameter swelling factor of 3 during pyrolysis and the assumption that the char particle was at terminal velocity and standard correlations for drag on a sphere were used to develop an empirical expression for Re.

$$Re = 13.6 \times (\text{Initial Diameter})^{2.05} \tag{15}$$

Figure 1 shows the typical behavior during char burning. The mass of char carbon decreases with time as the carbon is converted to gases. The total mass of the char particle drops off and goes through a minimum as the carbon is depleted and then increases as sulfide is reoxidized to sulfate. The reduction efficiency, which characterizes the state of the sulfur in the particle rises during char burning, reaches a maximum at about the point of carbon depletion, and then falls off at a constant rate because of sulfide reoxidation. The particle diameter decreases greatly as burning proceeds and reaches the diameter of a smelt drop as the carbon is depleted.

Char burning can be characterized by two parameters: the time for 99% char carbon burnup, $t_{99}$, and the maximum increase in reduction efficiency, $\Delta E$. The effect of process variables on these two quantities can provide considerable insight into the nature of black liquor combustion in a recovery boiler. The two most important process variables are the initial black liquor drop diameter and the temperature. Figure 2 shows the effect of drop diameter and temperature on $t_{99}$ and $\Delta E$. The spacing between points indicates that at a given temperature, both $t_{99}$ and $\Delta E$ increase with increasing drop diameter in a nearly linear manner. As temperature increases, the gain in reduction increases in an exponential manner, while the time for carbon burnout shortens at a slower rate. It is evident that bigger drops contribute much more to reduction than do smaller drops. It is also apparent that high temperature is more important than drop size in getting good reduction.

Figure 2 also shows that, at a given temperature, the relation between reduction gain and char burnout time is nearly linear. This is to be expected. The reduction reaction takes place homogeneously

12

throughout the particle at a rate dependent on carbon concentration but independent of the external gas environment. The longer the time allowed for this to occur, the more reduction takes place. <u>At a given temperature, any variable that shortens the char burnout time will result in less reduction</u>. The effect of temperature on the sulfate reduction kinetics is so great that higher temperature results in more reduction even though it also shortens char burnout times.

The effect of gas composition on char burning was examined by making changes in gas concentrations around the base case conditions and determining the effects on $t_{99}$ and $\Delta E$. $H_2O$ and $CO_2$ were varied by $\pm 5\%$, $O_2$ by $\pm 3\%$ and $H_2$ and CO by $\pm 2\%$ on an absolute basis. The average rates of change over this range are summarized in Table 1. Both $H_2O$ and $CO_2$ showed non-linear behavior, with low concentrations giving about 50% greater changes than high concentrations.

Increasing $H_2O$ and $CO_2$ concentrations increases carbon gasification rates which shorten burning times and result in less reduction. $H_2O$ has a larger effect than $CO_2$. Both $H_2$ and CO suppress gasification rates slightly and this increases burning times and gives more reduction. The effects are not very large.

The $O_2$ concentration, over the range from 2 to 8%, has no effect on burning times and maximum reduction gain at temperatures of 1300°K or higher, and only a minor effect at 1200°K. This apparently surprising result can be readily explained. At the conditions that are typical for char burning in a recovery furnace, gasification by $H_2O$ and $CO_2$ is responsible for carbon removal. The combustible CO and $H_2$ coming from the particle consume the $O_2$ in the boundary and effectively prevent it from reaching the particle itself until the carbon is nearly depleted. The effects of oxygen concentration are very apparent after the carbon is depleted. Rates of reduction loss by sulfide reoxidation are 4.3, 10.8, and 17.2 %/sec for oxygen concentrations of 2, 5, and 8% respectively.

## VALIDITY OF MODEL

There are three elements of the char burning model predictions that need to be validated. These are char burning rates (burnout times), the suppression of oxidation by combustible gasification products, and reduction efficiency gains. There are no experimental data available giving both burning times and sulfur reduction during char burning in mixed $O_2$, $H_2O$ and $CO_2$ atmospheres which could be used to validate the complete model. There are data available on each of these individual elements that can establish model validity.

There are some data (7) on the weight changes occurring when a char particle was burned in air which show the decrease to a minimimum as carbon is burnt out and then the weight regain characteristic of sulfide oxidation. However, the total weight loss is greater than can be accounted for by carbon removal alone, apparently because of cocurrent sodium evolution. Rate equations to handle this effect are not yet available. Another problem with these data is that the model predicts that temperature has a very large effect, particularly on reduction, and the temperature of the burning particles were not measured. In an oxidizing environment, particle temperatures can exceed furnace temperatures by up to 400°K (8).

Frederick (15,16) has measured char burning times for different temperatures and gas compositions in a quiescent, thermal radiation-dominated environment and has been able to successfully predict these times with a char burning model using essentially the same treatment of mass transfer and chemical kinetics that have been incorporated in the current char burning model.

Table 2 shows rate data for carbon oxidation obtained by Grace (11) in a laboratory study of char bed burning. These data show that rates of carbon release by direct oxidation and gasification were additive in the absence of water vapor (which catalyzes CO oxidation). However, carbon release rates for $O_2$ - $H_2O$ mixtures were no greater than for dry $O_2$ alone and the rates for $O_2$ - $CO_2$ - $H_2O$ mixtures were less than for $O_2$ - $CO_2$. Sutinen et al. (17) were able to predict these carbon oxidation rates within ±

7% on average using a char bed burning model very similar to the one described here. We believe this is strong evidence that reactions between $O_2$ and combustibles close to the char burning surface decrease or eliminate the $O_2$ flux at the surface and that a similar effect takes place during char particle burning.

The ability of the model to predict reduction is dominated by the reliability and accuracy of the sulfate reduction kinetic model. The sulfate reduction rate model has little effect on carbon burnout rates but it has a big effect on reduction (e.g. if the sulfate reduction rate constant is doubled, the base case value for $t_{99}$ is lowered from 3.205 to 3.11 seconds while $\Delta E_R$ is nearly doubled from 17.73% to 33.92%).

High reduction efficiencies in the recovery furnace are generally easy to obtain, and it appears that the current model is underpredicting reduction efficiency. However, there are currently no data available which would provide a firm basis for increasing the reduction rates. Cameron's (14) results, which are the source of the rate equation used in the model, were obtained under conditions of very low carbon concentrations in a mass of molten inorganic smelt. The char carbon was produced by pyrolyzing black liquor and then crushing the char before adding it to the smelt. Some loss in char carbon reactivity may have occurred during these steps. Thorman and Macur (18) obtained reduction rate data with much larger quantities of char carbon suspended in molten smelt. However, they found that the measured reduction rates depended on the amount of stirring in their reactor, and the rates were generally lower than those predicted by Cameron. Li and van Heiningen (19) obtained data on sulfate reduction at low temperatures where the sulfate is in the solid phase. The applicability of these data to the temperature region of interest is questionable.

## CONCLUSIONS

1.  The model appears to underpredict sulfate reduction. The capability to predict reduction is dominated by the reliability and accuracy of the sulfate reduction kinetic model. There is a need for good rate data on sulfate reduction under the conditions applicable to kraft char burning.

2.  Gasification of char carbon by reaction with $H_2O$ and $CO_2$ is the most important means for carbon release under typical recovery furnace conditions. Sulfate reduction is responsible for only a minor part of the carbon release. Direct carbon oxidation by reaction with $O_2$ is insignificant because $O_2$ is prevented from reaching the particle surface until the carbon is depleted due to reaction with $H_2$ and CO coming from the particle.

3.  Under the normal range of recovery furnace conditions, the rate of carbon burnup is not enhanced by increased $O_2$ concentrations. Consumption of $O_2$ by combustible products of gasification reactions prevents direct oxidation of the char carbon.

4.  The $H_2$ and CO from char carbon gasification by $H_2O$ and $CO_2$ provide a protective effect to preserve reduction, since they prevent $O_2$ from reaching the char surface where it could oxidize sulfide until the carbon is depleted. This is significant in obtaining high reductions.

5.  New experimental data are needed to fully validate the char burning model. These experiments should include mixed gas atmospheres and measurement of the sulfur reduction state at intermediate times dring char burning.

## NOMENCLATURE

$A_p$      external surface area of char particle, $cm^2$

$C_i$      concentration of species i in bulk gas, $mols/m^3$

[C]      moles of fixed carbon in the particle at any time, mols

D      char particle diameter, cm

$\mathcal{D}$      diffusivity of gases, $cm^2/sec$

E      reduction efficiency = $Na_2S/\{Na_2S + Na_2SO_4\}$ at any time

f      fraction of CO in the gas produced by the sulfate-carbon reaction

I      mole inorganic in the particle, mols $Na_2$, (assumed constant)

$k_g$      film mass transfer coefficients for reacting gases, cm/sec

$k_i$      apparent first order rate constant for carbon gasification reaction

$M_T$      Thiele modulus

$P_i$      partial pressure of gases

p      fraction of the $O_2$ reaching the surface that reacts with fixed carbon

$R_{O2}$      rate of mass transfer of $O_2$ to the particle that would occur if there were no gas phase reactions in the boundary layer, mol $O_2/sec$

$R'_{O2}$      net rate of $O_2$ transfer to the particle after reactions with combustibles in the boundary layer, mol $O_2/sec$

$R_{CO2}$      rate of $CO_2$ reaction with fixed carbon in the particle, mol $CO_2/sec$

$R_{H2O}$      rate of $H_2O$ reaction with char carbon in the particle, mol $H_2O/sec$

$R_V$      rate of flow of pyrolysis volatiles from the particle, mol V/sec

$R_{SO4}$      rate of reaction between C and $Na_2SO_4$ , mol $Na_2SO_4/sec$

$R_S$      rate of oxidation of $Na_2S$ to $Na_2SO_4$, mol $Na_2S/sec$

$R_{m,i}$      rate of gas transport, mols/sec

Re      Reynolds number, UD/v, dimensionless

S      sulfidity of the inorganic = moles sulfur per mole inorganic

Sc      Schmidt number, $\upsilon/\mathcal{D}$, dimensionless

Sh      Sherwood number, $kD/\mathcal{D}$, dimensionless

T      temperature, °K

[SO4]      sulfate concentration = $S \times I \times (1 - E)$

t      time, sec

U      relative velocity between gas and char particle, cm/sec

$\eta$      effectiveness factor to account for the effects of intraparticle diffusion.

$\upsilon$      kinematic viscosity of gas

## REFERENCES

1. Smoot, L.D. and Smith, P.J., *Coal Combustion and Gasification*, Plenum, New York (1985)

2. Bartok, W. and Sarofim, A.F. *Fossil Fuel Combustion*, John Wiley and Sons, New York (1991)

3. Li, J. and van Heiningen, A.R.P., *Ind. Eng. Chem. Res.* 29(9):1776-1785 (1990)

4. Li, J. and van Heiningen, A.R.P., *Ind. Eng. Chem. Res.* 30(7):1594-1601 (1991)

5. Walsh, A.R. and Grace, T.M., *J. of Pulp & Paper Science* 15(3):J84-J89 (1989)

6. Jones, A.K. and Chapman, P.J., *Tappi J.*, 76(7):195-202 (1993)

7. Grace, T.M., Cameron, J.H. and Clay, D.T., *Tappi J.* 69(10):108-113 (1986)

8. Frederick, W.J. and Hupa, M., *Combustion Chemistry Research Group Report 93-3*, Abo Akademi University, Turku, Finland (1993); also to be pulished as a U.S. Department of Energy Report

9. Adams. T.N. and Frederick, W.J., *Kraft Recovery Boiler Physical and Chemical Processes*, American Forestry and Paper Institute, New York, NY (1988) p.131

10. Sjoberg, M. and Cameron, J.H., *AIChE Symposium Series*, 239(80):35-40 (1984)

11. Grace, T.M., Lien, S.J. and Brown, C.A., *Proceedings of 1992 International Chemical Recovery Conference*, TAPPI, Atlanta, GA p.539-550 (1992)

12. Mitchell, R.E., Kee, R.J., Glarborg, P. and Coltrin, M.E., *Twenty-Third Symposium (International) on Combustion*, The Combustion Institute, p 1169 (1991)

13. Reid, R.C., Prausnitz, J.M. and Poling, B.E., *The Properties of Gases and Liquids*, Fourth ed., McGraw-Hill Book Company, New York (1987)

14. Cameron, J.H. and Grace, T.M., *Ind. Eng. Chem. Fundam.* 24(4):443-449 (1985)

15. Frederick, W.J., *U.S. DOE Report DOE/CE/40637-T8 (DE90012712)* (1990)

16. Frederick, W.J., Kulas, K.C., Clay, D.T., Hupa, M. and Noopila, T., *Proc. 1989 International Chemical Recovery Conference*, CPPA, Montreal, Que. (1989)

17. Sutinen, J., Karvinen, R. and Frederick, W.J., *Coupling of Phenomena ina Char Bed to the Gas Field of a Lower Recovery Furnace*, in press.

18. Thorman, R.P. and Macur, T.S., *Proceedings of 1985 International Chemical Recovery Conference*, TAPPI, Atlanta, GA , p.451-458 (1985)

19. Li, J. and van Heiningen, A.R.P., *Proceedings of 1992 International Chemical Recovery Conference*, TAPPI, Atlanta, GA p.531-538 (1992)
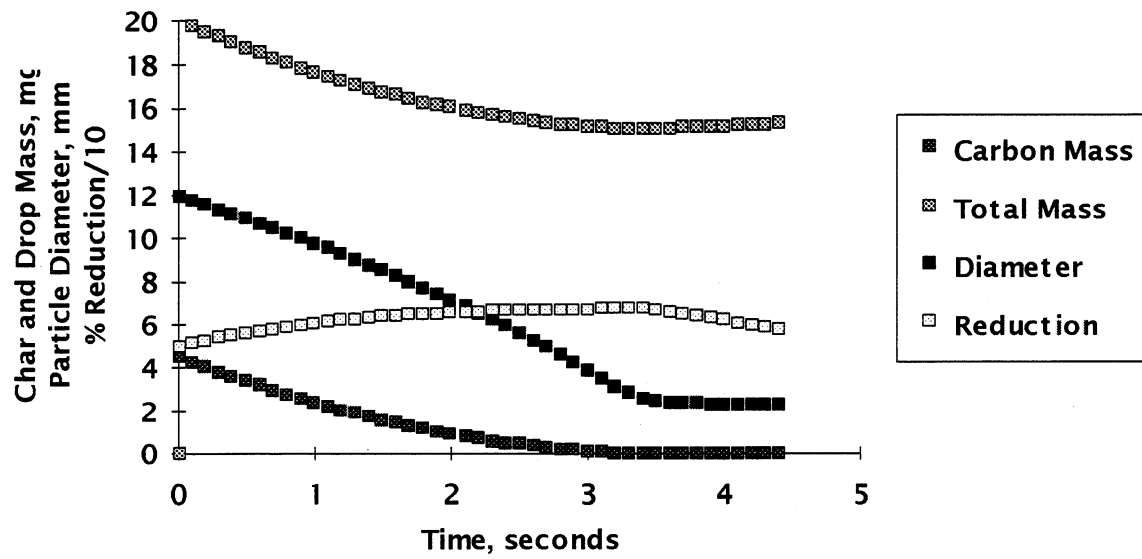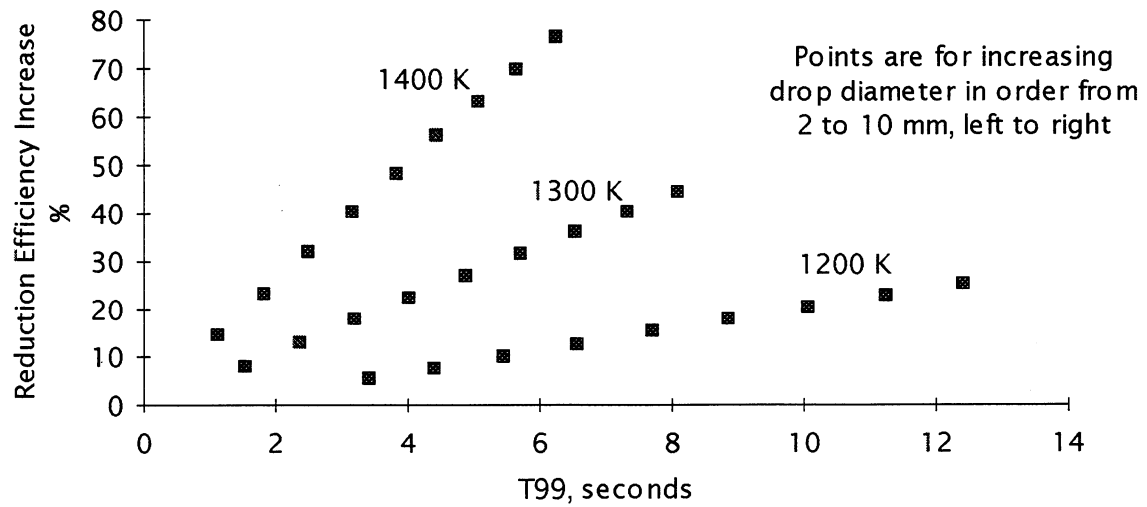
**Figure 1. Typical Char Burning Behavior.**



**Figure 2.** **Effect of Initial Drop Diameter and Temperature on Maximum Reduction and Char Burnup Time.**

## Table 1. Effect of Gas Composition on Char Burning

| Temperature, °K | Gas Changed | $dt_{99}/dX$, sec/% | $dE/dX$, % / % |
|---|---|---|---|
| 1200 | $H_2O$ | -0.191 | -0.39 |
|  | $CO_2$ | -0.122 | -0.25 |
|  | $O_2$ | -0.048 | -0.10 |
| 1300 | $H_2O$ | -0.128 | -0.73 |
|  | $CO_2$ | -0.088 | -0.49 |
|  | $H_2$ | +0.033 | +0.13 |
|  | $CO$ | +0.041 | +0.17 |
|  | $O_2$ | 0 | 0 |
| 1400 | $H_2O$ | -0.103 | -1.31 |
|  | $CO_2$ | -0.072 | -0.91 |
|  | $H_2$ | +0.013 | +0.13 |
|  | $CO$ | +0.015 | +0.15 |
|  | $O_2$ | 0 | 0 |

## Table 2
### Effect of $CO_2$ and $H_2O$ on Char Bed Burning

| $O_2$ % | $H_2O$ % | $CO_2$ % | Carbon Flux gmol/sec/cm$^2$ | $CO/(CO+CO_2)$ | Temperature °C |
|---|---|---|---|---|---|
| 14 | 0 | 0 | $24.35 \times 10^{-6}$ | 0.504 | 961 |
| 14 | 0 | 10 | $32.45 \times 10^{-6}$ | 0.638 | 932 |
| 14 | 10 | 0 | $24.86 \times 10^{-6}$ | 0.011 | 990 |
| 14 | 10 | 10 | $28.09 \times 10^{-6}$ | 0.0 | 967 |