

**ROLE OF THE SULFATE/SULFIDE CYCLE IN CHAR BURNING -  
EXPERIMENTAL RESULTS AND IMPLICATIONS**

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**ABSTRACT**

Kraft char burns via a sulfate/sulfide cycle. The char carbon reacts with sulfate to form sulfide and gaseous CO<sub>2</sub> and CO. The sulfide, in turn, reacts with oxygen in combustion air to reform sulfate. The result of this cycle is an exothermic process in which the char carbon is burnt off and the sulfur compounds are reduced to sulfide. We developed quantitative, predictive equations for char burning which agreed well with experimental measurements of char particle burns.

This work indicates that a substantial fraction of the total burning load should take place on the surface of the char bed. Reduction is an inherent part of the char burning process, and is not jeopardized by combustion air impinging on the bed. Measured kraft char burning rates were much higher than those corresponding to typical boiler design hearth loadings, suggesting a large potential for increased bed burning rates. There are two keys to increased bed burning:

1. Providing an adequate supply of combustion air to the whole bed surface, matching the stoichiometric requirement of the fuel landing on the bed
2. Maintaining high temperatures in the bed surface zone

If these two requirements are met, all chemical functions in the lower furnace will take care of themselves.

**CHAR BURNING**

Burning of a black liquor drop in air occurs in three distinct stages: drying, volatiles burning, and char burning (1). These are described in Fig. 1. Char burning is the last stage in the burning process and occurs as a heterogeneous reaction between the char particle and the oxygen in the combustion air. There is no visible flame, but rather an intense glow at the reacting surface. The residual carbon burns away and the inorganic salts are reduced and smelted out. Char burning does not tend to begin until volatiles production ceases, permitting oxygen to reach the char particle.

Black liquor drop burning times are strongly influenced by the size of the liquor drop and the nature of the air-drop contact. For drops of the size range normally encountered in the furnace burning in air, burn times are about 5-10 s. Drying and char burning stages tend to be the slowest (1).

**Char Characteristics**

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

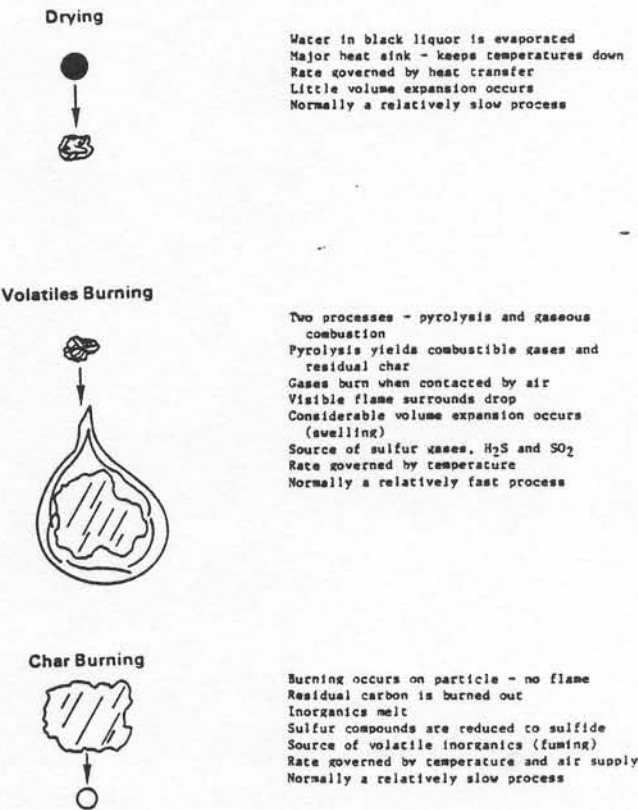


Fig. 1 Black liquor burning stages.

From a chemical standpoint, carbon is the dominant species in the char. Carbon is the excess reactant. There is more than enough carbon present

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**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<sub>2</sub>S and SO<sub>2</sub>  
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

Fig. 1 Black liquor burning stages.

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 (CO<sub>2</sub>) in the product gas. About twice as much air is needed if the char carbon is burned to CO<sub>2</sub> 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<sub>2</sub> split. Very limited data on the gas composition just above the bed in a recovery furnace gives CO/CO<sub>2</sub> = 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 <sub>2</sub> :	3430 Btu/lb
Smelt fully reduced, all CO:	910 Btu/lb

#### Bed Burning

The definition of char used in this paper 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.

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 of the burning process. This tends to blur the distinctions between the process steps.

Prediction of the composition and heating value of the partially burnt liquor landing on the bed is beyond the scope of present knowledge. This has its biggest impact on char bed material and energy balance calculations. It appears to be a reasonable first approximation to identify bed burning with char burning. All of the conclusions derived from understanding char burning are directly applicable to interpreting bed behavior.

#### SULFATE/SULFIDE CYCLE

Kraft char burns via a sulfate/sulfide cycle. The carbon in the char reacts with sulfate, reducing it to sulfide and forming CO<sub>2</sub> 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.

#### Description

The concept of the sulfate-sulfide cycle is illustrated in Fig. 2. Oxygen comes in from the combustion air and reacts with sulfide (Na<sub>2</sub>S). This oxidizes sulfide to sulfate (Na<sub>2</sub>SO<sub>4</sub>). The sulfate carries the oxygen over to the carbon where it reacts to form CO<sub>2</sub> 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.

#### Sulfate - Sulfide Cycle

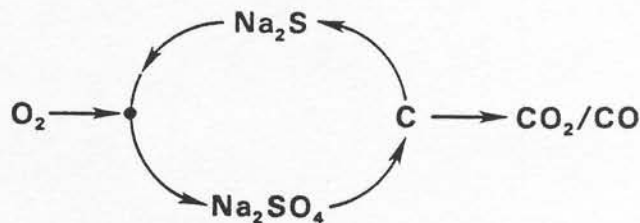


Fig. 2 Schematic of sulfate-sulfide cycle.

## Significance

The significance of the sulfate-sulfide cycle is that it permits two apparently contradictory processes, carbon burnup and sulfate reduction, to take place simultaneously in the furnace. It is entirely possible to burn off char carbon in an oxygen containing atmosphere while still achieving very high degrees of sulfur reduction. The only necessary condition for this to occur is for the rate of the carbon-sulfate reaction to exceed the rate of oxygen supply. The carbon-sulfate reaction rate increases exponentially with increasing temperature. The high temperatures required to insure a sufficiently high carbon-sulfate reaction rate tend to be self generated because char burning (even with net overall reduction) is an exothermic process. It is not necessary to maintain a gaseous reducing zone (oxygen deficient atmospheres) in the lower furnace in order to get good reduction. In fact, starving the lower furnace for air is counterproductive because it results in low bed temperatures and lower rates of reduction.

## QUANTITATIVE ANALYSIS OF CHAR BURNING

The sulfate/sulfide cycle can be treated quantitatively. The following assumptions are made:

1. The only significant chemical species in char are C, Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>4</sub>, and Na<sub>2</sub>CO<sub>3</sub>.
2. Fume formation and sulfur gasification are neglected.
3. The only gaseous species of interest are O<sub>2</sub>, CO<sub>2</sub>, and CO.

The second assumption is useful because it makes Na<sub>2</sub>CO<sub>3</sub> and total alkali a constant and also makes the sum of Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>4</sub> constant. This is a good first approximation for treating char carbon burnup and sulfate reduction. Even though fuming is significant in a recovery furnace, its effect on carbon burnup and reduction is minor. Sulfur gasification occurs before char is formed.

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

$$[C] = \text{moles char carbon/mole Na}_2 \text{ (alkali)}$$

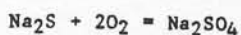
$$r = \text{reduction efficiency} = \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4} \text{ (in moles)}$$

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

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<sub>2</sub> is

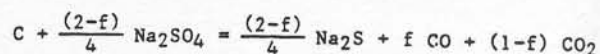


Let R<sub>0</sub> = rate of above oxidation in moles O<sub>2</sub>/mole Na<sub>2</sub>, time

then 1/2 R<sub>0</sub> = rate of Na<sub>2</sub>SO<sub>4</sub> production by this reaction

1/2 R<sub>0</sub> = rate of Na<sub>2</sub>S 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.

Let R<sub>C</sub> = rate of C-Na<sub>2</sub>SO<sub>4</sub> reaction in moles C/mole Na<sub>2</sub>, time

then *f*R<sub>C</sub> = rate of CO production by C-Na<sub>2</sub>SO<sub>4</sub>

(1-*f*)R<sub>C</sub> = rate of CO<sub>2</sub> production by C-Na<sub>2</sub>SO<sub>4</sub>

$\frac{(2-f)}{4} R_C$  = rate of Na<sub>2</sub>SO<sub>4</sub> depletion by C-Na<sub>2</sub>SO<sub>4</sub>

$\frac{(2-f)}{4} R_C$  = rate of Na<sub>2</sub>S production by C-Na<sub>2</sub>SO<sub>4</sub>

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

$$\begin{aligned} &\text{rate of production} - \\ &\text{rate of consumption} = \\ &\text{rate of accumulation.} \end{aligned}$$

Only two material balances are needed, given the assumptions that are made. Balance for carbon and sulfide totally describe the system (Na<sub>2</sub>CO<sub>3</sub> doesn't change and Na<sub>2</sub>SO<sub>4</sub> is known if Na<sub>2</sub>S is known).

Carbon balance:

$$\text{Rate of production} = 0$$

$$\text{Rate of consumption} = R_C$$

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

$$\therefore R_C = \frac{-d[C]}{dt} \quad (1)$$

Sulfide balance:

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

$$\text{Rate of consumption} = 1/2 R_0$$

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

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

### Carbon-Sulfate Rate

The rate of reaction between sulfate and three different types of carbon (pulverized graphite, kraft char and soda char) was found to be represented by Eq. (3). This was determined in a laboratory pool reactor described in Ref. (2) and (3).

$$\frac{d[SO_4]}{dt} = -k_1' \left( \frac{[SO_4]}{k_2 + [SO_4]} \right) [C] e^{+k_3 \left( \frac{\Delta T}{1+\Delta T/T_R} \right)} \quad (3)$$

where  $[SO_4]$  = sulfate concentration  
 $[C]$  = carbon concentration  
 $k_1', k_2, k_3$  = rate constants in Eq. (3)  
 $T_R$  = reference temperature = 1200°K  
 $\Delta T$  = temperature difference =  $T - 1200^\circ K$

Best fit values for the parameters in Eq. (3) are given in Table 1.

Table 1 Rate parameters for carbon-sulfate reactions.

	$(T_R = 1200^\circ K, \Delta T \text{ in } ^\circ C)$		
	$k_1',$ $s^{-1}$	$k_2,$ mole/L	$k_3,$ $^\circ C^{-1}$
Kraft char	$6.3 \times 10^{-3}$	0.022	0.0102
Pulverized graphite	$4.8 \times 10^{-4}$	0.026	0.0154
Soda char	$1.7 \times 10^{-2}$	0.041	0.0139

The effect of carbon concentration, sulfate concentration and temperature on the reaction rate is illustrated in Fig. 3. A key feature of the carbon-sulfate rate behavior is that the rate is independent of sulfate concentration for all reduction efficiencies up to 95%. Sulfate concentration does not have a major effect on the reaction rate until reduction efficiencies exceed 99%.

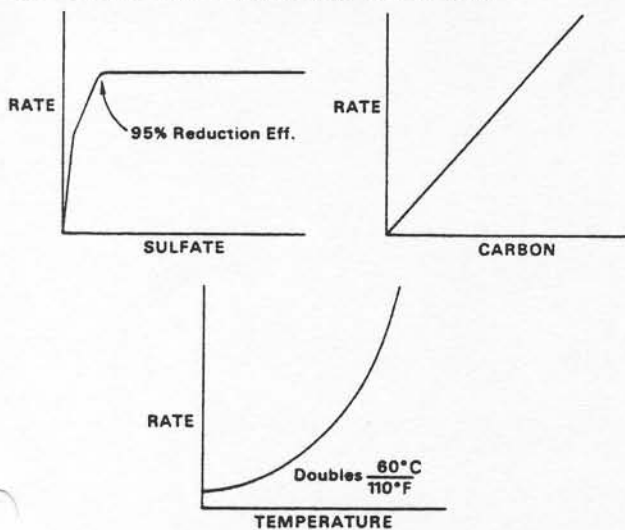


Fig. 3 Effect of parameters on carbon-sulfate rate.

### Sulfide Oxidation Rates

Sulfide oxidation in molten carbonate is an inherently fast reaction. In experiments 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. 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.

If the oxygen supply is mass transfer limited we might have

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

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

### Predicted Behavior

A predictive set of equations for burning kraft char can be developed using the rate constants in Table 1 and assuming  $f = 0$  (no CO produced)

$$\frac{-d[C]}{dt} = 1.26 \times 10^{-2}$$

$$\left\{ \frac{(1-r)s}{0.0011 + (1-r)s} \right\} [C] e^{+0.0102\Delta T/(1+\Delta T/T_R)} \quad (5)$$

$$\text{and} \quad \frac{dr}{dt} = -\frac{1}{2s} \frac{d[C]}{dt} - \frac{R_0}{2s} \quad (6)$$

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

In deriving Eq. (5) and (6), use was made of the fact that  $[SO_4]$  in moles/mole  $Na_2 = s(1-r)$ , and  $k_2 = 0.022 \text{ mole/L} = \frac{0.022 \text{ mole/L}}{20 \text{ mole } Na_2/L} = 0.0011 \text{ mole/mole } Na_2$ .

A generalized solution can be written for Eq. (5) 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

$$[C] = [C]_0 e^{-\int_0^t k''(T)f(r)dt'} \quad (7)$$

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

Equation (6) can be solved directly by integration.

