

Mathematical model for the release of inorganic emissions during black liquor char combustion

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TO IMPROVE THE DESIGN AND operation of modern recovery boilers, manufacturers and engineers alike need a validated computational model for black liquor combustion. Accurate, numerically efficient submodels need to be worked out first, as they become the building blocks of a large-scale model.

In the building of such a model for the incineration of black liquor, two tasks can be defined. The first task is to develop a model that can predict the fate of all chemical species of interest (C, H, O, S, Na, K, and Cl) during char combustion and gasification. The second task is to obtain experimental data relevant to modeling key processes at common furnace conditions.

Our objective here is to present submodels that describe the chemical species transitions of importance in recovery boilers. We introduce an improved char burning model that can accurately predict a number of specific phenomena in the gas environment of the furnace.

KEY PROCESSES

The key processes in black liquor char combustion are:

- Conversion of carbon-containing solid species to carbon-containing gases
- Release of sulfur gases and their recapture by fume
- Reduction of sulfur species
- Release of sodium, potassium, and chloride

- Temperature development of the particle
- Decrease in the size of the swollen char particles.

Previous models have not dealt properly with all of these processes. Earlier models that have been used for black liquor droplet calculations focused on carbon removal (1, 2), and a more recent model included sulfate reduction as well (3). These models have not dealt with sulfur, sodium, potassium, and chloride release in a comprehensive manner. The model presented here treats the char gasification, sulfur reactions, and fume formation processes simultaneously.

The model we describe here is an improved char burning model that can accurately predict the following phenomena in the gas environment of a typical recovery boiler:

- Changes in the mass of sodium, sulfur, potassium, and chloride in the particles
- Effect of initial particle size on the chemical element content of the particles
- Effects of particle size and temperature on fume formation.

CHEMICAL DESCRIPTION OF THE MODEL

Char burning involves the reactions that occur in a char-smelt particle. Each particle is taken as a miniature chemical reactor that interacts with the surrounding gases. The particle is considered to contain carbon and the following inorganic compounds:

ABSTRACT

A mathematical model has been developed for predicting the emissions of sodium, potassium, chloride, and sulfur during the combustion of a black liquor char particle. It accounts rigorously for element mass balances and includes calculations for particle temperatures. Predictions for the release of these elements agree well with experimental data. The model accurately predicts the burning times for black liquor char in combustion gases. It also predicts increases in fume formation with increasing particle temperature and decreasing particle size.

Application:

This validated element-based combustion model was developed to improve large-scale computational combustion models. The model could provide a basis for improving the design and operation of recovery boilers.

Na_2CO_3 , K_2CO_3 , Na_2S , Na_2SO_4 , NaCl , and KCl . The model includes reactions for the vaporization of sodium, potassium, and chloride, and it includes reactions for the release of sulfur as COS and H_2S , both of which occur during char burning (4). The total number of moles of inorganic material in the char decreases during char burning.

The reactions taken into consideration are listed as Reactions A–K in the “Reactions” box. Reactions A, B, and C are heterogeneous reactions between furnace gases and char carbon. Reactions D, E, and F, the reduction reactions, are treated as homogeneous reactions that occur in the phase of condensed smelt-char. In Reaction F, the variable stoichiometry indicated by the use of the parameter “ f ” reflects the fact that both CO and CO_2 can be products of the sulfate-carbon reaction.

Reaction G is treated as a heterogeneous reaction between gas-phase oxygen and sulfide, with the sulfide being oxidized back to its sulfate form. Reactions A and G are assumed to be totally controlled by mass transfer (5, 6). Reactions B and C are treated as controlled by external mass transfer first, intraparticle diffusion second, and chemical kinetics third. Reactions D and E are assumed to be reversible reactions, with the forward rate being controlled by chemical kinetics. Reactions H and I are controlled by film mass transfer, assuming that the vapor partial pressures in the particle boundary layer are at chemical equilibrium with the solid phase. Reactions J and K are assumed to be at chemical equilibrium according to Raoult's law.

Reduction reactions between sulfate and reducing gases such as CO or H₂ are not included in this treatment. Experimental work has shown that the rates of these reactions are several orders of magnitude less than the rates of reactions between carbon and sulfate gases (7).

In addition to reactions that occur with smelt-char components, there are also gaseous reactions that may occur in the boundary layer adjacent to the char-smelt phase. These gaseous reactions are listed as Reactions L-S.

CO and H₂ are produced through gasification of carbon by CO₂ and H₂O(g) and by the reactions of sulfate and carbonate with carbon. These species are consumed by oxygen through Reactions L and M. The elemental alkali species that are generated from carbonate reduction in Reactions D and E react with oxygen in Reactions N and O. The oxidized alkali species are recaptured by reaction with SO₂ and CO₂ to reform carbonate and sulfate in Reactions P, Q, and R.

CARBON BURN-OFF AND SULFATE REDUCTION MODELS

The rate of carbon removal from the char particle proceeds through either combustion or gasification at

typical recovery boiler conditions. In a recovery boiler in which the partial pressures of CO₂ and water vapor are normally higher than that of O₂, Reactions B and C are responsible for converting char carbon to CO. The CO and H₂ produced react with O₂ in the boundary layer, and all oxygen is prevented from reaching the particle surface. That is the case when the gasification reactions generate enough combustible volatiles for the oxygen to react completely. When oxygen does reach the surface, it reacts much more readily with active carbon sites than do CO₂ and H₂O(g), as discussed in more detail elsewhere (3).

The overall consumption rate of carbon is determined by gasification with CO₂ and H₂O(g) or by oxidation with O₂, whichever is greater at any point during combustion (8). The access of the reacting gaseous species to the pore surfaces of the char particle is controlled by film mass transfer first and pore diffusion second. The carbon release calculations are described in greater detail elsewhere (3).

The change of sulfide concentration in the particle is calculated from a sulfur balance:

$$\frac{d[\text{Na}_2\text{S}]/dt}{d[\text{Na}_2\text{S}]_{\text{consumed}}/dt} = \frac{d[\text{Na}_2\text{S}]_{\text{formed}}/dt}{d[\text{Na}_2\text{S}]_{\text{consumed}}/dt} \quad (1)$$

where t is for time in seconds. The reduction efficiency, E , is defined as the fraction of sulfur in the smelt that is in the form of sulfide:

$$E = [\text{Na}_2\text{S}]/([\text{Na}_2\text{S}] + [\text{Na}_2\text{SO}_4]) \quad (2)$$

where $0 < E < 1$ and E is dimensionless.

By differentiating Eq. 2 with respect to the sulfide concentration, we obtain the overall rate of change in reduction efficiency. The sum of the concentrations of sulfide and sulfate was assumed to be constant. The reduction efficiency calculations are described in more detail elsewhere (3).

MODELS FOR SODIUM, POTASSIUM, AND CHLORIDE RELEASE

Sodium, potassium, and chloride release from black liquor char proceeds by the parallel reaction paths of (a) formation of elemental sodium and potassium vapor via reduction of their carbonates and (b) evaporation of NaCl and KCl. Atomic sodium quickly reacts with the species in the complex chemical environment surrounding the reacting char surface to yield bound molecular states, especially when H₂O(g), H₂, and O₂ are present (9). Hence, we treated carbonate reduction as an essentially irreversible chemical reaction. The existence of NaCl in the vapor phase has been confirmed for coal fuels in 10% and 20% oxygen at 1200K (10). At these conditions, kinetics calculations showed that steady state would be achieved rapidly for a system of sodium, chlorine, oxygen, and hydrogen.

The overall rate of the generation of sodium vapor through carbonate reduction was assumed to be controlled by chemical kinetics, pore diffusion, and resistance to film mass transfer in that order (11). The rate was calculated according to Eq. 3, where i is either Na or K vapor.

$$1/R_i = 1/R_{mi} + 1/\eta_i R_{ci} \quad (3)$$

where

R = gas constant, J/(mol K)

R_{mi} = rate of gas transport of species i , mol/s

R_{ci} = kinetic rate of reaction of species i , mol/s

η_i = effectiveness factor to account for the effects of intraparticle diffusion, dimensionless.

The rate of mass transfer of sodium vapor was calculated by Eq. 4, in which i represents the leaving gas species.

$$R_{mi} = k_{g,i} A_{ext} C_i \quad (4)$$

where

$k_{g,i}$ = film mass transfer coefficient of species i , cm/s

A_{ext} = external surface area of char particle, cm²

C_i = concentration of species i in gas film, mol/m³.

The mass transfer coefficient $k_{g,i}$ was evaluated using a Sherwood number correlation. C_{Na} in the gas film was calculated using the software Chemsage (12). The rate-limiting effect of intraparticle diffusion was accounted for with an effectiveness factor based on the Thiele modulus.

$$\eta_i = \tanh(M_{\text{Ti}})/M_{\text{Ti}} \quad (5)$$

where

M_{Ti} = Thiele modulus, number of experimental data points, dimensionless.

In Eq. 5, the Thiele modulus is defined according to Eq. 6.

$$M_{\text{Ti}} = (D/6) (k_i/\mathcal{D}_i)^{1/2} \quad (6)$$

where

k_i = apparent first-order rate constant for carbon gasification reaction,

1/s

$\mathcal{D}_i$ = diffusivity of gas species i , cm²/s.

In Eq. 6, the constant k_i is defined according to Eq. 7.

$$k_i = R_{\text{ci}}/(V_p C_i) \quad (7)$$

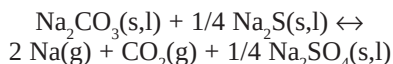
The kinetic rate of Na₂CO₃ reduction in black liquor char reported by Li and van Heiningen (13) is described by Eq. 8.

$$R_{\text{Ci}} = d[\text{Na}_2\text{CO}_3]/dt = 10^9 [\text{Na}_2\text{CO}_3] \exp(-244000/RT) \quad (8)$$

To determine the rate of production of K(g) from potassium carbonate reduction, we used a rate equation analogous to Eq. 8 but with the ratio of K/Na in the particle adjusted.

Inhibition of carbonate reduction by CO or CO₂ was neglected because much of the experimental data (14) shows no evidence of suppression at 1000°C in a typical recovery boiler environment (20% CO₂ and H₂O(g), 10% CO and H₂). However, results from experiments with CO₂ being the only major gaseous species (15–20% CO₂) do show that the reduction process is inhibited at 800°C and 900°C (14, 15).

Reduction of Na₂CO₃ may also proceed by reduction with sulfide:



However, the equilibrium sodium vapor partial pressure from the reduction of Na₂CO₃ with carbon is much greater than that obtained by reduction with Na₂S. Therefore Na₂CO₃ will be reduced by Na₂S only after the fixed carbon has been consumed—that is, not during char burning.

Since black liquor is a fuel that contains Na, K, and Cl, fuming involves the vaporization of NaCl and KCl. Experimental work with molten salt pools indicates that sodium chloride vaporization is a process controlled by mass transfer (16), whereas the smelt is an ideal system and the gas film is saturated with sodium chloride. During these conditions, Raoult's law applies, as expressed in Eq. 9, where a is NaCl(g,l) or KCl(g,l).

$$y_a P_{\text{total}} = x_a P_a^{\text{sat}} \quad (9)$$

where

y_a = mole fraction of species a in the vapor phase, dimensionless

P_{total} = atmospheric pressure, bar

x_a = mole fraction of species a in the liquid phase, dimensionless

P_a^{sat} = partial pressure of species “ a ” at saturation

The rates of NaCl and KCl vaporization were calculated by Eq. 4 under the assumptions that mass transfer across the gas film adjacent to the burning particles was the rate-limiting step and that the vapor pressures of NaCl and KCl were negligible in the bulk gas beyond the gas film.

The partial pressures of NaCl(g) and KCl(g) at the particle interface were assumed to be in chemical equilibrium with an inorganic phase consisting of Na⁺, K⁺, Cl[−], CO₃^{2−}, S^{2−}, and SO₄^{2−} in the particle. In the results presented here, P_{NaCl} and P_{KCl} were calculated using the chemical equilibrium program HSC Chemistry (17), in which the inorganic phase was treated as an ideal solution.

The rate of sodium release, $d\text{Na}/dt$, was calculated as the sum of the rate of sodium loss from the reduction of Na₂CO₃ and from the evaporation of NaCl, according to Eq. 10.

$$d\text{Na}/dt = d\text{NaCl}/dt + d\text{Na}_2\text{CO}_3/dt \quad (10)$$

The rate of potassium release, $d\text{K}/dt$, is obtained analogously by Eq. 11.

$$d\text{K}/dt = d\text{KCl}/dt + d\text{K}_2\text{CO}_3/dt \quad (11)$$

The overall Cl release rate is given by the sum of NaCl and KCl vaporization, according to Eq. 12.

$$d\text{Cl}/dt = d\text{NaCl}/dt + d\text{KCl}/dt = k_{g,\text{NaCl}} A_{\text{ext}} (P_{\text{NaCl}} + P_{\text{KCl}}) \quad (12)$$

SULFUR RELEASE MODELS

Li assumed that the rate of formation of COS is controlled by film mass transfer and that the concentration of COS is at thermodynamic equilibrium at the particle surface (18).

$$R_{\text{COS}} = k_{g,\text{COS}} A_{\text{ext}} [\text{COS}]_{\text{eq}} (1 - X_s) \quad (13)$$

	700— 899°C	900— 1100°C
A	16.1	12.6
B	12307	8514
C	16.5	12.9
D	16507	12585

I. Values for A, B, C, and D

	Weight, % in solids	Weight, % in char
C	35.0	31.2
H	3.1	2.0
O	35.0	38.7
Na	22.7	19.0
K	0.62	1.4
S	2.9	4.0
Cl	0.67	0.8
UnAc.	0.01	2.9
Total	100.0	100.0

UnAc. = unaccounted for.

II. Elemental composition of black liquor solids and char

where

$$R_{\text{COS}} = \text{rate of reaction of Na}_2\text{S to COS, mol Na}_2\text{S/s}$$

$$X_s = \text{fraction of sulfide that has reacted away, dimensionless}$$

$$[\text{COS}]_{\text{eq}} = \text{equilibrium conc. of COS, mol/m}_3 = K_{\text{C,COS}} [\text{CO}_2]_2 \text{ and } K_{\text{C,COS}} = e^{-A+(B/T)}$$

Likewise, it is assumed that there are no internal diffusion resistances in H_2S formation and that the rate is limited by film mass transfer and the equilibrium partial pressure of H_2S .

$$R_{\text{H}_2\text{S}} = k_{\text{g, H}_2\text{S}} A_{\text{ext}} [\text{H}_2\text{S}]_{\text{eq}} (1 - X_s) \quad (14)$$

where

$$[\text{H}_2\text{S}]_{\text{eq}} = \text{equilibrium conc. of H}_2\text{S, mol/m}_3 = K_{\text{C, H}_2\text{S}} [\text{CO}_2][\text{H}_2\text{O}], \text{ and } K_{\text{C, H}_2\text{S}} = e^{-C+(D/T)}$$

Weight, mg	Temp., °C	Char burning time, s	
		Experimental	Calc.
2	900	$7.4 \pm \text{na}^*$	7.6
10	900	13.5 ± 4.4	9
2	900	$10.8 \pm \text{na}^*$	11
10	900	20 ± 0.1	16.5

Mean square difference = 22.1%.
*Extrapolated value. na = not available.
Gas composition: 20% H_2O , 4% CO .

III. Experimental and calculated char burning times for stagnant gas experiments

O_2	Gas, mole % CO_2	Char burning time, s	
		Experimental	Calc.
	20	90 ± 5	88.0
2	20	24 ± 2	30.3
5	20	14 ± 1	21.2
10	20	7.5 ± 0.5	10.9
16.8	20	4 ± 0.3	3.6

Mean square difference = 16.6%.
*Extrapolated value. na = not available.

IV. Experimental and calculated char burning times for single-droplet experiments

$[\text{CO}_2]$ and $[\text{H}_2\text{O}]$ are partial pressures evaluated in the particle boundary layer.

The equations for $K_{\text{C, COS}}$ and $K_{\text{C, H}_2\text{S}}$ were evaluated for the tempera-

ture range of 900–1100°C, based on data generated from the software (17). We evaluated the parameters A, B, C, and D through optimization to fit the equilibrium constants for Eq. 8 and Eq. 9. Table I shows the values for these parameters for two temperature ranges.

MODEL PREDICTIONS AND COMPARISONS WITH EXPERIMENTAL DATA

The experimental data for carbon, sodium, and sulfur were obtained in two sets of experiments. At Oregon State University (OSU), a laminar entrained-flow reactor (LEFR) was used for particles measuring about 100 μm . Single-droplet reactors were used at Åbo Akademi University (ÅAU) for droplets of 2–3 mm (14).

Experimental data for sodium, potassium, and chloride release were

obtained from LEFR experiments at OSU. Dry particles of black liquor solids with diameters in the range of 90–125 μm were pyrolyzed in 100% N_2 , in 4% O_2 , and in 21% O_2 at 700–1100°C. Table II gives the elemental composition of the OSU liquor.

The particle heating rate was of the order of 10^4 °C/s, and the residence time was 0.6–0.8 s. The samples were quenched with nitrogen in a water-cooled probe to stop the reactions. The solid products of combustion were collected as char ($> 3 \mu\text{m}$) and fine particles ($< 3 \mu\text{m}$). These solid products were analyzed for Na, K, and Cl content. The experimental data for sodium, potassium, and chloride release were obtained at OSU from the fume collected.

At ÅAU, two different types of reactors were used: a stagnant gas reactor and a convective flow reactor. Black liquor droplets (generally 2–3 mm in diameter) were pyrolyzed at 800°C or 900°C in different gas mixtures. The droplets were 76.1% and 82.3% in dry solids content, and

Gas	Mole %	Temp., °C	Char burning time, s	Experimental results for Na loss, %	Calculated sodium loss, %		
					Mass transfer	Kinetics only	Overall
H ₂ O	15	800	15	-3 ± 1.4		0.473	0.462
	15	900	15	4 ± 7.1		5	4.8
CO ₂	1	900	85	17.4 ± 5.7		21.2	19.9
	2	800	85	4.0 ± 1.8		2.84	2.57
	2	900	85	7.6 ± 5.8		15.3	14.3
	4	900	100	14.5 ± 13.4		11.8	11
O ₂	1	800	115	1.3 ± 2.2	59.8	6.1	5.1
	1	900	115	24.8 ± 8.9	10.0	30.2	25.4
	4	800	200	0.3 ± 4.2	17.8	3.2	2.4
	4	900	20	67.4 ± 15.6	77.8	16.4	12
	7	800	20	23 ± na	10.1	3	2
	7	900	20	60.1 ± 27.6	47.5	16.9	10.4
N ₂	100	800	165	8 ± na		5.03	4.92
	100	900	165	36.5 ± 19.3		37	35.9
CO	4	900	165	37.9 ± 5.0		37	35.9
	12	800	20	0 ± na		0.63	0.616
	12	900	20	5.7 ± 3.8		6.6	6.3
	12	900	100	25.3 ± 3.4		26.4	25.5
	12	900	165	32.2 ± 8.0		37	36.9

na = not available.

V. Experimental and predicted sodium release for single-droplet experiments

they had the following elemental composition: 31.4% C, 19.1% Na, and 6.4% S. The experimental data on sodium loss were obtained at ÅAU from the char residue, and each amount of the sodium released is reported here as a percentage of that contained in the black liquor solids.

For the convective flow reactor, the particle surface temperature was calculated to be approximately 40° C below the furnace temperature. The gas stream entered at a lower temperature than that of the furnace, and the gas flow did not attain the temperature of the furnace before it reached the particle. The temperatures of the particles were therefore determined by the net rate of the heat input by radiation from the furnace and heat removal by convection to the gas. A detailed description of the estimation of particle temperature can be found elsewhere (14).

Carbon release

The validity of the carbon release model was established at ÅAU (14, 19). Char burning times measured in a stagnant gas reactor and in a single-droplet reactor were compared with the corresponding times calculated with the model. In **Tables III and IV**, the predicted times are given at 99% carbon conversion. In Table IV, droplets were assumed to have 35% carbon initially, a dry solids content of 60%, and a weight of 6 mg at 800°C.

The mean square difference is an indication of the overall agreement with the model. As Eq. 15 shows, it is expressed as the percentage of the average of the experimental data.

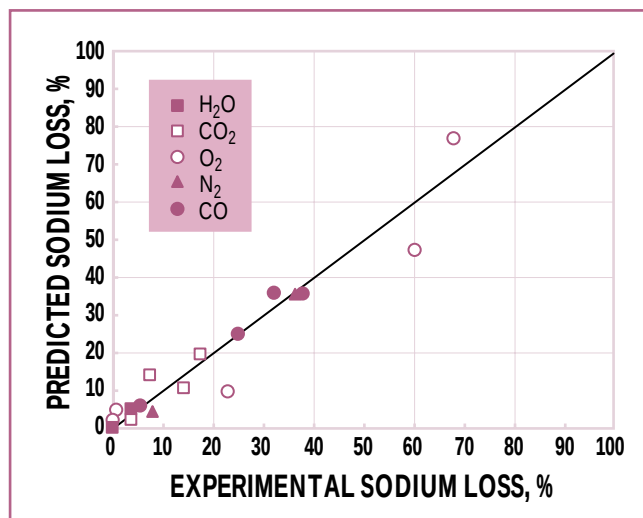
$$\text{Mean square difference, \%} = \frac{[\sum(\text{exp} - \text{calc})^2 + n]^{0.5}}{(\text{exp avg}) \times 100} \quad (15)$$

where n is the number of experimental data points.

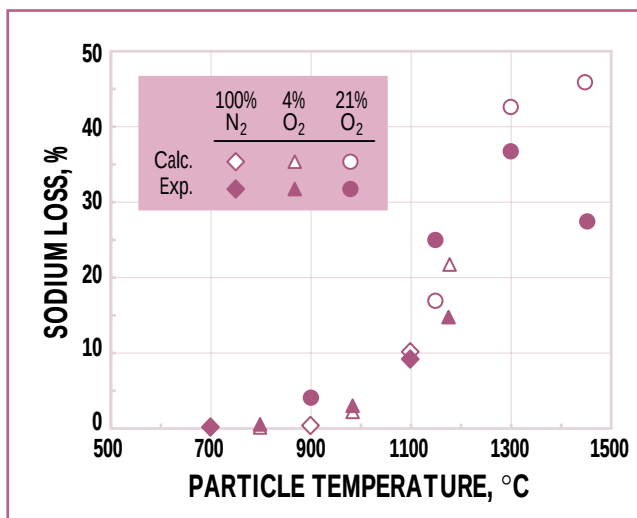
The mean square differences for the data in Tables III and IV are 22.1% and 16.6%, respectively. These data show that the predicted char burning times agree well with the experimental data. The theoretical char burning times are calculated on the assumption that only CO₂ is generated from sulfate reduction. If only CO₂ is produced from sulfate reduction, the char burning times are somewhat lower.

Sodium release

Single droplets. Table V summarizes the experimental data for sodium release and the model predictions for the single-droplet experiments. The experiments were carried out for particles with diameters of 2–3 mm. One data point represents the average of eight measurements from experiments on droplets



1. Sodium loss, predicted vs. experimental, from the data in Table V



2. Sodium loss as a function of actual particle temperature for the 100-μm particles

with particle weights between 10 mg and 20 mg. The theoretical results were calculated for an average droplet weight of 18 mg.

The data show a greater loss of sodium at a higher temperature. There is no increase in sodium loss when oxygen, water vapor, or CO₂ are present, compared to the amount of sodium that droplets lose when heated in an environment of carbon monoxide or nitrogen.

The data in CO₂ at 900°C suggests that CO₂ may be suppressing sodium volatilization at 900°C, but there is no indication that CO suppresses sodium volatilization at this temperature. The experimental char burning times listed in Table V are longer in most cases than the actual burn-out times for fixed carbon. The loss of sodium is assumed to be negligible after carbon is completely converted. In these instances, our model predictions agree well with the measured sodium losses.

The sodium lost during devolatilization has been accounted for. The experimental amount of sodium released during char burning was calculated as the amount of sodium in the black liquor solids minus that released during devolatilization minus that remaining in the char after the indicated char burning time.

The sodium released during devolatilization was taken to be 13% at 900°C and 18% at 800°C. For water vapor, the experiments showed that 19% of the sodium was released during devolatilization at 900°C and that 12% was released at 800°C.

Figure 1 is a plot of the data in Table V for sodium loss based on calculated values versus experimental results. The graph shows a good fit for the data. Three of the data points for oxygen (open circles) appear to have a sizable difference between experimental and predicted sodium loss. In referring to Table V, we see that the difference would be even higher if chemical kinetics were limiting the overall reaction rate. However, if the sodium release at these conditions is controlled by film mass transfer, then we obtain a reasonable agreement between experimental and predicted sodium loss.

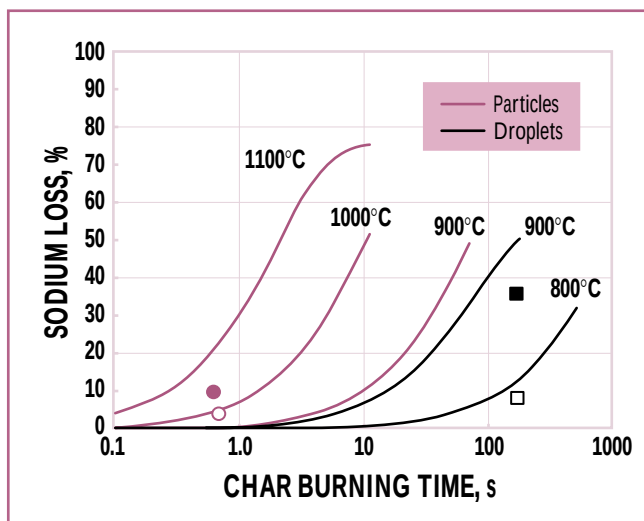
This consideration could describe the actual case if a significant temperature gradient were to exist within the particle. Pertinent literature indicates that there is a temperature difference of 100°C or more between the core of the particle and the surface for black liquor droplets of 2–3 mm burned in air at 800°C (20). Verrill *et al.* have shown that the release of sodium may indeed be

enhanced by the presence of oxygen (21). Therefore, we calculated the sodium losses for experiments carried out in oxygen on the assumption that the reactions are controlled by film mass transfer only. These values are indicated in the table and are the ones used for the oxygen data points in the figure.

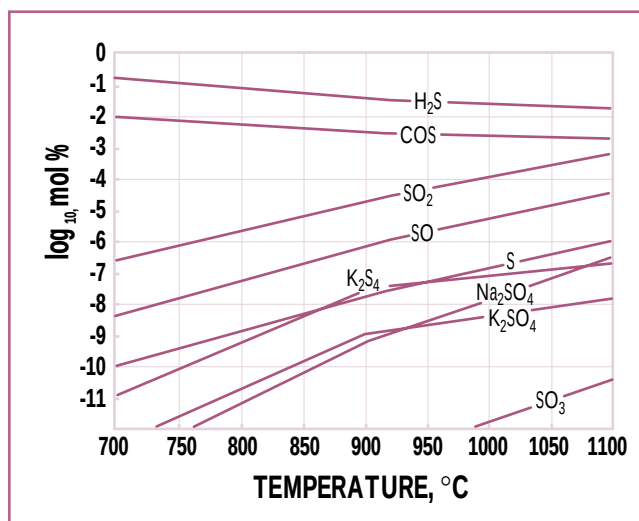
Particles of 100 μm. Table VI summarizes the data for sodium release and the model predictions for the LEFR experiments on particles of 100 μm. The agreement between experimental and theoretical sodium loss is generally good except at high concentrations of oxygen, as with the data for the droplets.

Figure 2 shows the experimental sodium loss as a function of the actual particle temperature for the 100-μm particles. The particle temperature increases with increasing oxygen concentration. Both experimental and predicted losses of sodium increase rapidly at oxygen concentrations above 4%. The particle temperature estimation is based on the method of Reis (22).

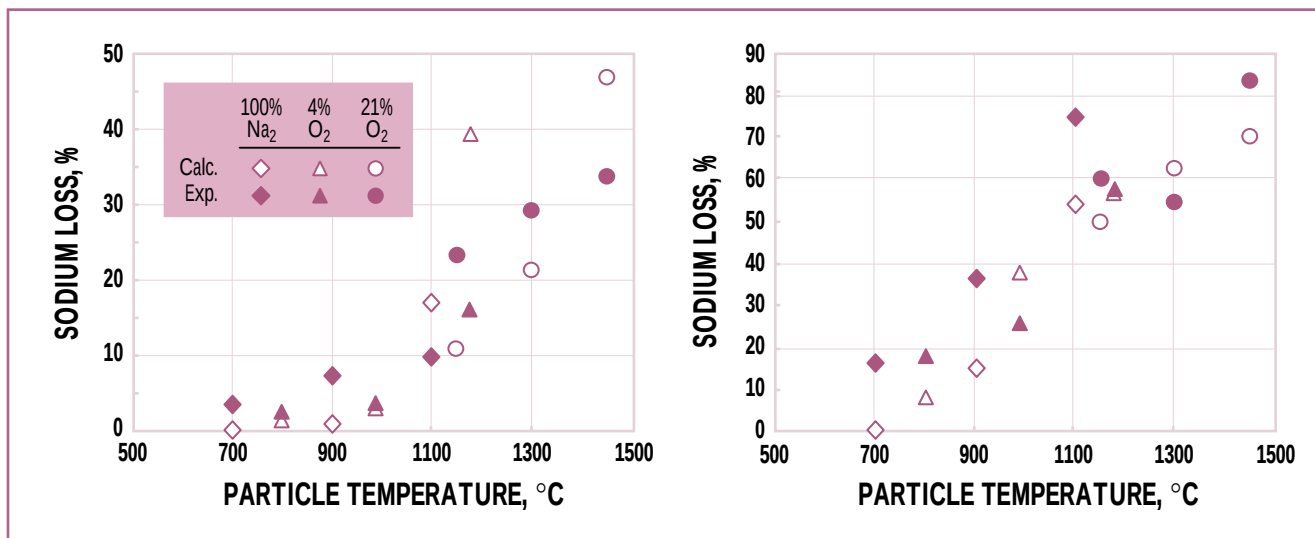
One should avoid comparing LEFR data directly with single-droplet data because of a significant difference in reactor residence time. Sodium losses in the LEFR were less than with the single droplets at simi-



3. Sodium loss as a function of particle size and char burning time in 100% N_2



5. Thermodynamic equilibrium mole fractions of main sulfur gas species in 5% H_2O , CO_2 , and CO



4. Experimental and calculated losses for potassium (left) and for chloride (right) at actual particle temperatures

lar conditions. Table VI shows a sodium loss of 2.8% in 4% O_2 at 900°C in the LEFR, whereas the single-droplet furnace yields a sodium loss of 67% at similar conditions. If the residence times were the same, one would actually obtain a higher sodium loss for the smaller particles.

This effect of particle size is illustrated in Fig. 3. Small particles yield more sodium than large particles yield for the same char burning time. The figure has four data points, and it shows solid curves that were generated by the model. Calculations are based on the assumption that the par-

ticle temperature is the same as the furnace temperature. In the figure, three of the data points are close to their responding curves, and the filled square is for the 100- μm particle at 1100°C.

Potassium and chloride release

The release of potassium and chloride was modeled as the competing processes of (a) evaporation of alkali metal chlorides and (b) vaporization of sodium and potassium via the reduction of Na_2CO_3 and K_2CO_3 . Table VII summarizes the data for potassium and chloride release during char burning. The predicted val-

ues are based on the method of Reis (22). The table shows that the agreement between experimental and calculated values is generally reasonable, though not as good as for sodium.

For potassium, the predictions are always low at low temperatures and high at high temperatures. The poor agreement at 1100°C is probably the result of a high prediction of the rate of potassium carbonate reduction. The poor agreement at 700°C could arise from the reduction rate being underestimated, as a result of the modified equation used to

Gas	Mole %	Furnace temp., °C	Particle temp., °C	Time, s	Exp.	Sodium loss, calc.
N ₂	100	700	700	0.79	0.2	0.1
	100	900	900	0.7	4.1	0.5
	100	1100	1100	0.63	9.6	10.4
O ₂	4	700	799	0.79	0.4	0.1
	4	900	986	0.7	2.8	2.1
	4	1100	1175	0.63	15	22
	21	700	1149	0.79	25.3	17.1
	21	900	1297	0.7	36.8	42.6
	21	1100	1448	0.63	27.7	45.9

Mean square difference = 54.6.

VI. Experimental and predicted sodium release for LEFR experiments

Gas	Mole %	Temp., °C	Time, s	POTASSIUM, %		CHLORIDE, %	
				Exp.	Calc.	Exp.	Calc.
N ₂	100	700	0.79	3.4	0.1	16.2	0.2
	100	900	0.7	7.2	1	36.7	15
	100	1100	0.63	9.8	16.9	75.1	54.5
O ₂	4	700	0.79	2.4	1.2	17.5	8
	4	900	0.7	3.5	2.8	26.1	37.7
	4	1100	0.63	15.9	39.1	57.8	56.5
	21	700	0.79	23.1	10.7	60.7	50.2
	21	900	0.7	29.2	21.4	55.5	62.6
	21	1100	0.63	33.6	46.7	83.7	70.5

Mean square differences = 75.2% for K and 27.6% for Cl.

VII. Experimental and predicted potassium and chloride release for LEFR experiments

determine the reduction rate of sodium carbonate. This modified equation is used because no experimental data are available yet for potassium carbonate reduction. Consequently, the rate of potassium carbonate reduction is predicted to be more important at 1100°C than it really is, and vice versa at 700°C. The graph on the left in **Fig. 4** shows how much potassium is released experimentally and theoretically at the actual particle temperature.

For chloride, the agreement is generally reasonable except when only nitrogen is present. The cause may be attributable to experimental

error. The graph on the right in **Fig. 4** shows the theoretical and experimental chloride release values as a function of actual particle temperature.

Sulfur release

The sulfur release models give fair predictions of the rates of H₂S and COS formation from char particles when the results are compared with the data obtained when both H₂O(g) and CO₂ are present. H₂S and COS formation can account for all the sulfur released at these conditions. However, these models do not apply if no CO₂ or H₂O(g) is present. **Table VIII** summarizes the data for

sulfur release during char burning. The droplet temperature was 900°C.

The scatter between the experimental and predicted values may be attributable to a difference between the gas composition within the particle and the external, bulk concentration. This difference is valid for the larger particles, the 2–3-mm droplets. However, the hypothesis remains to be tested with small particles in LEFR experiments at conditions similar to those for the data listed in **Table VIII**.

The models predict that the rates of H₂S and COS release will decrease with increasing temperature as a result of a decrease in the equilib-

CO ₂	GAS, MOLE %		SODIUM, %	
	H ₂ O	CO	Exp.	Calc.
10	5		14	16.1
10	15		16	33.6
10	10	10	28	33
5	5	10	37	12.1
5	10	10	36	19.6

Mean square difference = 59.9.

VIII. Experimental and predicted sulfur release from single-droplet experiments

rium partial pressures of H₂S and COS. This finding probably accounts for the higher sulfur release observed in colder lower furnaces in recovery boilers. However, sulfur loss is overpredicted at high H₂O(g) concentrations and is underpredicted at low CO₂ concentrations. These discrepancies could indicate that all sulfur release mechanisms are not considered.

For example, direct vaporization of SO, SO₂, and SO₃ has been found in preliminary studies in mass spectrometry experiments with black liquor (23). Thermodynamic equilibrium calculations predict that the concentration of SO₂ becomes increasingly important at higher temperatures, as Fig. 5 shows. Thus, SO₂ may further enhance the release of sodium and potassium by depleting Na₂O and K₂O through Reactions R and S in the gas film surrounding the particle. (For the predictions of Fig. 5, the particle smelt was assumed to have the following composition: 66.31% C, 0.43% NaCl, 0.01% KCl, 10.26% Na₂CO₃, 0.18% K₂CO₃, 11.23% Na₂S and Na₂SO₄, 0.18% K₂S and K₂SO₄.)

DISCUSSION

This unified model is the first model developed for the release of inorganic emissions during black liquor char burning. The model's ability to predict is best for sodium, both for large and for small particles (Tables V and VI).

Carbonate reduction, the main release mechanism for sodium and potassium, is an irreversible reaction

in the typical recovery boiler because elemental sodium and potassium react rapidly in the gas phase with oxygen, CO₂, and SO₂.

For potassium, the agreement is reasonable but not as good as for sodium. The potassium release model lacks a reduction rate equation that is based on experimental data. The insufficient experimental data that are available have not been reproduced rigorously. Moreover, the data are not easy to obtain. There are relatively small amounts of potassium in the black liquor initially, which makes it difficult to measure the quantities accurately.

The calculated release of chloride when oxygen is present is quite good, but in an inert atmosphere the predicted values are much lower than the experimental values. The difference at lower oxygen concentrations has yet to be explained.

The sulfur release model overpredicts sulfur loss with high H₂O(g) concentrations and underpredicts at low CO₂ concentrations. This problem may need the most attention in future modeling efforts.

Greater inorganic emissions are expected from smaller particles at a given reaction time. This result would arise from the smaller resistance attributable to the greater influence of pore diffusion and film mass transfer. The Thiele modulus number (Eq. 6) becomes smaller with decreasing particle diameter. Thus, the effectiveness factor approaches unity (Eq. 5). The mass transfer coefficient increases as the

Element	Mean square difference
Carbon	
O ₂ +CO ₂	16.6
H ₂ O+CO	22.1
Chloride	27.3
Sodium	
Large particles	27.6
Small particles	54.6
Sulfur	59.9
Potassium	75.2

IX. The mean square differences for the different element models

diameter decreases, according to the definition of the Sherwood number.

Table IX summarizes the mean square differences for all the different elements accounted for. It shows that chloride and sodium have the best agreements of the inorganic elements. Potassium and sulfur have the poorest agreements.

Potassium and chloride release can also be expressed in terms of enrichment factors. Increasing K or Cl release increases enrichment if the loss of sodium is assumed to be constant. Reis and coworkers have found that both potassium and chloride enrichment decrease as particle temperature increases (24). Vakkilainen and coworkers discovered that SO₂ can increase Cl volatilization (25), but this finding has not been taken into account in this model for the release of chlorides.

CONCLUSIONS

This unified (or more comprehensive) model contains submodels that can accurately predict the release of sodium, sulfur, potassium, and chloride during the char combustion of black liquor. The burning times for black liquor char combustion agree well with experimental data.

Data for single particles of 2–3 mm show, on a per unit mass basis, less fume formation than do particles measuring 100 μm. This apparently surprising result is attributable to the difference in residence time and to the fact that smaller particles have

less resistance to pore diffusion and film mass transfer.

With respect to black liquor char burning, the following general conclusions can be drawn from the model predictions and experimental data:

- The release of sodium, potassium, and chloride increases with increasing particle temperature.
- Sulfur release decreases with increasing particle temperature.
- Fume generation increases with decreasing particle size.
- In sodium and potassium volatilization, carbonate reduction is more important than the

vaporization of the chlorides at elevated temperatures. The reaction rates of carbonate reduction are more sensitive to temperature than are the vapor pressures of NaCl and KCl.

- At high oxygen concentrations and furnace temperatures, the internal particle temperatures may be higher than measured particle surface temperatures. Hence, fume formation at high oxygen concentrations is essentially limited by film mass transfer.

The implications to recovery boiler operations are important. First, higher operational temperatures in the lower furnace and the increased air supplied there may decrease the release of sulfur. Second, more fume may be generated as a result of an increase in the vaporization of sodium and sodium chloride and of potassium and potassium chloride. This outcome leads to lower enrichment because sodium

vaporization increases faster with increasing temperature than does the vaporization of NaCl or KCl. Conversely, lower temperatures and oxygen concentrations, as sometimes used to combat NO_x, will decrease the rate of fume formation but will increase K and Cl enrichment. **TJ**

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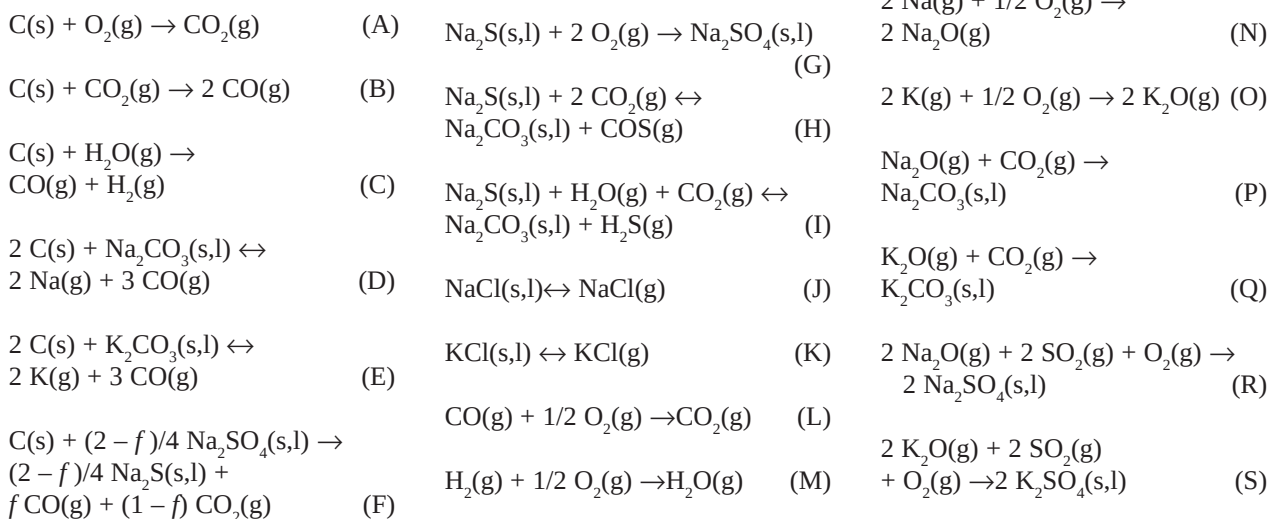
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KEYWORDS

Alkali metals, bibliographies, black liquors, chlorides, chlorine compounds, combustion, emission, halides, materials balance, mathematical models, models, nonmetals, potassium, sodium, spent liquors, sulfur.

REACTIONS



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