Effects of temperature and oxygen concentration on potassium and chloride enrichment during black-liquor combustion

Victor V. Reis, William J. Frederick, Kaj J. Wåg, Kristiina Iisa, and Scott A. Sinquefield

ABSTRACT: The release of potassium and chloride was measured during pyrolysis and combustion of dry black-liquor solids in a laminar-entrained-flow reactor at 700–1100°C. Experiments were made with dry black-liquor solids particles (90–125 μm) in N_2, 4% O_2, and 21% O_2. Combustion products were collected and analyzed for Na, K, and Cl content. Enrichment of potassium and chloride was greatest at 700°C in N_2. Enrichment decreased with increasing temperature or O_2 concentration. In all cases, enrichment was greatest for chloride. Enrichment was modeled as the competing processes of (a) evaporation of alkali-metal chlorides and (b) vaporization of sodium and potassium via reduction of Na_2CO_3 and K_2CO_3. The decrease in enrichment with increasing temperature or O_2 concentration is attributed to the greater temperature dependence of Na_2CO_3 reduction. The results imply that the conditions that reduce enrichment—higher temperatures or increased air in the lower furnace—will increase the total amount of fume generated.

KEYWORDS: Bibliographies, black liquors, chlorides, combustion, laminar flow, oxygen, potassium, pyrolysis, reactors, sodium, solids content, temperature.

Potassium and chloride are two important nonprocess elements in kraft pulping. Both play an important role in deposition and hardening of deposits in recovery boilers *(1, 2)*.

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The fume particles collected in recovery boilers are typically enriched by a factor of 2–3 in potassium and chloride *(1)*. By enrichment, we mean that the potassium content of the fume particles relative to their sodium and potassium content has increased when compared with the same ratio in the black liquor. Thus the potassium enrichment factor for fume particles is defined as the ratio of the concentration of potassium to that of sodium plus potassium in fume divided by the ratio of potassium to sodium plus potassium in the black liquor, or

$$\text{potassium enrichment factor} = \{[K]_{fume}/([K]_{fume} + [Na]_{fume})\}/\{[K]_{BLS}/([K]_{BLS} + [Na]_{BLS})\} \quad (1)$$

(Note that the variables for this and all other equations are defined in the Nomenclature at the end of this article.)

An analogous definition for the chloride enrichment is

$$\text{chloride enrichment factor} = \{[Cl]_{fume}/([Cl]_{fume} + [Na]_{fume})\}/\{[Cl]_{BLS}/([Cl]_{BLS} + [Na]_{BLS})\} \quad (2)$$

Two mechanisms of potassium and chloride enrichment have been discussed in the literature. In three separate studies *(3–5)*, enrichment factors were estimated or implied based on equilibrium considerations. In these studies, the inorganic sodium, potassium, and chloride species in the char bed were assumed to be in chemical equilibrium with the combustion gases. The resulting

I. Elemental composition of dry black-liquor solids

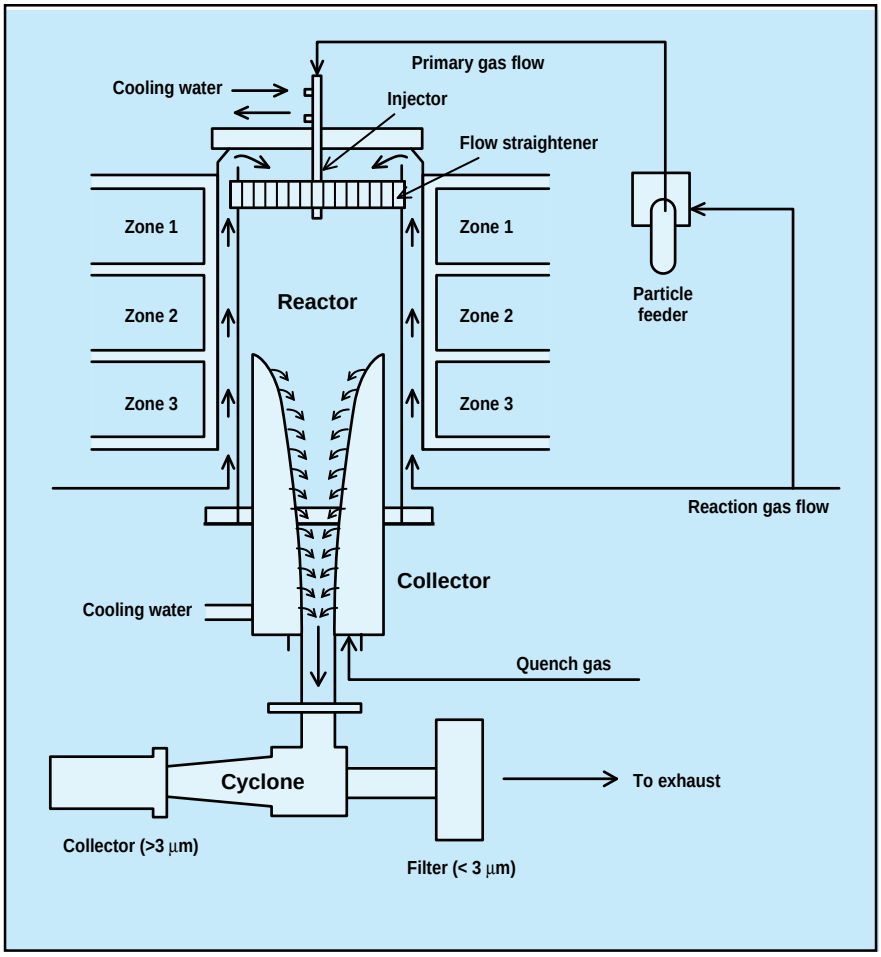
Element	*Content (dry basis), wt.%*
Carbon	34.90
Hydrogen	3.05
Oxygen *	35.21
Sodium	22.65
Sulfur	2.90
Potassium	0.62
Chloride	0.67

* Calculated by difference

II. Experimental conditions for the LEFR

Size of kraft BLS	90–125 μm
Reactor temp.	700–1100°C
Oxygen content	0, 4%, 21%
Residence time	0.6–0.8 s
Feeding rate	0.5 g BLS/min
Heating rate	≈10^4 °C/s
Chemical analysis	Specific-ion electrode and capillary electrophoresis

1. Schematic of the OSU laminar-entrained-flow reactor



equilibrium calculations predicted enrichment factors that are an order of magnitude higher than those measured in recovery boilers.

Cameron *(6)* suggested that reaction-enhanced sodium vaporization from molten smelt was an important source of recovery-boiler fume and, further, that vaporization of sodium and potassium chloride is responsible for the potassium and chloride enrichment observed in the fume. He modeled the vaporization process by assuming that the vaporization of sodium chloride is an equilibrium process, that the smelt is an ideal system, that Raoult's law can be used to predict the vapor pressure of NaCl in equilibrium with the molten salts, and that the gas stream is saturated with sodium chloride. Cameron's data for sodium chloride vaporization rates from molten salt pools agreed well with his calculated rates. However, he did not measure or try to predict potassium or chloride enrichment factors.

The work presented here had two objectives:

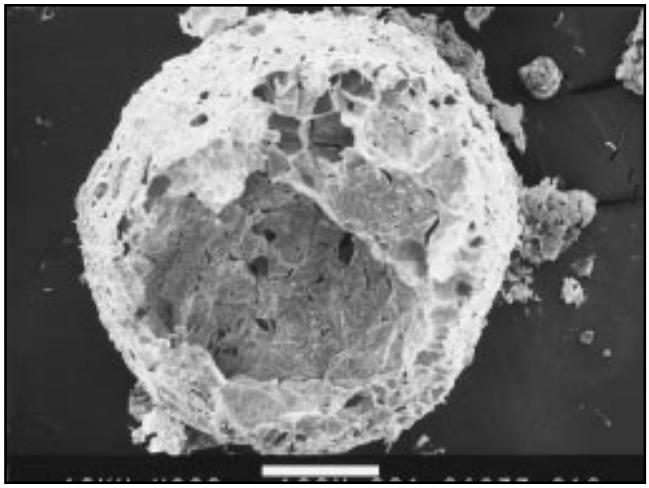
1. Measure potassium and chloride enrichment in fume generated from pyrolysis and combustion experiments over a wide range of experimental conditions.
2. Develop a numerical model of the chemical processes involved in enrichment.

This paper presents new findings on the release of potassium and chloride during black-liquor combustion in a laboratory flow reactor and interprets those results with respect to enrichment of these species in recovery boilers.

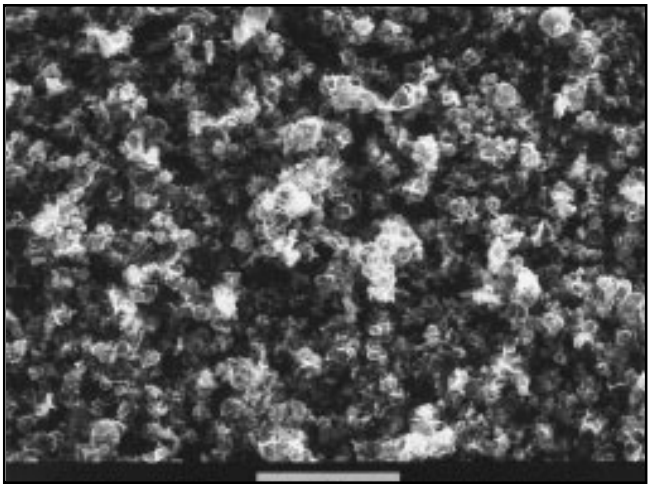
Experimental

The pyrolysis and combustion experiments were conducted in a laboratory-scale laminar-entrained-flow reactor (LEFR). A schematic of the apparatus used in the experiments is shown in **Fig. 1**. Black-liquor solids are carried in the primary gas flow [typically 0.15 L/min at normal temperature and pressure (NTP)], which flows from the particle feeder to the reactor injector. The primary flow enters the reactor at the center, coaxially with the preheated secondary gas flow [typically 20 L/min (NTP)]. The particles and gases flow downward through the hot zone of the reactor in a narrow laminar col-

2. SEM micrograph of a typical black-liquor char particle collected in the cyclone in a pyrolysis run at 700°C for 0.8 s in N_2 with dry black-liquor solids



3. SEM micrograph of typical post-cyclone filter-catch material from pyrolysis of dry black-liquor solids at 700°C for 0.8 s in N_2



III. Reproducibility of the Na, K, and Cl contents of the fine-particle samples collected in typical replicate experiments

Run	Furnace temp., °C	O_2 content, %	Elemental content of fine particles, %*				
			Na	K	Cl	K/Na	Cl/Na
18	700	0	0.21	4.12	21.0	19.60	100.0
19	700	0	0.19	3.06	16.9	16.10	84.70
3	900	4	3.03	3.90	28.8	1.29	9.50
4	900	4	2.51	3.18	23.4	1.27	9.32
7	1100	21	29.70	40.30	95.4	1.36	3.21
8	1100	21	25.60	26.90	72.0	1.05	2.81

* Percent of element in black-liquor solids

umn. When they reach the collector, they are quenched with nitrogen to stop the reactions. Most of the quench gas [typically 15 L/min (NTP)] is fed into the first 2 cm of the collector, while the rest of the gas [typically 5 L/min (NTP)] flows through the remaining porous wall of the collector. This is done to avoid deposition of the aerosol particles on the cold collector walls. The residence time is set by moving the collector up or down or by changing the gas flow rates.

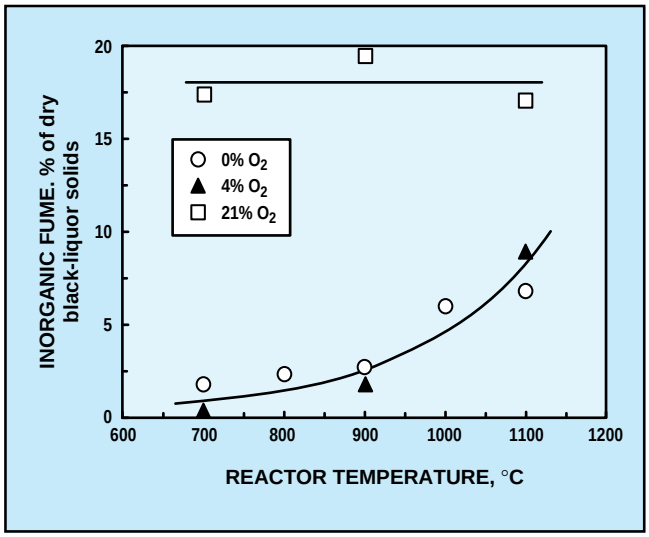
After the quench, the products of reaction are separated. Particles larger than 3 μm in diameter (inorganic residue, char, or both) are removed by a cyclone, and the fine particles (fume) are collected on filters located before the exhaust duct.

For the experiments, we used dried particles of a southern pine kraft black liquor. The original liquor was dried in an oven, ground in a jar mill, and sieved to the desired 90–125-μm diam. **Table I** shows the composition of the dry black-liquor solids. All of the experiments presented in this work were performed under the conditions described in **Table II**.

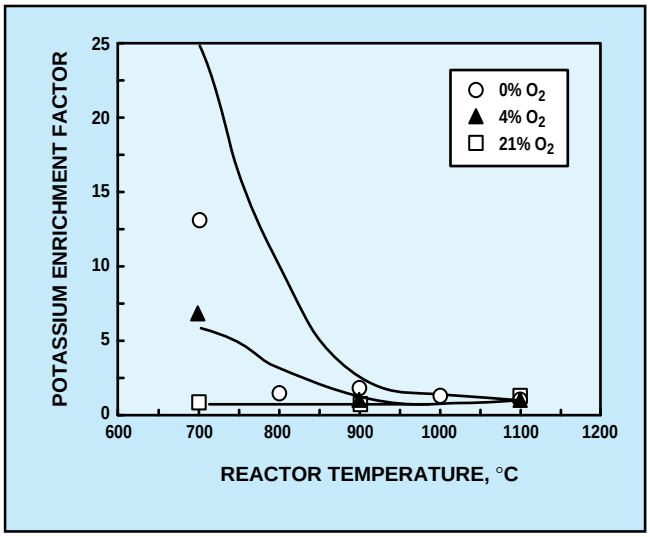
The residence time and black-liquor-solids feeding rate in Table II are nominal values. The residence times differed slightly in runs at different temperatures because the gas flow rates at standard conditions were kept the same in all runs. The actual residence times were calculated using a computational mode for LEFRs developed by Flaxman *(7)*. The calculated residence times were 0.80 s at 700°C, 0.75 s at 800°C, 0.70 at 900°C, 0.65 s at 1000°C, and 0.60 s at 1100°C.

The concentrations of sodium, potassium, and chloride in the fume samples were determined by capillary electrophoresis and ion-selective electrodes. Electrodes from different manufacturers were used for potassium and sodium analysis (Corning) and chloride analysis (Orion). Capillary electrophoresis analyses were performed in a CES-1 capillary electrophoresis system (Dionex) using a conventional fused-silica capillary (50 cm x 50-μm ID). All injections were hydrostatic and performed by raising the sample vial 100 mm above the level of the destination vial for 30 s. The cation and anion electrolyte buffers were obtained from the manufacturer of the

4. Fume generation as a function of reactor temperature at three levels of oxygen. Solid lines are trend lines.



5. Potassium enrichment factor as a function of reactor temperature at three levels of oxygen. Solid lines are predicted enrichment factors.



electrophoresis system (Dionex). Detection of cations was carried out with an ultraviolet (UV) lamp at 215 nm and separation voltage of 20 kV; anions were detected using a UV lamp at 250 nm and separation voltage of 30 kV.

Replicate runs were made at most of the experimental conditions. Typical data for the sodium, potassium, and chloride collected as fine particles on the filter are shown in **Table III** for a wide range of furnace temperature and oxygen content. As the data in Table III show, the amounts of sodium, potassium, and chloride collected per mass of black-liquor solids fed in these runs were reasonably reproducible, as were the ratios of K/Na and Cl/Na in the fine particles collected.

The material-balance closure for sodium, potassium, and chloride was computed as the sum of these elements collected in the cyclone and as filter catch. The closures for sodium and potassium were not good, averaging 49% and 62%, respectively, as seen in **Table IV**. The chloride closure was much better, 107% of the chloride input. The main loss of sodium and potassium increased—and correlated strongly—with increasing mass collected in the cyclone per mass of black-liquor solids fed. The fractions of sodium, potassium, and chloride collected as fine particles were much less variable than were those collected in the cyclone. The high chloride balance closure in Table IV is attributable mainly to the fact that much more of the chloride in the black-liquor solids was volatilized in the experiments than were sodium or potassium. Based on these considerations, we concluded that we had collected nearly all of the fine particles generated.

IV. Sodium, potassium, and chloride material-balance closure for the LEFR runs

Furnace temp., °C	*O_2 content, %*	*Material-balance closure, %**		
		Na	*K*	*Cl*
700	0	43	58	113
700	4	50	66	82
700	21	61	59	108
900	0	38	53	114
900	4	26	65	135
900	21	75	68	97
1100	0	63	85	...
1100	4	...	...	...
1100	21	36	46	101
Averages		49	62	107

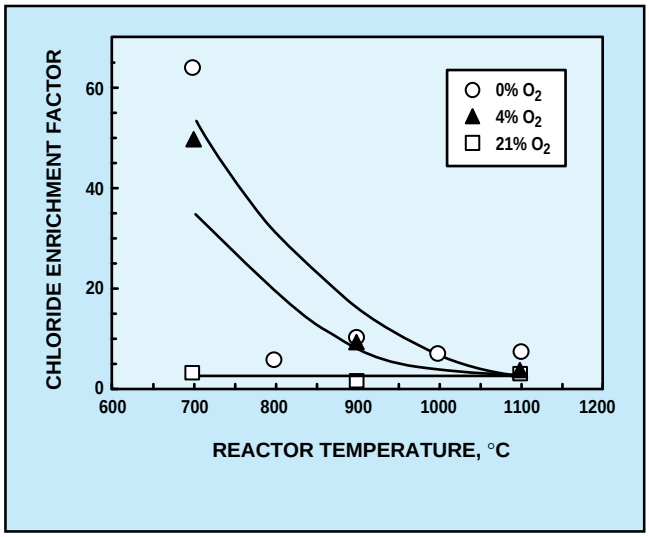
* Percentage of each element in black-liquor solids recovered as cyclone or filter catch. Data are averages of at least two runs at each experimental condition.

Results and discussion

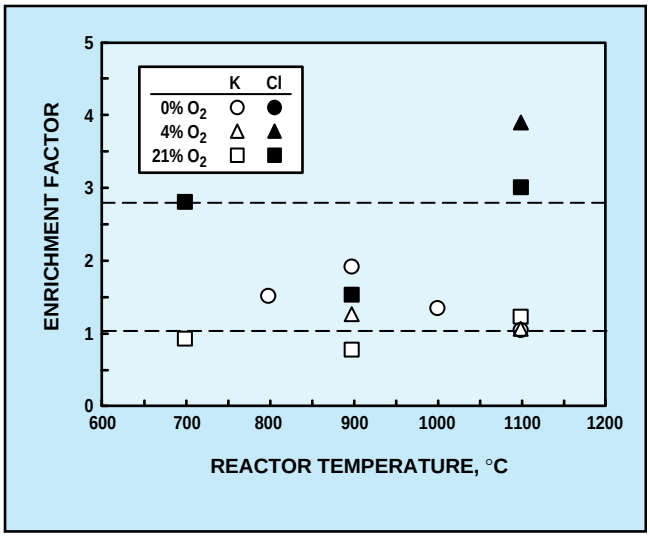
Particle characteristics

Figures 2 and 3 are scanning-electron micrographs (SEMs) of typical char and fume, respectively. The char particles produced were uniformly spherical and very porous. In contrast, the fume particles were very small (about 1 μm) and nonporous, similar in size and appearance to those measured by others in recovery boilers and laboratory experiments *(8–10)*.

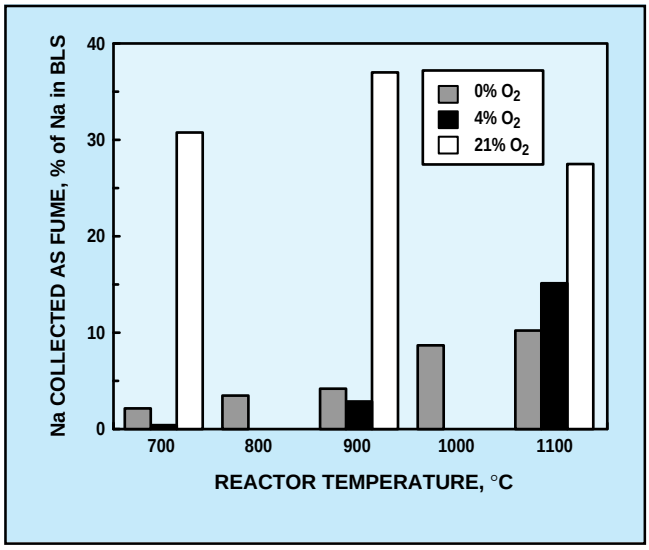
6. Chloride enrichment factor as a function of reactor temperature at three levels of oxygen. Solid lines are predicted enrichment factors.



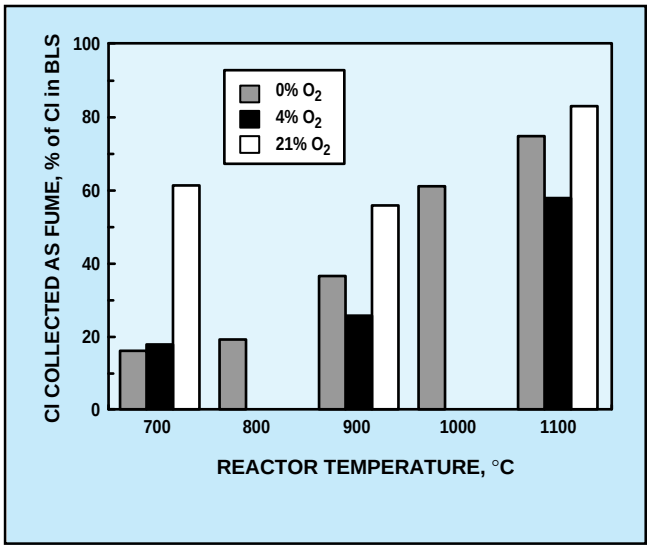
7. Potassium and chloride enrichment factors as functions of reactor temperature at three levels of oxygen



8. Sodium collected as fume during pyrolysis of 100-μm dry black-liquor particles in N_2 in an LEFR at 0.6–0.8-s residence time



9. Chloride collected as fume during pyrolysis of 100-μm dry black-liquor particles in N_2 in an LEFR at 06.–0.8-s residence time

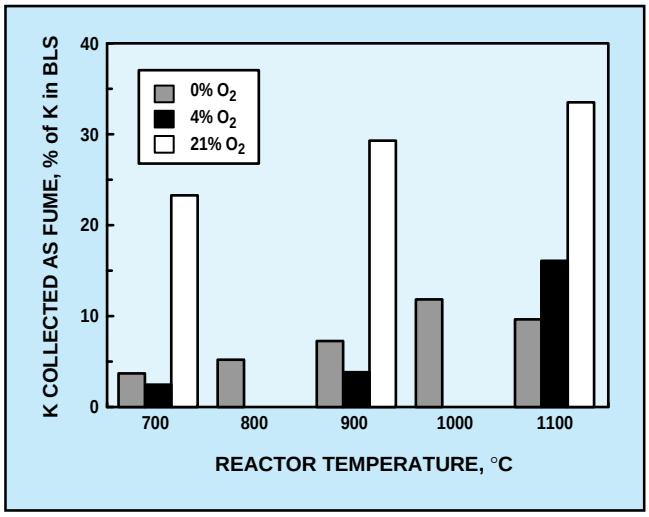


The solid black-liquor particles, when pyrolyzed, swelled to about four times their initial diameters. The swelling characteristics of the original black liquor were also determined at 800°C in air using the method of Noopila and Hupa *(11, 12)*. With the larger (≈ 2 mm) droplets, the liquor swelled by about three times its initial droplet diameter to a maximum specific swollen volume of 35 cm^3/g dry black-liquor solids. The difference in swelling in nitrogen vs. that in air is at least partly the result of inhibited swelling at the higher temperatures that occur when particles are burned in air *(13)*.

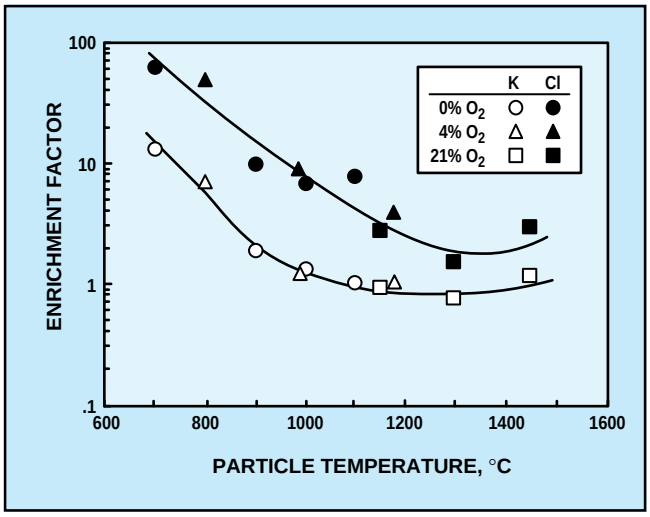
Fume generation

In each experimental run, the amounts of sodium, potassium, and chloride released as fume were calculated based on the sodium, potassium, and chloride contents of the solids collected on the fine-particle filter. The filter catch collected from pyrolysis experiments consisted of sodium and potassium salts as well as fixed carbon. It was assumed that all the alkali metal (potassium and sodium) not in the form of chloride salt was in the form of either carbonate or sulfate. The content of carbonate, sulfate, and fixed carbon in the solids collected on the fine-particle filter was calculated based on these analyses and assumptions and on chemical element and charge balances. The NaCl content of the fine-particle-filter samples decreased with increasing furnace temperature and O_2 content, although the total

10. Potassium collected as fume during pyrolysis of 100-μm dry black-liquor particles in N_2 in an LEFR at 0.6–0.8-s residence time



11. Effect of particle surface temperature on potassium and chloride enrichment factors at three levels of oxygen. Particle temperature was estimated according to Eq. 3.



amount of NaCl in the fume per gram of black-liquor solids increased.

The material collected on the fine-particle filter was either fume (combustion runs) or fume and fixed carbon (pyrolysis runs). This is supported by Fig. 3 and other SEM micrographs of the filter samples, the data analysis presented in **Table V**, and the particle-size-distribution data reported by Kauppinen *et al. (8)* and Mikkanen *et al. (14)*. From this point, we refer to the inorganic mass collected on the fine-particle filter—as determined by the analysis presented in Table V, excluding fixed carbon—as fume.

Figure 4 shows the ratio of fume collected from the black-liquor solids fed at various temperatures and oxygen contents. The results show that the amount of fume at oxidizing conditions is considerably higher than in reducing conditions. It also shows that temperature has a great effect on fuming, especially at lower oxygen content, where fuming is an order of magnitude higher at 1100°C than at 700°C.

Potassium and chloride enrichment

Using the definitions in Eqs. 1 and 2, we calculated the potassium and chloride enrichment factors for several experimental conditions. For potassium, the greatest enrichment factor, about 13, was obtained at 700°C in nitrogen (zero O_2), as shown in **Fig. 5**. At higher temperatures, the potassium enrichment factors were smaller, decreasing to the point that no potassium enrichment occurred at 1100°C. For particles burned in air, there was virtually no potassium enrichment at any temperature. The solid lines in Fig. 5 are enrichment factors predicted from a mechanistic model that is discussed in the next section of this paper.

For chloride, a similar trend was found, but even higher enrichment factors were obtained, as seen in **Fig. 6,** which shows that the chloride enrichment factor peaked at about 65 in nitrogen at 700°C. As in Fig. 5, the solid lines in Fig. 6 are enrichment factors predicted from a mechanistic model that is discussed in the next section of this paper.

The enrichment factors below five for both potassium and chloride are plotted on an expanded scale in **Fig. 7**. For particles burned in air or at 1100°C in 4% O_2, the chloride enrichment factor averaged 2.8 and did not seem to be affected by the reactor temperature.

Proposed mechanism

Cameron *(6)* suggested that evaporation of sodium and potassium chloride is responsible for the potassium and chloride enrichment observed in the fume. However, NaCl and KCl evaporation alone would result in much higher enrichment factors than were observed in our experiments or in recovery boilers. Another route for sodium and potassium volatilization is reduction of their carbonates, producing elemental Na and K. Reduction of carbonates by carbon has been established as the mechanism by which the alkali-metal catalyst is lost during heat treatment of alkali-impregnated carbons prior to gasification of carbon with CO_2 or water vapor *(15, 16)*. Li and van Heiningen *(17)* showed that Na_2CO_3 reduction occurs in black-liquor char at temperatures above 700°C. In their experiments, the sodium loss from the char was in proportion stoichiometrically to the extent of carbonate reduction. Their rate data indicate a strong temperature dependence of the carbonate-reduction reaction.

We modeled sodium, potassium, and chloride volatilization from black-liquor char as proceeding by the parallel reaction paths of evaporation of NaCl and KCl, and formation of elemental sodium and

V. Composition of filter catch

Furnace temp., °C	O_2 content, %	Fume, * wt.% of BLS	Composition, mass %					
			Na	K	Cl	SO_4	CO_3	Fixed C
700	0	2.80	17.6	4.53	12.80	19.6	3.47	42.3
700	4	0.30	28.6	4.93	39.20	...	...	...
700	21	17.3	40.3	0.97	2.86	13.5	42.40	...
800	0	4.04	18.7	0.77	3.11	34.7	0.59	42.1
900	0	3.73	25.6	1.38	7.83	42.9	1.06	21.2
900	4	1.81	34.7	1.21	9.69	43.8	10.60	...
900	21	19.5	42.8	1.63	1.23	0	54.30	...
1000	0	8.26	23.9	0.88	4.97	43.1	0.68	26.5
1100	0	7.53	30.7	0.70	7.61	48.1	4.16	13.1
1100	4	9.01	37.5	1.09	4.31	29.1	28.0	...
1100	21	17.1	36.9	1.21	3.29	33.1	25.50	...

* Fume designates the inorganic fraction of the filter catch as determined by analysis for Na, K, and Cl and using the calculation procedure described in the text.

A-I. Assumed initial composition of inorganic residue in char particles (values used in the model calculations)

Species	Moles/particle
NaCl	1.865×10^{-10}
KCl	3.052×10^{-12}
Na_2CO_3	4.500×10^{-9}
K_2CO_3	7.772×10^{-11}
NaX *	9.849×10^{-9}
KX *	1.585×10^{-10}

* X indicates either sulfur or sulfide.

potassium vapor via reduction of their carbonates. The rates of NaCl and KCl vaporization were calculated by assuming that (a) mass transfer across the gas film adjacent to the burning particles was the rate-limiting step and (b) vapor pressures of NaCl and KCl in the bulk gas were negligible. Details of the model are presented in the Appendix at the end of this paper.

The theoretical enrichment factors, based on our model, are compared with the experimental data in Figs. 5 and 7. The agreement between the theoretical and experimental enrichment factors is generally quite good. The poorest agreement is at 700°C and no oxygen (100% N_2), where the theoretical values are high for potassium and low for chloride.

The main reason for the high enrichment factors at 700°C in N_2 is the low sodium-release rate via Na_2CO_3 reduction at 700°C. In **Fig. 8**, we show the sodium in fume as a percentage of the sodium initially in the black-liquor solids vs. reactor temperature at three oxygen contents. As temperature increased, the sodium released increased by as much as 18 times from 700°C to 1100°C in N_2 or 4% O_2. The release of chloride increased by only a factor of about 3.5 at the same conditions, as seen in **Fig. 9**. The behavior of potassium, shown in **Fig. 10**, falls between that of chloride and sodium, increasing by about a factor of six at the same conditions. It is released as potassium chloride by volatilization and also as potassium vapor by the carbonate-reduction mechanism.

Figure 8 shows that the release of sodium fume in air is high, even at lower temperatures. There are two effects that could be acting simultaneously to increase the amount of sodium being released by carbonate reduction. One is the oxygen-enhanced fuming mechanism *(6, 18)*, and the other is the temperature of the burning char particles.

It has been reported that small particles burn at higher temperatures in air as compared with those in no oxygen or in 4% O_2. Frederick *et al. (19)* measured the surface temperature for larger char particles (3–10 mm) during char burning at several O_2–N_2 mixtures in an 800°C furnace. They concluded that surface temperature for droplets burned in air increased by 300–400°C above the furnace temperature during char burning, but only by about 40–50°C at 4% O_2 content. This agrees quantitatively with the particle-temperature data reported by Hurt and Mitchell *(20)* for approximately 100-µm coal particles. The particle temperature would increase with increasing oxygen content in the gas phase, but it would be roughly independent of particle size if burning were controlled by transport of oxygen to the external particle surface, as proposed by Frederick *(21)*. We therefore modeled particle burning as controlled by boundary-layer mass transfer of oxygen and estimated the particle temperature as suggested by Levenspiel *(22)*.

$$T_p = T_g + [(\Delta H_c R_c)/h_{eff}] \qquad (3)$$

Details of the particle-temperature calculations are discussed in the Appendix and by Reis *(23)*.

At the much higher particle temperatures achieved when burning in

air, Na_2CO_3 reduction proceeds rapidly, and sodium release is high compared with that of particles burned in 4% O_2 or pyrolyzed in N_2. The enrichment factor is highly dependent on the rate of sodium carbonate reduction, which increases sharply with temperature. This resulted in a large fraction (25–35%) of the sodium in the black-liquor solids being volatilized at the higher furnace temperatures and O_2 content, and it explains why there was almost no potassium enrichment in air at any temperature. **Figure 11** shows the effect of particle surface temperature on the potassium and chloride enrichment factors.

The data obtained in this work suggest that the increase in sodium, potassium, and chloride release with increasing oxygen content is a temperature effect resulting from the higher particle temperatures at higher O_2 partial pressures. For the small particles used in this study, the carbonate-reduction mechanism is limited by reaction kinetics, with intraparticle diffusion and film mass transfer playing only a minor role. However, for the much larger char particles that are produced by firing typical size (2–3 mm) droplets in a recovery boiler, intraparticle diffusion of the alkali-metal species and their transport across the gas boundary layer surrounding the particles could be important in the overall rate of sodium and potassium volatilization. If so, the oxygen-enhanced mechanism proposed by Cameron *(18)* could play a more important role on the release of sodium.

This work has several implications for recovery-boiler operations. Boilers can experience severe plugging or corrosion from high enrichment of potassium and chloride. Such problems can be alleviated by increasing the temperature in the lower furnace. However, higher burning temperatures tend to increase total fume production, as seen in Fig. 4. In boilers where plugging is caused by fume production rather than potassium and chloride enrichment *per se*, increasing the burning temperature in the lower furnace could exacerbate the problem.

Conclusions

Experiments performed in a laminar-entrained-flow reactor (LEFR) showed that potassium and chloride enrichment during black-liquor combustion can be very high, depending on the temperature and the oxygen content of the gas. At lower temperatures and oxygen content, enrichment factors were 65 for chloride and 13 for potassium. Operation of recovery boilers at higher temperatures and increased air in the lower furnace may reduce enrichment of potassium and chloride. However, the reason for lower enrichment at higher temperatures is the increased volatilization of sodium, which also results in an increase in total fume production.

The main reason for higher enrichment factors at lower temperatures and reducing conditions is the low sodium release rate by the Na_2CO_3 reduction mechanism. The gas-composition effect on enrichment is mainly a temperature effect resulting from higher surface temperatures when particles burn in gases containing higher levels of oxygen.

The mechanism of potassium and chloride enrichment involves volatilization of NaCl and KCl and reduction of Na_2CO_3 and K_2CO_3 to metallic Na and K. For droplets of the size fired in recovery boilers, intraparticle diffusion and film mass transfer may also be important. Based on this mechanism, it is possible to predict potassium and chloride enrichment during black-liquor pyrolysis and combustion.

Appendix: Theoretical model for potassium and chloride enrichment

Sodium, potassium, and chloride volatilization from black-liquor char were modeled as proceeding by the parallel reaction paths of (a) evaporation of NaCl and KCl and (b) formation of elemental sodium and potassium vapor via reduction of their carbonates. The rates of NaCl and KCl vaporization were calculated by assuming that (a) mass transfer across the gas film adjacent to the burning particles was the rate-limiting step and (b) the vapor pressures of NaCl and KCl in the bulk gas were negligible, so that

$$dCl/dt = dNaCl/dt + dKCl/dt = A_{ext}(k_{g,NaCl}P_{NaCl} + k_{g,KCl}P_{KCl}) \quad (A.1)$$

The partial pressures of NaCl and KCl at the particle interface were assumed to be in equilibrium with an inorganic phase consisting of the Na^+, K^+, Cl^-, CO_3^{2-}, S^{2-}, and SO_4^{2-} in the particle. In the results presented here, P_{NaCl} and P_{KCl} were calculated using a chemical equilibrium program *(24)*.

The rate of sodium volatilization, dNa/dt, was calculated as the sum of the rate of sodium volatilization from reduction of Na_2CO_3 plus the rate of evaporation of NaCl. Reduction of Na_2CO_3 was treated as a reversible chemical reaction occurring within the particle. A kinetic rate equation for Na_2CO_3 reduction in black-liquor char (Eq. A.2) was developed from the data of Li and van Heiningen *(17)*. This equation was used in the model to predict the rate of sodium vapor formation.

$$dNa_v/dt = -2\,d[Na_2CO_3]/dt = 2 \times 10^9\,[Na_2CO_3]\exp(-244000/RT) \quad (A.2)$$

The possible effects of diffusion within the pores of the particle and of transport across the gas boundary layer surrounding the particle were estimated to determine whether they would be important for the swollen (≈ 400 μm) char particles in the experimental study by Reis *(23)*. The overall rate of sodium vapor evolution, accounting for these transport effects, was very nearly the same as when they were ignored. We therefore treated the overall rate of sodium volatilization via Na_2CO_3 reduction as being controlled by

$$\frac{\left[\int\left(\frac{d\,\mathrm{NaCl}}{dt}\right)dt + \int\left(\frac{d\,\mathrm{KCl}}{dt}\right)dt\right]}{\left[\int\left(\frac{d\,\mathrm{Na}}{dt}\right)dt + \int\left(\frac{d\,\mathrm{NaCl}}{dt}\right)dt + \int\left(\frac{d\mathrm{K}}{dt}\right)dt + \int\left(\frac{d\mathrm{KCl}}{dt}\right)dt\right]} \frac{\left([\mathrm{Na}]_{\mathrm{BLS}} + [\mathrm{K}_{\mathrm{BLS}}]\right)}{[\mathrm{Cl}]_{\mathrm{BLS}}} \quad \text{(A.9)}$$

$$\frac{\left[\int\left(\frac{d\,\mathrm{KCl}}{dt}\right)dt + \int\left(\frac{d\,\mathrm{K}}{dt}\right)dt\right]}{\left[\int\left(\frac{d\,\mathrm{Na}}{dt}\right)dt + \int\left(\frac{d\,\mathrm{NaCl}}{dt}\right)dt + \int\left(\frac{d\mathrm{K}}{dt}\right)dt + \int\left(\frac{d\,\mathrm{KCl}}{dt}\right)dt\right]} \frac{\left([\mathrm{Na}]_{\mathrm{BLS}} + [\mathrm{K}_{\mathrm{BLS}}]\right)}{[\mathrm{K}]_{\mathrm{BLS}}} \quad \text{(A.10)}$$

chemical kinetics and proceeding via Eq. A.2. While this is valid for the small black-liquor char particles used in this study, it would not be valid for the much larger char particles that are produced by firing typical size (2–3 mm) droplets in a recovery boiler.

Mass-transfer coefficients for the alkali-metal species were estimated from the Sherwood number correlation in Eq. A.3 *(25)*.

$$\mathrm{Sh} = k_g D/D_p = 2 + 0.569(\mathrm{Gr}\,\mathrm{Sc})^{1/4} + 0.347(\mathrm{Re}\,\mathrm{Sc}^{1/2})^{0.62} \quad \text{(A.3)}$$

Diffusivities of the alkali-metal species at the temperature of interest were estimated using the following correlation between diffusivity and molecular weight for a wide range of chemical species *(23)*.

$$D = 1.0662 \times 10^{-4}\,\mathrm{MW}^{-0.483}[(T/273) + 1]^{1.75} \quad \text{(A.4)}$$

where MW is the molecular weight of the diffusing species and T is the temperature in °C.

The temperature of the burning char particles was calculated assuming that the rate of burning was controlled by the rate of transport of oxygen to the external particle surface and that the temperature gradient in the radial direction was negligible. For these conditions, the particle temperature can be estimated using Eq. 3. The heat of reaction used in Eq. 3 was the heat of formation of CO, and the rate of carbon burning was calculated as

$$R_c = (k_{g,O2}P_{O2})/\mathrm{R}(T + 273) \quad \text{(A.5)}$$

The effective heat-transfer coefficient was calculated as

$$h_{eff} = (k\mathrm{Nu}/D_p) + [\sigma(T_p^4 - T_g^4)/(T_p - T_g)] \quad \text{(A.6)}$$

where

$$\mathrm{Nu} = 2 + 0.39\mathrm{Gr}^{0.25} + 0.37\mathrm{Re}^{0.6} \quad \text{(A.7)}$$

and

$$k = 0.0238 + (6.85 \times 10^{-5}\,T_f) + (1.614 \times 10^{-8}\,T_f^2) \quad \text{(A.8)}$$

The rate of potassium volatilization, $d\mathrm{K}/dt$, was calculated as the sum of the rate of potassium volatilization from reduction of K_2CO_3 and from evaporation of KCl. Since no kinetic data exist for K_2CO_3 reduction in black-liquor char, the rate of reduction of K_2CO_3 was calculated as the rate of sodium vapor production predicted by Eq. A.2 multiplied by the ratio of K/Na in the particle.

In the model, the theoretical chloride enrichment factor was defined in terms of the rates of sodium chloride and potassium chloride vaporization and the rates of sodium and potassium vapor production by sodium and potassium carbonate reduction, as seen in Eq. A.9.

chloride enrichment factor = (see eq. A.9)

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

A theoretical potassium enrichment factor was also defined in terms of the rates of potassium chloride volatilization, potassium carbonate reduction, carbonate reduction, and NaCl volatilization.

potassium enrichment factor = (see eq. A. 10)

Li and van Heiningen *(17)* showed that CO and CO_2 can suppress sodium carbonate reduction at temperatures up to 800°C. More recent data *(26)* indicate that suppression may not occur at higher temperatures. We did not account for the suppression of sodium carbonate reduction by CO and CO_2 in the model presented here. The concentrations of CO and CO_2 resulting from the pyrolysis products were low, on the order of 1000 ppm or less, and we expected the suppression effects to be negligible.

In calculating enrichment factors, the initial char particles were assumed to consist of the inorganic residue from a 100-μm particle (of the composition given in Table I) plus fixed carbon. The inorganic composition was assumed initially to have the composition shown in **Table A-I**, which is consistent with the data in Table I. The fixed carbon was assumed to be present in adequate supply to maintain carbonate reduction throughout the 0.6–0.8-s reaction time. A time step of 0.1 s was used in the calculations, and the particles were assumed to be isothermal during the entire reaction period. ■

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Nomenclature

A_{ext}	= external surface area of a particle, m^2
D_p	= particle diameter, m
D	= diffusivity, m^2/s
Gr	= Grashof number
h_{eff}	= effective heat-transfer coefficient
ΔH_c	= heat of formation of CO, kJ/kg
k	= thermal conductivity, J/mKs
k_g	= mass-transfer coefficient, mol/m^2 bar s
MW	= molecular weight, g/mole
Nu	= Nusselt number
P	= pressure, bar
R	= ideal gas constant, 8.314 J/mol K
R_c	= rate of conversion of fixed carbon in char to CO
Re	= Reynolds number
Sc	= Schmidt number
Sh	= Sherwood number
T	= temperature, K
T_f	= film temperature $[(T_g + T_p)/2]$, K
T_g	= bulk gas temperature, K
T_p	= particle temperature, K
t	= time, s
$[Na]_{BLS}$	= Na concentration in black-liquor solids, mol Na/g BLS
$[K]_{BLS}$	= K concentration in black-liquor solids, mol K/g BLS
$[Cl]_{BLS}$	= Cl concentration in black-liquor solids, mol Cl/g BLS
$[Na]_{fume}$	= Na concentration in fume, mol Na/g fume
$[K]_{fume}$	= K concentration in fume, mol K/g fume
$[Cl]_{fume}$	= Cl concentration in fume, mol Cl/g fume
dNaCl/dt	= rate of chloride or sodium released by NaCl vaporization, mol/s
dKCl/dt	= rate of potassium or chloride released by KCl vaporization, mol/s
dNa/dt	= rate of sodium released by carbonate reduction, mol/s
dK/dt	= rate of potassium released by carbonate reduction, mol/s
dNa_v/dt	= rate of sodium vapor formation, mol/s
dCl/dt	= rate of chloride released by carbonate reduction, mol/s
σ	= Stefan–Boltzmann constant, 5.67×10^{-8} J/m^2sK