Dust and flue gas chemistry during rapid changes in the operation of black liquor recovery boilers: Part 2—Dust composition

TARJA TAMMINEN, TOR LAURÉN, KAUKO JANKA, AND MIKKO HUPA

ABSTRACT: This is the second of three papers concerning dust and flue gas chemistry of two kraft recovery boilers during rapid changes in boiler dynamics. This paper presents the results of the changes in fume composition, especially the behavior of potassium and chloride during the tests. The purpose of these studies was to shed new light on the formation and composition of fume during rapid changes in boiler operation.

In these dynamic tests the dust composition (sodium, potassium, and chloride) behaved mainly in the similar way in both boilers. About 6%-9% of the input sodium was released in fume in these tests. Some 11%-15% of input potassium and 25%-35% of input chloride were found in fume. The release of sodium from the char bed surface during the total interruption of black liquor flow was about 300 mg Na/s per m² of floor area in both boilers.

The composition of size fractionated dust samples (Na, K, Cl, SO_4, CO_3) analyzed either with IC and ICP-MS or SEM/EDXA showed equal trends as the operating conditions of the boilers were changed.

Application: This work adds insights on the topic of dust composition in kraft recovery boilers.

Part I of this study described the results of dust formation during rapid changes in boiler load, including fume formation during char bed burning as the black liquor flow was totally interrupted. The first part also described the two kraft recovery boilers involved in these tests, the on-line measurement systems used in mill measurements, and the procedure of the transient tests, i.e., rapid changes in boiler load including a total interruption of black liquor flow.

Part II concerns dust composition, especially the behavior of potassium (K) and chloride (Cl) contents in dust during rapid changes in boiler operation. It also evaluates particle size distributions of dust in different operating conditions and compares dust composition results analyzed with SEM/EDXA to results analyzed with IC and ICP-MS methods.

COMPOSITION OF BLACK LIQUORS

For this study, we used online measurements of flue gas composition (dust and gaseous emissions) from two Finnish kraft recovery boilers. The floor area for boiler A was 104 m² and 164 m² for boiler B. The maximum load of boiler A is 2200 metric tons black liquor solids (BLS)/day; and for boiler B it is 3300 metric tons BLS/day. In these tests, both boilers burned softwood liquors. **Table I** shows the elemental analysis of the fired black liquors. The dry solids content of the liquor ranged from 71%-74% in boiler A and 78%-80% in boiler B.

		BOILER A	BOILER B
Dry solids	%	71.0	79.0
Elemental analysis of ds			
C	%	31.8	31.0
H	%	3.3	3.1
N	%	0.067	0.056
Na	%	20.8	20.6
K	%	2.4	2.8
S	%	6.1	6.3
Cl	%	0.4	0.2
HHV calorimetric	MJ/kg	12.65	12.67

I. The elemental analysis of the black liquors.

COMPOSITION OF DUST

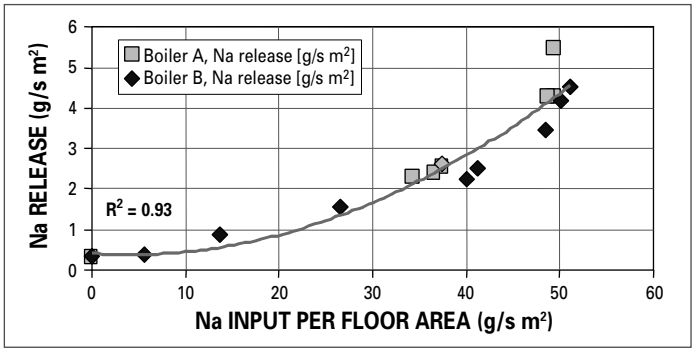
Results and discussion

We analyzed the sodium, potassium and chloride contents of dust continuously with a recently developed online dust analyzer (see Part I). The analyzer measured dust concentration (g/Nm³) in flue gases, and sodium, potassium and chloride contents in dust as weight fractions (Na, K, Cl wt-%). The principle of the operation of the online analyzer is described elsewhere [1, 2].

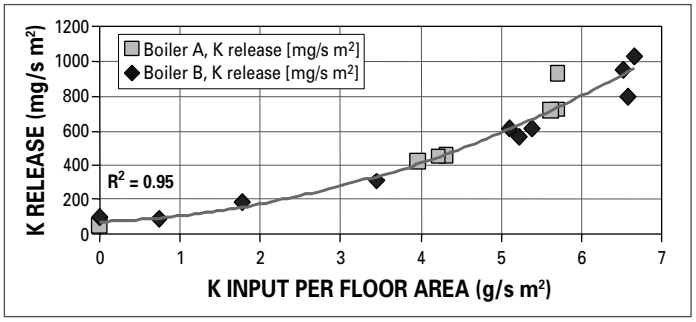
We took the measurements from the flue gas duct just before the flue gas enters the electrostatic precipitators. In that location, the dust in flue gases is mainly submicron fume.

In these transient tests, we altered the boiler load by changing the number of black liquor guns operating, but kept the spraying pressure constant. In that way, we changed the number of black liquor droplets introduced to the furnace in these tests. To compare the release of Na, K, and Cl in the different size boilers, we divided the mass flow results of each element with the floor area of the boilers. **Figures 1-3** plot the release of sodium, potassium, and chloride to the flue gases per the floor area of the boiler [Na, K, Cl, g/s m²] against the input mass flow of the same element.

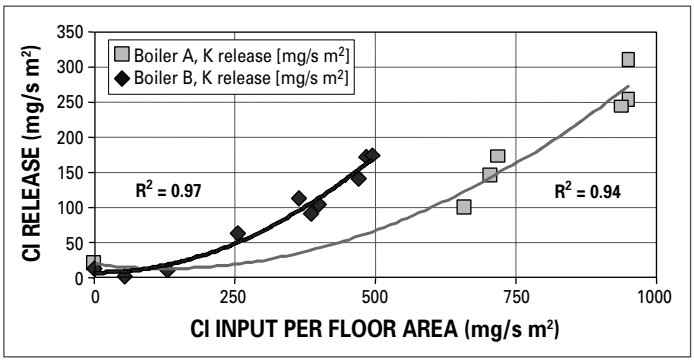
About 6%-9% of the input sodium was released in fume in these tests. We found 11%-15% of input potassium and 25%-35% of input chloride in fume. The release of Na and K was similar in the



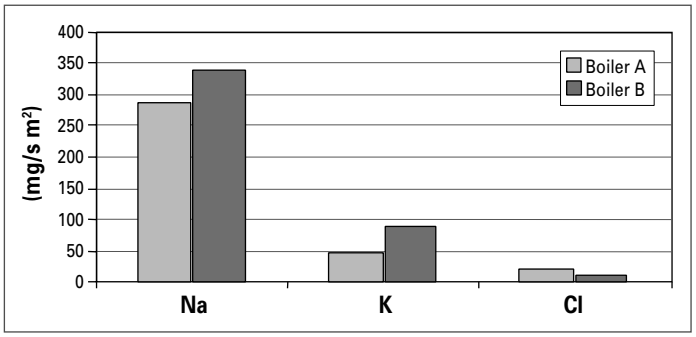
1. Na release [g/s m²] to the dust as a function of Na input in BLS in boiler A and boiler B.



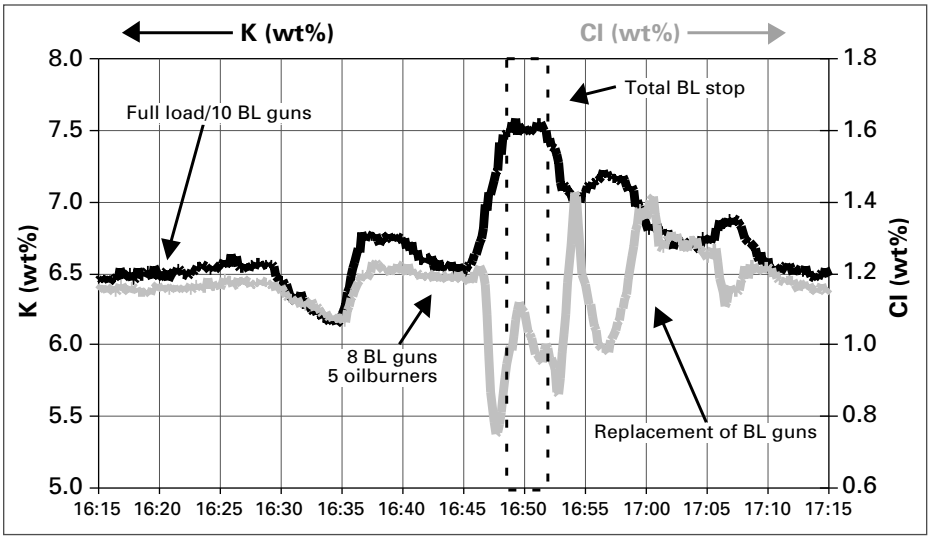
2. K release [g/s m²] to the dust as a function of K input in BLS in boiler A and boiler B.



3. Cl release[g/s m²] to the dust as a function of Cl input in BLS in boiler A and boiler B.



4. Na, K and Cl release from the char bed surface per square meter of floor area [mg/s m²] during the total interruption of black liquor flow.



5. K and Cl (wt-%) in dust during the total interruption of BL flow in boiler B.

two boilers as the boiler load was increased, i.e., the input of the element was increased. In boiler B, a higher portion of input chloride was released to the dust than in boiler A (Fig. 3). However, the actual chloride content in dust in boiler B was lower than in boiler A due to different mass flows of alkali compounds (Na, K).

The release results for the elements at the point where the input of Na, K, and Cl into the furnace is zero in Figs. 1-3, are from the tests where the black liquor flow was totally interrupted. During those tests, the measured dust amounts and Na, K, and Cl were released from the char bed surface. The release of sodium in both boilers was about 300 mg/s per floor square meter. In boiler B, more potassium was released per square meter and in boiler A, more chloride during the liquor stop test (**Fig 4**).

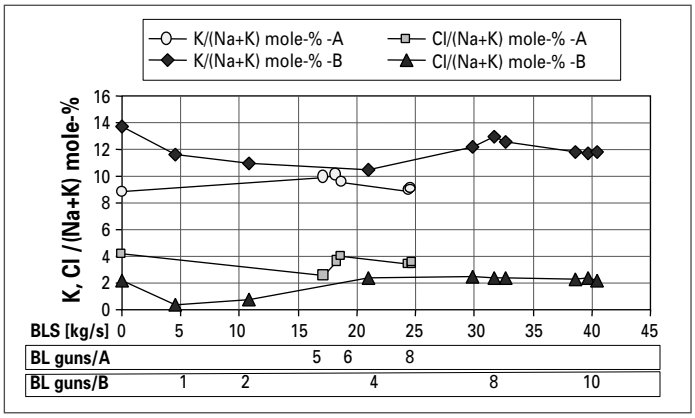
Figure 5 shows the initial signal of the composition of dust (K, Cl, wt-%) measured online during load reduction followed by the total liquor interruption in boiler B. It shows that the potassium content in dust increased from 6.5 to 7.5 wt-% when the black liquor flow was interrupted. This may indicate that the release of potassium from the char bed surface was different from the release of sodium, leading to the enrichment of potassium in dust. Another interesting point is that the chloride did not follow the potassium. This indicates that potassium may form other components besides potassium chloride (KCl), which has been thought to be the main component for potassium. This was a single result at one boiler, but it gives interesting ideas for researchers struggling with the mechanisms of alkali release.

Table II shows the release and composition information of fume during the total interruption of black liquor flow.

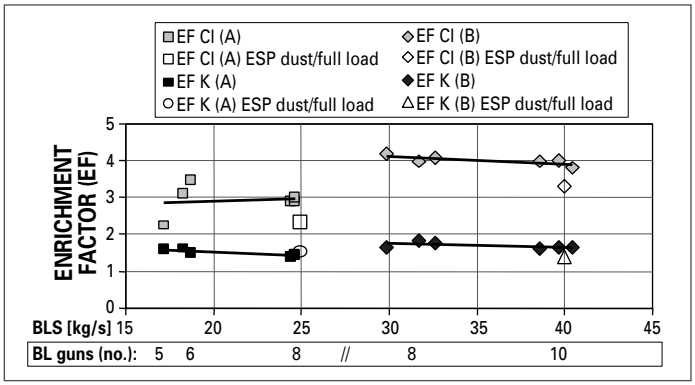
Potassium and chloride contents in dust are often expressed as mole-% of the total alkali (Cl, K/[Na+K]). The dust composition, K, and Cl content as a fraction of total alkali, did not vary much as the boiler load was changed from full load to part load (**Fig. 6**). During the start up of boiler B (1→ 2→ 4 liquor guns)

	BOILER A	BOILER B
Total dust [g/s]	100.0	200.0
Na [g/s]	29.7	55.6
K [g/s]	4.9	15.0
Cl [g/s]	2.07	2.2
Na/(Na+K) mole-%	91.2	86.3
K/(Na+K) mole-%	8.8	13.7
Cl/(Na+K) mole-%	4.1	2.2
Na [mg/s m²]	286.0	337.0
K [mg/s m²]	47.0	91.0
Cl [mg/s m²]	20.0	13.0
Total dust [mg/s m²]	962.0	1212.0

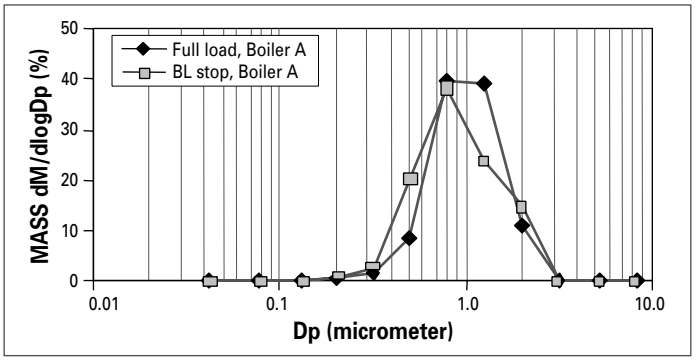
II. The amount of fume and Na, K and Cl released from char bed during the rapid black liquor interruption -tests in both boilers.



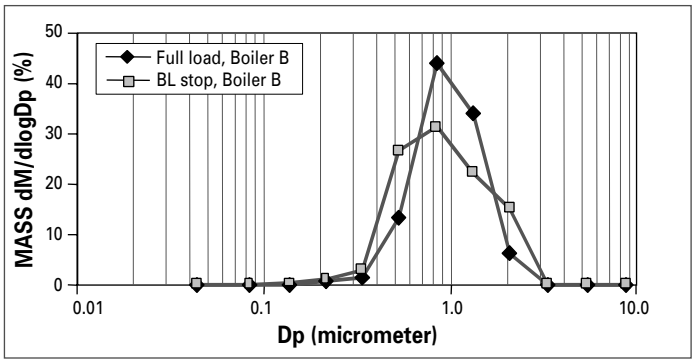
6. Dust composition (Cl, K/[Na+K]) as a function of boiler load in both boilers.



7. K and Cl enrichments as a function of boiler load in the boilers. Also, enrichment factors calculated from ESP dust samples during full load operation are shown.



8. Particle size distribution in full load and during the total interruption of BL flow in boiler A.



9. Particle size distribution in full load and during the total interruption of BL flow in boiler B.

the potassium and chloride contents in dust did vary before leveling up to the steady level. The higher potassium level during the total liquor flow interruption in bioler B (zero BLS flow) is also seen in Fig. 6 (comparable to Fig 5.)

We calculated the enrichment factors of potassium and chloride as the boiler load changed from full load to part load. We defined potassium and chloride enrichments here as the relative amount of potassium and chloride in the fume (using total alkali as the basis) relative to that in the initial BLS. The enrichments of potassium and chloride were calculated using the as-fired liquor composition, online measurements of dust composition, and ESP dust sample analyses.

Potassium enrichment showed a slight decrease as the boiler load increased in both boilers. The enrichment factor for potassium (EFK) was within the range of 1.4-1.6 in boiler A and 1.4-1.8 in boiler B. In boiler B, chloride enrichment slightly decreased with an increase in boiler load (EFCl 3.7-4.2). In boiler A, the chloride enrichment varied more (EFCl 2.2-3.5) and did not show any clear trend (**Fig. 7**).

The trends of increasing dust load (or sodium release) and decreasing enrichment factors of potassium and chloride as the boiler load was increased agree with measurements in a boiler with stable operation described by Janka et al. in [3]. Those findings were explained by the dilution effect of increased release of sodium (i.e., increased fuming).

PARTICLE SIZE DISTRIBUTION

Results and Discussion

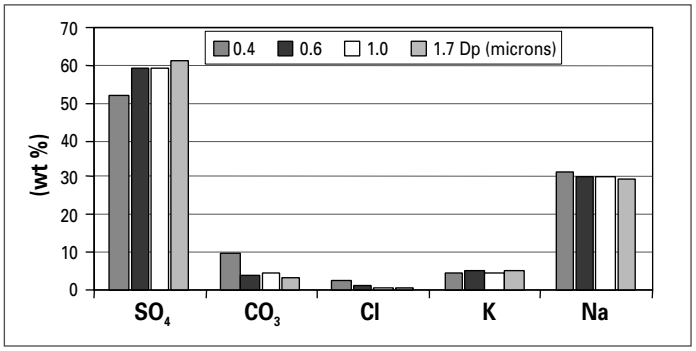
We measured particle size distribution of fume online with an electrical low-pressure impactor (ELPI) device during each test. The particle size did not change when we reduced the boiler load by taking off liquor guns. When the black liquor flow was totally interrupted, the particle size distribution showed a slight broadening toward smaller particle size fractions (**Figs. 8 and 9**).

Normally, the initially formed fume particles collide with each other and form agglomerates [4]. The concentration of fume in the flue gases was in full load 15-20 g/Nm³, but during the liquor interruption, the concentration was only one-tenth part (1.5-2 g/Nm³) relative to the full load. Due to the lower concentration, the fume particles had less opportunity to form agglomerates and the particle size distribution of fume changed during the liquor interruption.

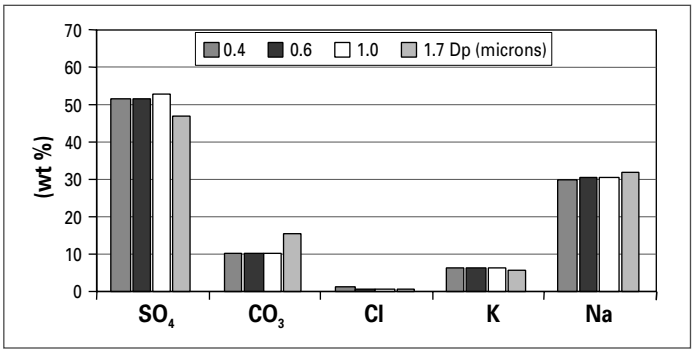
COMPOSITION OF SIZE FRACTIONED DUST SAMPLES

Results and discussion

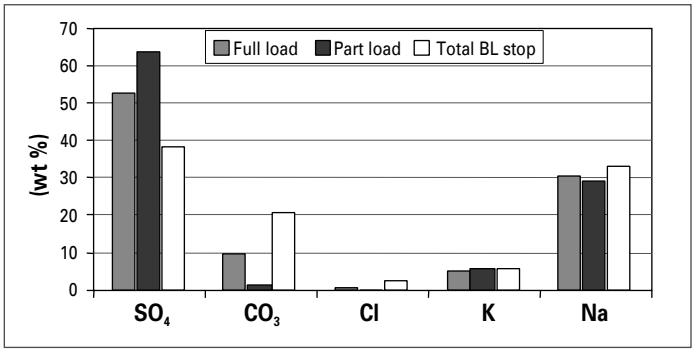
We obtained size-fractionated dust samples with a 13 stage low pressure impactor. The analyzed components were Na, K, Cl, S,



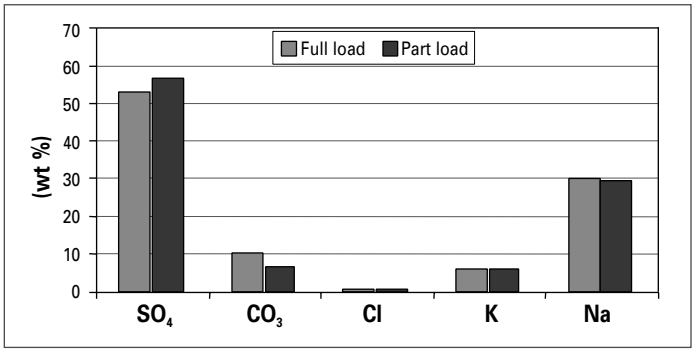
10. Composition of the size fractionated dust samples (SEM/EDXA). Dust samples are taken during the full load of the boiler A.



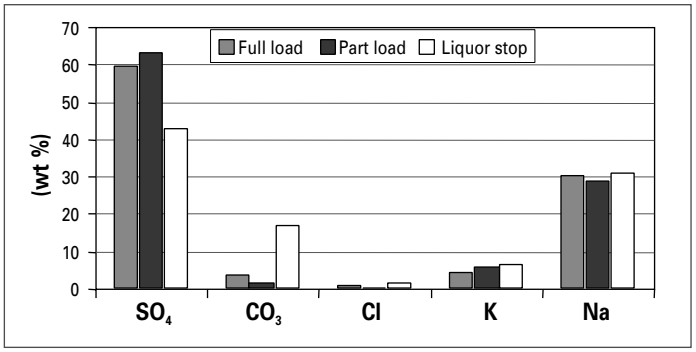
11. Composition of the size fractionated dust samples (SEM/EDXA). Dust samples are taken during the full load of the boiler B.



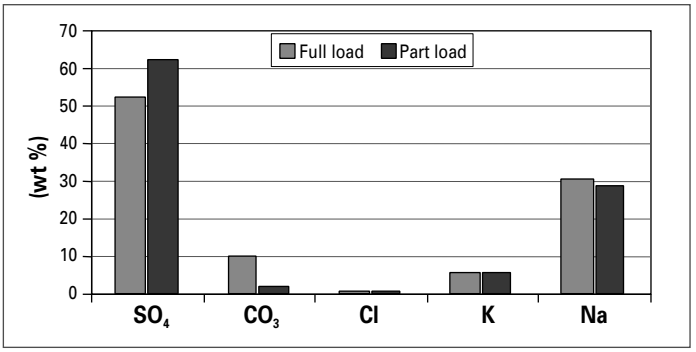
12. Dust composition (Dp 1 µm) during full load, part load, and black liquor stop in boiler A. ICP-MS and IC methods.



13. Dust composition (Dp 1 µm) during full load and part load in boiler B. ICP-MS and IC methods.



14. Dust composition (Dp 1 µm) during full load, part load, and black liquor stop in boiler A. SEM/EDXA.



15. Dust composition (Dp 1 µm) during full load and part load in boiler B. SEM/EDXA.

	BOILER A	BOILER B
Full load	0.8	0.8
Part load	1.0	0.8
BL stop	0.5	–

III. S/(Na+K)$_2$ mole ratio in one micron size dust particles in different operating conditions.

or SO_4. Sodium and potassium were analyzed with an inductively coupled plasma mass spectrometer (ICP-MS) and chloride and sulfate with ion chromatography (IC). We calculated carbonate (CO_3) as a balance. The results were cross-checked through anion-cation balance calculations. To compare different analysis methods, we also analyzed these samples using a scanning electron microscope with energy dispersive X-ray analyzer (SEM/EDXA). The size fractionated dust samples are not the easiest to analyze because the amount of one sample is very small.

Both methods (SEM/EDXA and laboratory methods) gave equal composition for the dust samples. The dust was formed mainly from sodium sulfate (Na_2SO_4). In full load, there was a miniscule concentration of carbonate in dust, usually under 10 wt-%. In the dust from boiler B, the carbonate content was slightly higher than in boiler A. The concentration of chloride was slightly higher in the smallest size fractions (<1µm) of dust (**Figs. 10 and 11**).

Because 1 micron sized dust seemed to be the main fraction in precipitator dust (see Figs. 8 and 9), we analyzed the composition of that dust fraction in different operating conditions in more detail. **Figure 12** shows the compositions of 1 micron size particles (Dp 1µm) during full load (24 kg BLS/s), part load (18 kg BLS/s), and during black liquor interruption in boiler A. We analyzed these dust samples using IC and ICP-MS methods.

Figure 12 shows that as the boiler load was reduced from full to part load, the SO_4/CO_3-composition of the particles changed. Carbonate in particles disappeared when operating with part load, and the sulfur-to-alkali ratio in fume increased (Table II). This is discussed further in Part III.

The 1 micron size particles released from the char bed during the total black liquor interruption contained twice as much carbonate compared to the particles that originated mostly in black liquor droplets during full load operation. This indicates that the in-flight release (from liquor droplets or char particles) also dominates the sulfur release.

Figure 13 shows that in boiler B there seemed to be no remarkable difference in particle composition (Dp 1 µm) whether the boiler load was higher (40 kg BLS/s) or lower (32 kg BLS/s), although, carbonate content shows a slight decrease during part load operation. Unfortunately, the size fractionated dust sampling was failed during the total BL stop in boiler B.

We analyzed the same 1-micron sized dust samples (Figs. 12 and 13) with SEM/EDXA (**Figs. 14 and 15**). These results generally agreed with the results analyzed with IC and ICP-MS, although we saw slight differences in the weight-% of the elements. Both analyzing methods showed the same trends in dust composition as the operating conditions were changed. The SEM/EDXA may be suitable for qualitative and quantitative analysis of size fractionated dust samples.

The sulfur-to-alkali-mole ratio $(S/(Na+K)_2)$ in these 1 micron size fume particles was 0.8 in full load operation of the boilers. As the load was reduced, the $S/(Na+K)_2$ ratio increased to unity in boiler A (**Table III**). This result was consistent with the SO_2 results, which we will discuss in Part III (gaseous emissions). In the particles released from the surface of the char bed the sulfur-to-alkali-mole ratio was low $(S/(Na+K)_2=0.5)$.

CONCLUSIONS

This paper is the second of three papers concerning dust and flue gas chemistry of kraft recovery boilers during rapid changes in boiler dynamics. Here we present the results of fume composition, especially the behavior of K and Cl. The purpose of these studies was to shed new light on the formation and composition of fume during rapid changes in boiler load. For the first time, dust concentrations and composition (K, Cl) were measured online.

In these dynamic tests the dust composition (Na, K, Cl) behaved mainly in the similar way in these two boilers. Both boilers were burning softwood liquor, although the dry solids contents of the black liquor were different (boiler A 71%-74%, boiler B 78%-80%). About 6%-9% of the input sodium was released in fume. Some 11%-15% of input potassium and 25%-35% of input chloride were found in fume.

The release of sodium from the char bed surface during the total interruption of black liquor flow was about 300 mg Na/s per floor square meter in both boilers. In boiler B, the increase in potassium content of dust during the liquor stop test indicated differences in the volatilization rates or mechanisms of potassium as compared to sodium.

The in-flight release of sodium and potassium from liquor droplets turned out to be the main source for fume formation. The SO_4 and CO_3 contents in dust released from liquor droplets or from the surface of the char bed indicated that the in-flight release may also be the main source for sulfur release.

During the complete interruption of black liquor flow the particle size distribution moved towards smaller size fractions. Coagulation and agglomeration of the particles decreased due to smaller concentration of fine dust particles in the flue gases.

The composition of size fractionated dust samples when analyzed with either IC and ICP-MS or SEM/EDXA showed equal trends as the operating conditions of the boilers were changed.

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Tamminen, Lauren, and Hupa are with Åbo Akademi University, Process Chemistry Group, c/o. Combustion and Materials Chemistry, Lemminkäisenkatu 14-18 B, 20520 Turku, Finland; Janka is with Kvaerner Pulping Oy, PL 109, 33101 Tampere, Finland; email Tamminen at tarja.tamminen@abo.fi or tarja.tamminen@enwin.fi.

Tamminen

Laurén

Janka

Hupa