Improving recovery boiler availability through understanding fume behavior

AINO LEPPÄNEN AND ERKKI VÄLIMÄKI

ABSTRACT: Unexpected recovery boiler shutdowns are rare, but they can cost millions of dollars in lost income. Sometimes the inorganic compounds in black liquor can cause sudden fouling or plugging problems that could not be predicted beforehand. The ash particles can be divided into two main types and size classes: carryover and fume. This paper focuses on the smaller fume particles that form through the condensation of alkali metal vapors and that deposit via different mechanisms than carryover. The location of fume deposition depends on several factors, such as flue gas and superheater temperatures, black liquor composition, and the flow field in the boiler.

This paper presents results obtained with a computational method that simulates fume formation in recovery boilers. The paper focuses on the effect of black liquor composition and elemental release on fume behavior and suggests how these observations should be taken into account when designing new boilers or retrofits. Moreover, the paper introduces the possible applications of the modeling method. These include, for example, troubleshooting of fouling problems in existing boilers, designing superheater configurations for new boilers, and positioning soot blowers.

Application: Boiler manufacturers and mills have new ways to predict their boiler's tendency for fume formation when the black liquor composition changes.

Reliable operation of modern, extremely large recovery boilers is a top priority. Unexpected boiler shutdowns are rare, but they can cost millions of dollars in lost income due to interrupted pulp production. The ash in black liquor is often the reason for these shutdowns because the ash can cause sudden fouling or plugging problems that could not be predicted.

Black liquor contains a high amount (about 30%) of ash-forming elements; the most important are sodium (Na), sulfur (S), potassium (K), and chlorine (Cl). Although the aim in recovery boiler operation is to recover these elements in the smelt, some of them escape through vaporization in the hot boiler furnace. Later, when the flue gases cool down, ash-forming compounds may condense on the heat transfer surfaces or form fine particles, called fume. These fine particles form deposits on the steam tubes and thus decrease the rate of heat transfer from the hot flue gases to the steam. In the worst case, the deposits may initiate tube corrosion or grow so thick that the flue gas paths are plugged; both situations lead to an unexpected boiler shutdown.

It is difficult to capture and analyze the fine fume particles from the hot and corrosive recovery boiler flue gases, and often information is only obtained from the electrostatic precipitator (ESP). However, it is possible to simulate the behavior of the fume particles by computational methods. One method for this has been presented [1-3]; it is based on computational fluid dynamics (CFD), equilibrium chemistry, and fine-particle dynamics.

The method contains several simplifications and approximations, which were necessary to make the method applicable to large boiler geometries with reasonable computational cost. One of the limitations is the use of constant release factors for the ash-forming elements from the black liquor to the vapor phase because clear correlations as a function of temperature or other boiler parameters are not available in the literature. The release factors given by different publications vary significantly [4,5]. Therefore, this paper reports on an investigation of the sensitivity of the modeling results to these release factors. Moreover, the results indicate how real-life changes in black liquor composition or elemental release may affect fume behavior in the recovery boiler superheater area.

MODELING METHOD

The modeling method is presented more in detail in the references [1-3,6]. The model uses a commercial CFD program [7], as well as several custom submodels that are connected through the program's user-defined functions. The main submodels include the model for the chemistry between the different alkali metal compounds and the model for the aerosol dynamics.

Alkali metal chemistry

As mentioned earlier, the release of the ash-forming elements from black liquor to the gaseous phase is modeled with constant release factors. Here, the release factors are determined

as the fraction of an element in black liquor dry solids that is released to the flue gases and not trapped in smelt. The release factors in the base case of this model (**Table I**) are based on the information from [8-10], but adjusted slightly to correspond to the ESP ash measurements presented in [6].

In practice, the temperature of the lower furnace can affect the release and the enrichment factors. In general, a higher lower-furnace temperature increases the release of sodium, potassium, and chlorine but decreases the release of sulfur [11]. However, clear correlations as a function of temperature are not available in the literature.

After the release, the ash-forming elements react to form new compounds. Usually, the main compound in the recovery boiler fume is sodium sulfate (Na_2SO_4)[12]; however, potassium sulfate (K_2SO_4), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), sodium chloride (NaCl), and potassium chloride (KCl) are also important. In addition to these compounds, the gaseous compounds sulfur dioxide (SO_2), hydrogen chloride (HCl), sodium hydroxide (NaOH), and potassium hydroxide (KOH) are present in the upper furnace of the boiler. The global reactions of the sodium compounds are $2NaCl + SO_2 + H_2O + ½\ O_2 \rightarrow Na_2SO_4 + 2HCl$; $2NaOH + SO_2 + ½O_2 \rightarrow Na_2SO_4 + H_2O$; and $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$. The same reactions hold for potassium.

The state of the chemical reactions is determined by chemical equilibrium because the kinetic parameters of the reactions are not available. The reactions of the alkali metal compounds are assumed to reach equilibrium because the temperature in the recovery boiler is relatively high, and the residence times of the alkali metal compounds are assumed to be long enough to allow equilibrium to be reached. The equilibrium assumption has also been used by Jokiniemi et al. [12], Wessel and Baxter [13], and Kangas et al. [5] in the upper furnace of the recovery boiler.

The equilibrium state of each chemical reaction is calculated with thermodynamic software [14], where the method is based on the minimization of the Gibbs energy of a system. The software is not directly coupled to the CFD simulations, but a lookup table of discrete reaction values is calculated and used in the simulations. For simplification, the equilibrium reactions only proceed when the compounds are in the gaseous phase. The formation of the fume particles is determined by fine-particle dynamics, as explained in the next section.

Element	Na	S	K	Cl
Release, %	12.2	20	16.5	43

I. The release factors used in the original case.

Aerosol dynamics

The ash particles can be divided into two main types and size classes: carryover and fume. There is another particle mode in between these two size classes, called intermediate size particles (ISP). For simplification, ISP is considered a part of carryover in this work. Moreover, this paper focuses on the smaller fume particles that form through the condensation of alkali metal vapors. The size of the fume particles is <1 μm. The carryover particles, on the other hand, consist mainly of unburned black liquor and are much larger (>100 μm), which make their formation and deposition mechanisms completely different from fume. In addition, most of carryover is usually removed from the flue gases before the last superheaters and the boiler bank. In many large and modern recovery boilers, carryover is removed from the flue gases earlier, which makes the presented modeling method best applicable in such boilers.

Previously, the presented modeling method utilized the commercial software (Fine Particle Model, FPM) to simulate the aerosol dynamics in the recovery boiler. Later, a new model was built [15] on the basis of the approach presented in [16]. Like the FPM, the new model uses the Eulerian approach; that is, it treats the particles as populations, not individual particles, so that very high particle concentrations can be simulated. The new model enables more control of the modeling parameters, such as the under-relaxation factors of different processes, and has improved the simulation speed significantly. One simulation run for a superheater section of around 700,000 computational cells takes about 30 h with eight computer nodes, when the temperature and flow field have been calculated beforehand.

In this work, the aerosol dynamics model includes the condensation of alkali metal vapors onto particles together with coagulation and movement of the particles. Condensation determines the location of particle formation and the total particle mass. The formation of particle seeds from gases, called nucleation, is not modeled in this work. Instead, it is assumed that inert particle seeds always exist in the recovery boiler and that condensation can occur on those seed particles. In addition to particle formation, fume particle deposition on the superheater tube surfaces is modeled by the approach presented in [3,6].

Element	C	H	S	O	N	Cl	Na	K	Inert
Weight, %	33.5	3.4	6.5	34.5	0.1	0.06	20.8	0.9	0.2

II.Composition of black liquor (dry mass basis).

Boiler modeling

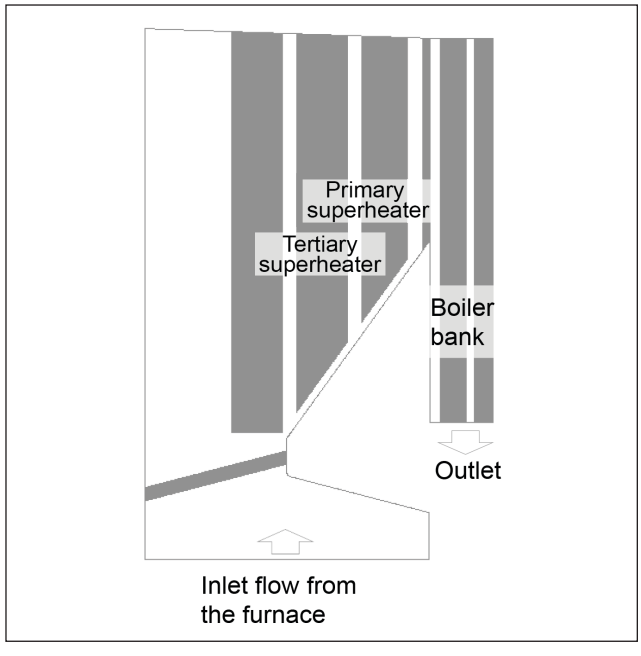
The boiler modeled in this work and the experimental results for model validation are presented in more detail in [6]. The model was found capable of predicting the fume particle composition relatively well in terms of Na, K, carbonate (CO_3), and SO_4 content. Unfortunately, it was not possible to measure the chlorine content of the fine particles inside the superheater area reliably, so the predicted chlorine content could be validated only at the ESP. One reason for the measurement difficulty was the low chlorine content of black liquor, which can be seen in **Table II**.

In this paper, the modeling case presented in [6] is modified in terms of the release factors of the ash-forming elements. This is done to investigate how sensitive the fume formation and deposition results are to the release factors. In addition, the results will indicate how changes in real-life conditions, such as the black liquor composition, may affect fume deposit composition. The sensitivity analysis is conducted by changing the mass fractions of sodium, sulfur, and chlorine entering the superheater area by 25% intervals. The changes are made for one element at a time because it is not known how the release factors of the different elements are connected.

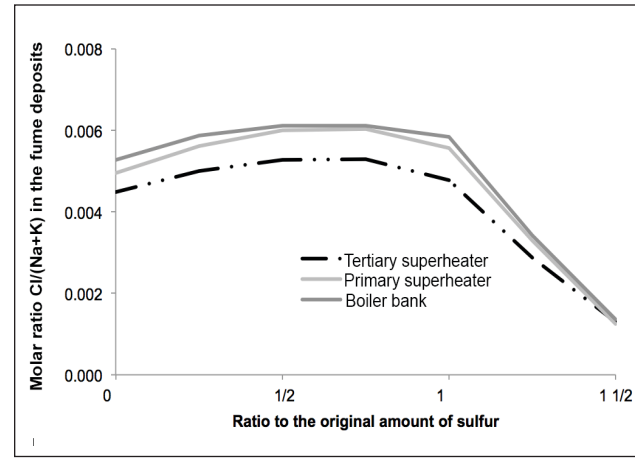
The modeling results are presented here only for the superheater area of the boiler since the model focuses on the fume particles, which become significant in that area. A 2-dimensional projection of the modeled 3-dimensional superheater area is shown in **Fig. 1**.

RESULTS AND DISCUSSION

The results are presented for the molar ratios of Cl/(Na+K) and K/(Na+K) in the fume deposits. The enrichment factors



1. Schematic of the superheater geometry and names of some superheater surfaces.



2. Molar ratio Cl/(Na+K) in the fume deposits at the primary and tertiary superheater and the boiler bank shown for different mass fractions of sulfur entering the superheater area.

are not presented because they are also dependent on the molar ratios in the black liquor. In this work, the changes in the amounts of different elements entering the superheater area are caused either by changes in the black liquor composition or changes in the elemental release factors, so the molar ratios in black liquor cannot be determined.

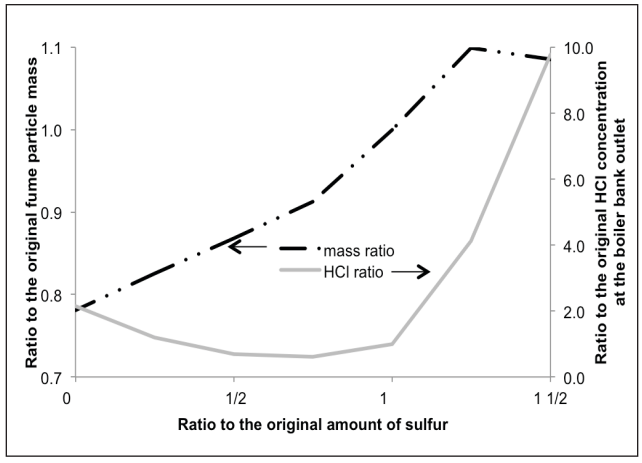
Changing the amount of sulfur

Changing the amount of sulfur entering the superheater area simulates either a change in the black liquor composition or a change in the amount of sulfur that is released from the black liquor to the flue gases. The release of sulfur should increase if the lower-furnace temperature decreases [11], contrary to the other ash-forming elements. For simplicity, the amount of the other elements is kept constant in these simulations.

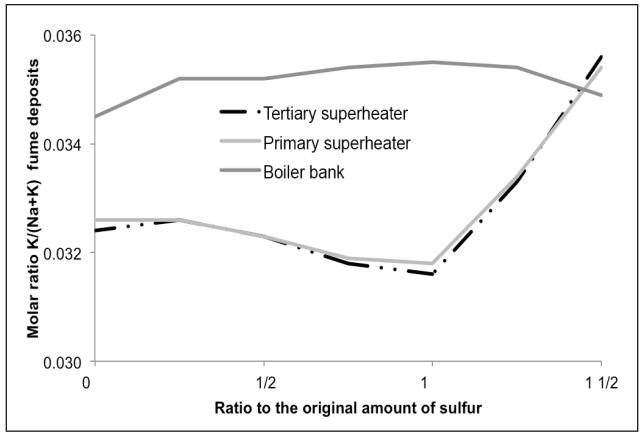
Figure 2 shows how the molar ratio Cl/(Na+K) in the fume deposits changes when the amount of sulfur entering the superheater area increases. The modeling results are shown as area-weighted averages for the fume deposits at the tertiary and primary superheaters and the boiler bank.

When there is less sulfur than in the original case, the fraction of chlorine in the fume deposits stays almost constant because most of the chlorine is present as alkali chlorides. However, when the amount of sulfur increases above the original amount of sulfur, the chlorine content in the fume deposits decreases. The experimental results of Frederick et al. [17] showed that the chlorine enrichment factor decreases when the SO_2 concentration increases, which supports the results in Fig. 2 for sulfur ratios above ¾. According to the results obtained in this work, there are two main reasons for the decreasing chlorine fraction, which can be seen in **Fig. 3**.

Figure 3 shows that the total particle mass increases when there is more sulfur entering the superheater area. This is expected because when there is more sulfur, the amount of alkali sulfates increases and the amount of alkali carbonates decreases. The alkali sulfates have a higher molar mass than alkali carbonates, which increases the total fume deposit mass



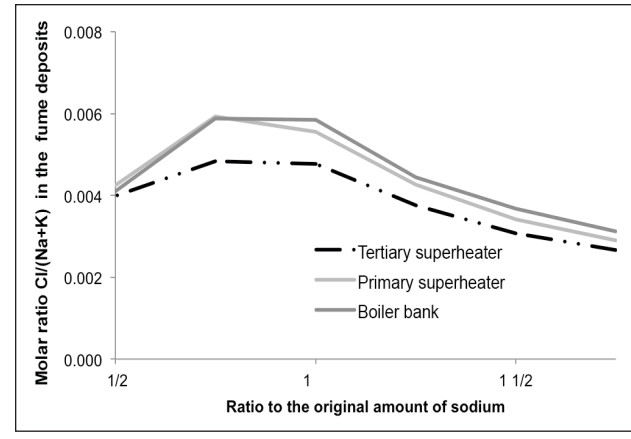
3. Ratio to the original fume particle mass (left axis) and ratio to the original hydrogen chloride concentration at the boiler bank outlet (right axis) shown for different mass fractions of sulfur entering the superheater area.



4. Molar ratio K/(Na+K) in the fume deposits at the primary and tertiary superheater and the boiler bank shown for different mass fractions of sulfur entering the superheater area.

and thus dilutes the chlorine mass fraction in the fume deposits. However, at the highest sulfur ratio (1½), the increase seems to stop as all alkalis are already bound to sulfates and the additional sulfur forms SO_2.

Another explanation for the decreasing Cl/(Na+K) ratio is related to the form of the chloride ions. When there is more sulfur than in the original case, more sulfates are formed and there is gaseous HCl present at the end of the boiler bank (Fig. 3). However, according to the modeling results, gaseous SO_2 emissions at the boiler bank outlet only occur with the highest sulfur ratio of 1½ because this boiler operates at such high temperatures that all sulfur dioxide is consumed at normal conditions. It seems that HCl emissions increase both toward lower and higher ratios of sulfur, but there is no clear explanation for this. One possibility is that at low sulfur ratios, according to equilibrium, alkali chlorides react with carbon dioxide to form alkali carbonates and HCl. However, this is uncertain because the equilibrium chemistry approach might not work at low- and zero-sulfur ratios.



5. Molar ratio Cl/(Na+K) in the fume deposits at the primary and tertiary superheater and the boiler bank shown for different mass fractions of sodium entering the superheater area.

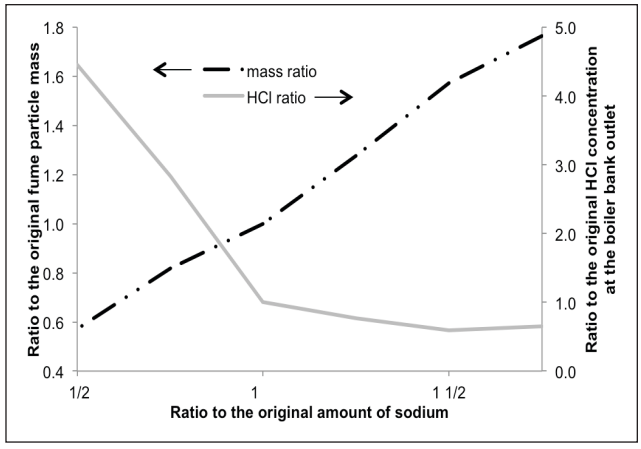
Figure 4 shows how the molar ratio K/(Na+K) changes in the fume deposits when the amount of sulfur entering the superheater area increases. The fraction of potassium remains practically constant when the amount of sulfur entering the superheater area changes. The same result has been obtained by Frederick et al. [17]. However, there is a slight increase in the molar ratio K/(K+Na) at the primary and tertiary superheater deposits at the higher sulfur ratios because more KCl is converted to K_2SO_4, which condenses earlier than KCl.

Changing the amount of sodium

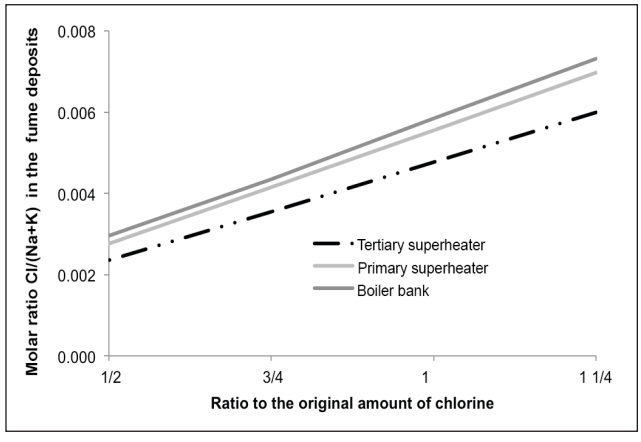
Changing the amount of sodium entering the superheater area simulates either a change in the black liquor composition or a change in the amount of sodium that is released from the black liquor to the flue gases. In real life, the release of sodium will increase if the lower-furnace temperature increases [11]. At the same time, however, the release of potassium and chlorine should increase and the release of sulfur should decrease, but these other factors are kept constant in these simulations.

Figure 5 shows how the molar ratio Cl/(Na+K) in the fume deposits changes when the amount of sodium entering the superheater area is changed. When there is much less sodium than in the original case (ratio ½), the Cl/(Na+K) ratio in the fume deposits decreases. This is because more chlorine is present as gaseous HCl than liquid or solid NaCl. On the other hand, when there is more sodium than in the original case, the ratio decreases again. This is because the amount of sodium carbonate in the fume particles increases and dilutes the chlorine mass fraction, as for sulfur (see Fig. 2). The same observation has been made by Frederick et al. [17].

These changes are also explained by the changes in the total fume particle mass and the HCl concentration at the boiler bank outlet, shown in **Fig. 6**. As could be expected, the K/(K+Na) molar ratio decreases when the amount of sodium entering the superheater area increases. The reason for the decreasing K/(K+Na) ratio is the dilution of potassium compounds by the sodium compounds, which has also been



6. Ratio of the original fume particle mass (left axis) and ratio of the original hydrogen chloride concentration at the boiler bank outlet (right axis) shown for different mass fractions of sodium entering the superheater area.

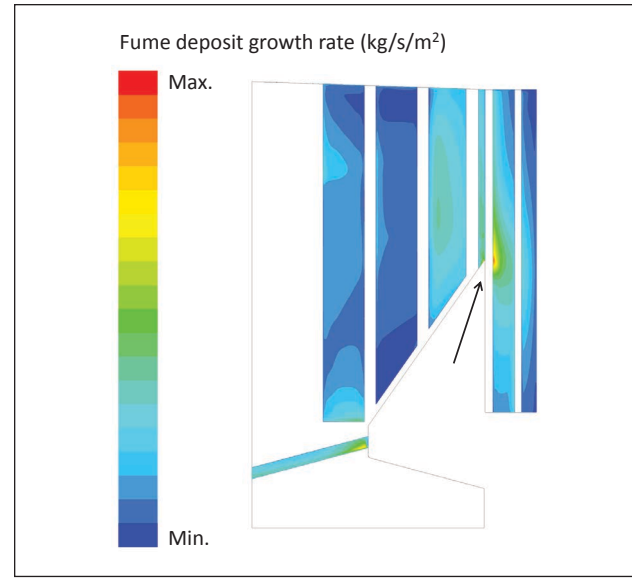


7. Molar ratio Cl/(Na+K) in the fume deposits at the primary and tertiary superheater and the boiler bank shown for different mass fractions of chlorine entering the superheater area.

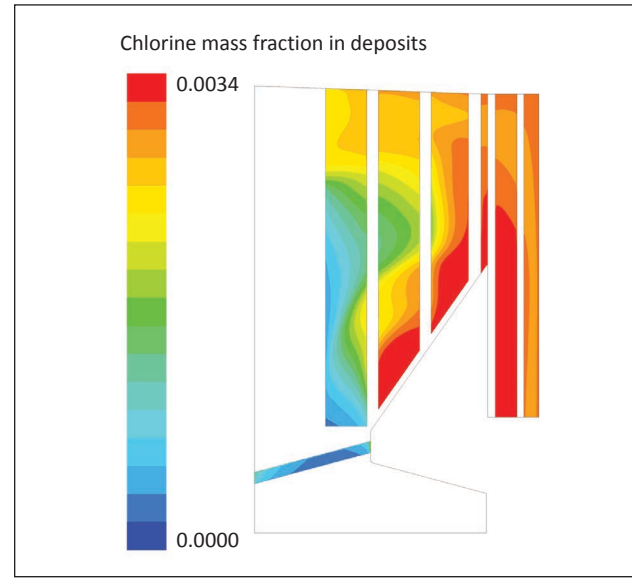
observed by Frederick et al. [17]. The results are self-evident and not shown here. The mass fraction of potassium entering the superheater area was also changed, but there were no significant changes in the Cl/(K+Na) or K/(K+Na) molar ratios, so the results are not shown here.

Changing the amount of chlorine

Figure 7 shows how the molar ratio Cl/(Na+K) in the fume deposits changes when the amount of chlorine entering the superheater area is changed. The amounts of the other ash-forming elements are kept constant. The molar ratio Cl/(Na+K) increases practically linearly when the amount of chlorine entering the superheater area increases. This means that the enrichment of chlorine stays constant, if we assume that the increased amount of chlorine follows from an increased amount of chlorine in black liquor. Overall, the amount of chlorine is highest at the boiler bank because there the temperatures are lower and all alkali chlorides have condensed to fume particles and deposits. The molar ratio



8. An example result for fume deposit growth rate in a recovery boiler superheater area.



9. An example result for chlorine mass fraction at deposits in a recovery boiler superheater area.

K/(K+Na) is not affected by the amount of chlorine entering the superheater area, so the results are not shown here.

POSSIBLE APPLICATIONS OF THE MODEL

The simulation tool has already been applied to real recovery boiler cases, and it has provided new insights into recovery boiler fouling. As an example, **Fig. 8** shows how the model predicts that fume deposit growth concentrates at the flue gas turning point at the boiler bank. The same phenomenon has been found in actual boilers. According to the modeling results, this phenomenon can be explained by the increased rate of deposition by thermophoresis, which is caused by a steep temperature gradient between the flue gas and the super-

heater surface [3,6]. At the flue gas turning point, however, turbulence also seems to enhance fume deposition.

Figure 8 also shows that the fume deposit growth would be the fastest at the primary superheater and the boiler bank for this particular boiler. These types of modeling results may help to troubleshoot fouling problems in existing recovery boilers, and to position soot blowers more effectively, for example. As another example, **Fig. 9** shows how the fume deposit chlorine content varies locally in the superheater area of a recovery boiler.

Predicting the chlorine content of fume deposits may help to identify causes for corrosion, or to plan new superheater configurations without a risk for corrosion. The simulations may also help to predict fume composition in a situation when the black liquor composition changes, as shown by the earlier results in this paper.

CONCLUSIONS

The primary goal of this work was to investigate the sensitivity of the modeling method presented in [1-3] to the mass fractions and the release factors of the ash-forming elements in black liquor. It is important to investigate this sensitivity, since the dependencies of the release factors of sodium, sulfur, potassium, and chlorine are not reliably known. The results in this paper are focused on fume formation and may not be applicable to boilers with high levels of carryover in the superheater area.

As could be expected, the fume deposit composition depends significantly on the released amount of each ash-forming element from the black liquor to the flue gases. For some elements this effect is linear, but not always. For example, a 25% underestimation in the sulfur release factor may result in a 40% overestimation in the molar ratio Cl/(Na+K) in the fume deposits (see Fig. 2). Thus, it is important to gain information from the release factors of the ash-forming elements that is as exact as possible.

In addition to the model sensitivity study, the results also indicate how some changes in the recovery boiler operation or black liquor composition may affect the composition of the fume deposits. For example, if the fraction of sulfur in the as-fired black liquor increases, it will most likely decrease the chlorine mass fraction in the fume deposits. However, it is more difficult to predict what would happen if the lower-furnace temperature would change, as this would affect the release of all the ash-forming elements at the same time.

Increasing the furnace temperature increases the amount of circulating dust [18,19]. In addition, the earlier simulation results obtained with the model indicate that increasing the flue gas temperature increases the overall fume deposition rate, even though the release rates would be constant [20]. Moreover, Reis et al. [21] and Wåg et al. [11] concluded that the reduction of sodium carbonate would increase faster with increasing temperature than the vaporization of NaCl and KCl, which would lead to the dilution of potassium and chlorine fractions in fume, but this should be confirmed. More information is needed on how the release of elements changes when the temperature of the furnace changes.

In addition to the furnace temperature, the conditions in the recovery boiler may also change as a result of lignin removal. Vähä-Savo et al. [22] showed that the sulfur content of reduced-lignin black liquor increases; however, the effect of lignin removal on sulfur release from black liquor is not clear. For eucalyptus, the release of sulfur seems to decrease when the lignin content is lower, but this is not observed for softwood. Vähä-Savo et al. also noted that when burning lignin-lean black liquors, it is important to maintain the temperature of the furnace, as a decrease in the furnace temperature may increase sulfur release. However, on the basis of the results presented, it seems possible that lignin removal may affect the chlorine content of the fume deposits, if the mass fraction of sulfur in the flue gases changes.

In conclusion, the presented modeling method can be used to estimate the effect of some operational changes in a recovery boiler on fume deposit growth rate and composition, but the reliability of these predictions is dependent on the reliability of the input parameters**. TJ**

ACKNOWLEDGEMENTS

The authors express their appreciation to Valmet Technologies Oy and Tampere University of Technology for financing this project.

LITERATURE CITED

1. Leppänen, A., Välimäki, E., and Oksanen, A., *TAPPI J.* 11(7): 9(2012).
2. Leppänen, A., Välimäki, E., Oksanen, A., et al., *TAPPI J.* 12(3): 25(2013).
3. Leppänen, A., "Modeling fume particle dynamics and deposition with alkali metal chemistry in kraft recovery boilers," Ph.D. dissertation, Tampere University of Technology, Tampere, Finland, 2015.
4. Saturnino, D.M. and Tran, H., "Factors affecting Cl and K enrichment in precipitator ash," *Congr. Expo. Anu. Celul. Pap., 44th*, Associacao Brasileira Tecnica de Celulose e Papel (ABCTP), São Paulo, 2011, p. 831.
5. Kangas, P., Koukkari, P., Lindberg, D., et al., *J. Sci. Technol. For. Prod. Processes* 3(3): 6(2013).
6. Leppänen, A., Tran, H.N., Taipale, R., et al., *Fuel* 129: 45(2014).
7. ANSYS Inc., *Fluent Release 14.5*, Canonsburg, PA, 2013.
8. Mikkanen, P., "Fly ash particle formation in kraft recovery boilers," D.Sc. (Tech.) dissertation, Helsinki University of Technology, Helsinki, 2000.
9. Mikkanen, P., Jokiniemi, J., Kauppinen, E., et al., in *AIChE Symposium Series*, Vol. 95, No. 322, American Institute of Chemical Engineers, New York, 1998, pp. 103–118.
10. Tamminen, T., Laurén, T., Janka, K., et al., *TAPPI J.* 1(6): 25(2002).
11. Wåg, K.J., Reis, V.V., Frederick, W.J., et al., *TAPPI J.* 80(5): 135(1997).
12. Jokiniemi, J., Pyykönen, J., Mikkanen, P., et al., *TAPPI J.* 79(7): 171(1996).
13. Wessel, R.A. and Baxter, L.L., *TAPPI J.* 2(2): 19(2003).

14. Thermfact/CRCT and GTT-Technologies, *FactSage Equilib Module*, Montreal and Herzogenrath, Germany, 2009.

15. Olin, M. and Leppänen, A., *Valmet Boiler Aerosol Model (VBAM) Manual*, Tampere University of Technology, Tampere, Finland, 2015, unpublished material.

16. Olin, M., Rönkkö, T., and Dal Maso, M., *Atmos. Chem. Phys.* 15(9): 5305(2015).

17. Frederick Jr., W.J., Dent, G., and Vakkilainen, E., "Effects of temperature and SO_2 on chloride and potassium enrichment factors in kraft recovery boilers," *Int. Chem. Recovery Conf.*, TAPPI PRESS, Atlanta, GA, USA, 1998, p. 945.

18. Mikkanen, P., Kauppinen, E.I., Pyykonen, J., et al., *Energy Fuels* 13(4): 778(1999).

19. Hupa, M., in *Kraft Recovery Boilers* (T. Adams, Ed.), TAPPI PRESS, Atlanta, 1997, pp. 39-57.

20. Leppänen, A., Tran, H., Välimäki, E., et al., *J. Sci. Technol. For. Prod. Processes* 4(1): 50(2014).

21. Reis, V.V., Frederick, W.J., Wåg, K.J., et al., *Tappi J.* 78(12): 67(1995).

22. Vähä-Savo, N., DeMartini, N., Ziesig, R., et al., *TAPPI J.* 13(8): 81(2014).

ABOUT THE AUTHORS

Fume particles and deposits may cause severe fouling and plugging problems in recovery boilers and lead to expensive boiler shutdowns. We wanted to continue our research on fume formation and predict how changes in black liquor composition or elemental release factors affect fume behavior.

This work continues the research presented in our two earlier *TAPPI Journal* articles and a recent doctoral dissertation by Aino Leppänen. However, this paper describes an extensive sensitivity study performed with respect to a changing black liquor composition. When black liquor composition changes, the elemental release factors of different liquor components may change, but this effect is not well known. We decided to investigate the sensitivity of our modeling method to these factors.

It seems that the effect of sulfur released in the lower furnace has a significant effect on fume composition; thus, it should be known as accurately as possible. For example, a 25% underestimation in the sulfur release factor may result in a 40% overestimation in the molar ratio Cl/(Na+K) in the fume deposits.

Boiler manufacturers and mills can use the results of this study to predict the effect of some operational changes (e.g., black liquor composition) on fume formation. This study found that incorrect estimations of elemental release factors can cause difficulties in fume composition modeling. Therefore, as a next step, it is important to gain more information on the elemental release factors of liquor components in the lower furnace of a recovery boiler.

Leppänen

Välimäki

Leppänen is product engineer and Välimäki is manager at Valmet Technologies Inc., Tampere, Finland. Previously, Leppänen was a postdoctoral researcher at Tampere University of Technology, Tampere, Finland. Email Leppänen at aino.leppanen@valmet.com.