

# Effect of Kaolin and Limestone Addition on Slag Formation during Combustion of Wood Fuels

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Ash-related problems have more than occasionally been observed in wood-fuel-fired boilers and also recently in wood-pellet burners. These problems can lead to reduced accessibility of the combustion systems as well as bad publicity for the market. The objectives of the present work were, therefore, to determine the effects of kaolin and limestone addition on the slagging propensities of problematic and problem-free wood fuels during combustion in residential pellet appliances (burners), thus contributing to the understanding of the role of kaolin and limestone in preventing slagging on furnace grates. Pellets with additive-to-fuel ratios between 0 and 0.7 wt %<sub>d.s.</sub> were combusted in three different types of burner constructions (10 kW): over-, horizontal-, and under-feeding of the fuel. The collected slag deposits from the under-fed burner as well as the corresponding deposited fly ash in the boiler were characterized with X-ray diffraction (XRD) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The initial sintering temperatures of the formed slags were also determined. By adding limestone with an additive-to-fuel ratio of 0.5 wt %<sub>d.s.</sub> to the problematic stemwood raw material (Si-enriched probably because of contamination of sand/soil), the severe slagging of the fuel could totally be eliminated. Adding kaolin to the problematic raw material gave a minor decrease in slagging tendency of the problematic raw material and a major increase in slagging tendency of the problem-free stemwood raw material. When adding limestone to the problematic raw material, the composition of the formed slag was changed from relatively low temperature melting silicates to high temperature melting silicates and oxides. On the other hand, kaolin addition to the problematic raw material changed the content of the slag from mainly Ca–Mg silicates to be dominated by K–Al silicates which have relatively low melting points. When introducing kaolin to the problem-free raw material, the high temperature melting Ca–Mg oxides react to form lower temperature melting Ca–Al–K silicates. Chemical equilibrium model calculations were used to interpret the experimental findings, and generally good qualitative agreements between modeling and experimental results were obtained.

## 1. Introduction

During recent years, an increasing interest in sustainable energy production has been seen globally. A major contribution to this is expected to come from biomass, as it is a renewable and CO<sub>2</sub>-neutral energy source. New and upgraded biomass fuels (i.e., pellets, briquettes, and powder) have become more common, and especially fuel pellets have proved to be well-suited for the small-scale residential market. The raw materials presently used are in general stemwood-based residues from sawmills and the wood-working industry, such as sawdust, planer shavings, and dry chips. The potential establishment of a sustainable residential pellet market will be dependent on preferences such as economic consideration and the attitudes of households. Pellets for residential heating provide possibilities of more

automated and optimized operating systems, approaching the user-friendliness of oil firing and also resulting in higher combustion efficiencies and fewer products of incomplete combustion (PIC) compared to traditional wood log firing.

However, ash-related operational problems such as slagging on the grates have more than occasionally been observed in wood-fuel plants in general and especially in pellet-fired burners and furnaces during recent years. These problems can lead to a reduced accessibility of the combustion system as well as to bad publicity for the residential pellet market.

Results from previous work<sup>1</sup> have showed that the operation of pellet burners are relatively sensitive to variations in the total ash content and to variations of the ash-forming elements in the fuel and that differ-

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(1) Öhman, M.; Boman, C.; Hedman, H.; Nordin, A.; Boström, D. *Proceedings Of The First World Conference on Pellets*; Stockholm, Sweden, September 2–4, 2002; pp 213–219.

ences in ash composition and resulting sintering tendency occur among stemwood-based pellets classified as "first-class" pellets according to the Swedish standard SS 18 71 20. A previous study<sup>2</sup> has also established that the slagging tendency of wood-pellets produced at a certain plant could vary over the operational season and that the Si content in the wood-pellets correlates well to the sintering tendencies in the burners. Furthermore, the increased production of wood-pellets in Scandinavia could give rise to competition of the raw material which in the end could affect the slagging tendencies of the produced pellets when raw materials other than first-class (not contaminated) stemwood are used.

Several authors have previously proposed the use of various kinds of mineral additives, for example, clay minerals,<sup>3–6,8</sup> lime-, and/or dolomite-based additives<sup>3,7,8</sup> to combat ash-related operational problems during combustion of biomass fuels. In a comparative study between kaolinite, bauxite, and emaltheite, kaolinite (the major substance in kaolin) proved to be the most efficient mineral/additive.<sup>6</sup> Combustion experiments have also previously been conducted where kaolin has been mixed into straw with positive results.<sup>5</sup> The initial melting temperature was increased by 250 °C by adding kaolin in a proportion corresponding to 20 wt % of the fuel ash content of the straw. In another study, the ash fusion temperatures of the ash formed during combustion were effectively increased when kaolin and lime were mixed with peat before pelletizing.<sup>8</sup> However, no studies have previously been published where the effects of kaolin and/or limestone addition to problematic (slagging) wood fuels have been qualitatively and quantitatively determined, nor the mechanism of the indicated positive effects described.

The objectives of the present work were therefore (i) to determine the effects of kaolin and limestone addition on the slagging tendencies of problematic and problem-free wood fuels during combustion in small-scale appliances, and (ii) to contribute to the understanding of the role of kaolin and limestone in preventing slagging on furnace grates. In addition, chemical equilibrium model calculations were used to interpret the experimental findings.

## 2. Experimental Section

The methodologies employed in the present study were the following:

(1) Initial combustion test runs (24 h) with varying kaolin and limestone additions (0–0.7 wt %<sub>d.s.</sub>) for one problematic wood fuel in one type of burner (see section 2.2.1).

(2) Subsequent combustion test runs for all additive/fuel/burner combinations, using the optimal additive-to-fuel ratio from methodology (1) above (see section 2.2.2).

(3) Chemical and visual analysis as well as quantification of the specific sintering temperature of the collected deposits,

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(5) Wilén, C.; Staahlberg, P.; Sipilä, K.; Ahokas, J. *Energy Biomass Wastes* **1987**, 10, 469–484.

(6) Turn, S. Q., et al. *J. Inst. Energy* **1998**, 71, 163–177.

(7) Nordin, A.; Leven, P. *Thermal Engineering Research Foundation* 1997, Report No. 607.

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**Table 1. Main and Ash-Forming Elements (given as oxides) of the Used Raw Materials (milled pellets)**

	testing method	problematic	problem-free
C <sup>a</sup>	LECO-CHN1000	51.1	51.9
H <sup>a</sup>	LECO-CHN1000	6.0	6.0
O <sup>a</sup>	by difference	42.3	41.8
N <sup>a</sup>	LECO-CHN1000	0.14	0.12
S <sup>a</sup>	SS 18 71 77	0.0084	0.0049
Cl <sup>a</sup>	SS 18 71 54	<0.01	<0.01
ash content <sup>a</sup>	SS 18 71 71	0.76	0.30
SiO <sub>2</sub> <sup>a</sup>	ICP-AES	0.263	0.0215
Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	ICP-AES	0.0068	0.0051
CaO <sup>a</sup>	ICP-AES	0.121	0.104
Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	ICP-AES	0.0063	0.0033
K <sub>2</sub> O <sup>a</sup>	ICP-AES	0.0823	0.0469
MgO <sup>a</sup>	ICP-AES	0.0298	0.0204
MnO <sub>2</sub> <sup>a</sup>	ICP-AES	0.0205	0.0134
Na <sub>2</sub> O <sup>a</sup>	ICP-AES	0.0039	0.0022
P <sub>2</sub> O <sub>5</sub> <sup>a</sup>	ICP-AES	0.0291	0.0091

<sup>a</sup> Dry basis, wt %.

using a previously developed controlled fluidized bed agglomeration (CFBA) method<sup>9</sup> (see sections 2.3 and 2.4).

(4) Finally, results from chemical equilibrium model calculations of the above raw materials and processes were used to interpret the experimental findings and elucidate the reasons and mechanisms behind the positive results obtained (see section 2.5).

**2.1. Fuels, Additives, and Appliances.** Two different pellet raw materials; milled non-slagging and milled slagging wood-pellets produced from softwood sawdust, were used in the study. From now on the different milled pellet grades will be called problematic and problem-free raw material. The reason for also including a problem-free raw material was to check the effect of the used additives on the slagging behavior of the non-sintering raw material. The slagging tendency of the selected raw materials/pellets were evaluated both by combustion in an over-fed pellet burner and by comparison of the inorganic characteristics of the pellets with the inorganic characteristics of approximately 40 other non-slagging and slagging wood-pellets which previously have been compiled in a database.<sup>2</sup> In this way, the selected raw materials were classified as normal problem-free and relatively severely slagging wood-pellets, respectively. The characteristics of the two raw materials (fuels) are shown in Table 1. The ash content in the problematic raw material is relatively high (0.76 wt %<sub>d.s.</sub>) in comparison to the ash content in the problem-free fuel (0.30 wt %<sub>d.s.</sub>) The difference is due to a higher Si content in the problematic fuel (see Table 1). This is most probably an effect of contamination of the raw material during handling, storage, or drying because no additives except steam and water were used during pelletization.

Both pellets were first milled and then re-pelletized in a conventional pellet equipment having a production capacity of 500–800 kg/h. Water and diluted additive suspensions (slurries) were supplied via two nozzles in the conditioning step, i.e., before the raw material input to the pelletizer. The additives used were a crystalline calcium carbonate slurry (65 wt %<sub>d.s.</sub>) and a kaolin slurry (78 wt %<sub>d.s.</sub>). The main constituent of the kaolin used was the mineral kaolinite, Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, with a small amount of halloysite Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>. To facilitate a good performance of the nozzle injection system, to increase the total reactive surface of the added additives, and to increase the adhesiveness to the raw material during the pelletizing process, particles of 1–2 μm were used in preparation of the slurries of both additives. Pellets with different additive-to-fuel ratios for both the different additives and the different raw materials were produced. The different additive-to-fuel ratios were achieved by varying the dilution

(9) Öhman, M.; Nordin, A. *Energy Fuels* **1998**, 12, 90–94.

**Table 2. Fuel Characteristics of the Studied Pellets in the Three Different Burners<sup>a</sup>**

pellet quality	moisture content (% wet basis) [SS 18 71 70]	ash content (wt % <sub>d.s.</sub> ) [SS 18 71 71]	additive-to-fuel ratio (wt % <sub>d.s.</sub> ) [difference in ash content]	bulk-density (kg/m <sup>3</sup> loose) [weight of a 12.5 L bucket]	density (kg/m <sup>3</sup> solid) [dimensions and weight measured for calculation of density]	durability (percentage of fine fractions < 3 mm of total weight) [SS 18 71 80]
problematic	7.2	0.76 ± 0.05	0	670	1270	0.4
problem-free	7.0	0.30 ± 0.05	0	680	1280	0.6
problematic + kaolin	5.5	1.14 ± 0.06	0.4	740	1200	1.2
problematic + limestone	5.4	1.29 ± 0.02	0.5	710	1260	0.7
problem-free + kaolin	8.0	0.58 ± 0.02	0.3	710	1180	0.7
problem-free + limestone	7.5	0.81 ± 0.04	0.5	700	1190	0.7

<sup>a</sup> Testing method in brackets.

ratio of the original additive suspension. The achieved additive-to-fuel ratio in the different produced pellet grades were determined by standard ashing of the raw material and the produced pellet. The physical characteristics of the produced pellet grades corresponded well to normal full-scale produced wood-pellets. The different pellet grades were also produced under similar conditions (e.g., total water content added to the process, production capacity, raw material particle fraction) in order to minimize variation in physical characteristics between the different produced pellet grades.

The deposit-/slagging formation during combustion of the different pellet grades were studied in three different commercial pellet burners (10–15 kW) installed in a reference boiler presently used for the national certification tests of residential pellet burners in Sweden. The burners are commonly used on the European market and also represents three different classes of burner design; with over-, horizontal- and under-feeding of the fuel.

**2.2. Combustion Procedure.** *2.2.1. Effect of Additive-to-Fuel Ratio.* Pellets of the problematic raw material with additive-to-fuel ratios of 0 to 0.7 w %<sub>d.s.</sub> were initially combusted in the over-fed burner in order to evaluate the effect of different additive-to-fuel ratios on the slagging tendency. Every combustion test run lasted for about 1 day (24 h) at a nominal load of 12 kW (continuous feeding), corresponding to a total pellet amount of 60–70 kg for every experiment. However, severe slagging/ash deposition in some of the experiments resulted in an unscheduled shut down before 24 h. Temperatures at three positions located on and in the vicinity of the burner grate were measured with shielded type N thermocouples. Continuous measurements of O<sub>2</sub>, CO<sub>2</sub>, CO, NO, and organic-bound carbon (OGC) were also performed with conventional instruments in the exhaust gas directly after the boiler. The amounts of deposited ash and slag in the burner as well as the deposited fly ash in the boiler were quantified after every experiment and the products collected for analysis.

*2.2.2. Experiments with an "Optimal" Additive-to-Fuel Ratio.* With the results from the above combustion tests, the most beneficial additive-to-fuel ratios were selected for the two different additives according to decreased slagging/deposition tendency in relation to increased ash-content of the produced pellet. Pellets with the desired additive-to-fuel ratio of 0.5 wt %<sub>d.s.</sub> were further produced using both the problematic and the problem-free raw material. Thus, four different pellet grades were produced. These pellets were further used in combustion experiments in all different burners. Because of difficulties of obtaining exactly the same production capacity during pelletization of the different pellet qualities, the desired additive-to-fuel ratio could not be achieved in the case of kaolin. A final additive-to-fuel ratio of 0.4 and 0.3 wt %<sub>d.s.</sub> were in this case obtained in the pellets produced using the problematic and the problem-free raw material, respectively. The characteristics of the used pellet grades are shown in Table 2. The experimental procedures of the combustion tests were the same as those described in section 2.2.1.

**2.3. Chemical and Visual Analysis of the Collected Deposits.** Previous work has shown that the elemental

distributions in the slag samples produced during combustion of different woody biomass pellets, i.e., pellets produced from bark, stemwood, branches, and tops, vary significantly between samples from different fuels but not between different burners.<sup>1</sup> Therefore, only the collected slag deposits from the under-fed burner, as well as the corresponding deposited fly ash in the boiler, were characterized with X-ray diffraction (XRD) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). However, deposited samples which contained less than 5 g of inorganic material were not subjected to the ICP-AES analysis. The slag deposits were also classified in four categories by visual and microscopic inspection using the following criteria:

- Category 1, non sintered ash residue, i.e., nonfused ash;
- Category 2, partly sintered ash, i.e., particles contained clearly fused ash;
- Category 3, totally sintered ash, i.e., the deposited ash was fused to smaller blocks;
- Category 4, totally sintered ash, i.e., the deposited ash was completely fused to larger blocks.

**2.4. Sintering Tests of the Collected Deposits/Slag.** Slag samples, which exceeded a weight of approximately 40 g, were collected and subjected to a sintering test in a bench-scale fluidized bed furnace in which the critical sintering temperature could be determined in a controlled manner. The method has previously been more thoroughly described,<sup>1,9,10</sup> and only a brief description is given here. The bench-scale reactor (5 kW), is constructed from stainless steel, being 2 m high, 100 mm, and 200 mm in bed and freeboard diameters, respectively. To obtain isothermal conditions in the bed, and to minimize the significant influence of cold walls in such a small-scale unit, the reactor is equipped with electrical wall heating elements, equalizing the wall and bed temperatures. The experiments were performed in a sand bed (400 g) consisting of 98% quartz. The bed was loaded by 20 g of an ash sample under normal fluidized bed combustion conditions. Initial test runs showed that the sintering temperature was independent of the ash sample amount, ranging from 10 to 40 g. Before loading, the ashes were crushed and sieved to an even distribution between 100 and 500 μm in all cases, which has good fluidization properties. The excess oxygen concentration was controlled to 6%<sub>dry</sub> by mixing propane and air in a combustion chamber prior to the air distributor. The bed temperature was set to 760 °C. Thereafter, the bed temperature was increased at a rate of 3 °C/min by external heaters in a homogeneous and controlled way until sintering or the maximum temperature 1050 °C of the experimental setup was reached.

The onset of sintering was determined by monitoring differential pressures and temperatures in the bed. The detection of initial bed particle cohesion was facilitated by Principal Component Analysis (PCA)<sup>11</sup> considering all bed-related variables (3 temperatures and 3 differential pressures) simultaneously.

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**Table 3. Elements and Solution Models Used in the Chemical Equilibrium Model Calculations<sup>a</sup>**

elements	C, H, O, N, S, Cl, P, K, Na, Ca, Mg, Fe, Mn, Si, Al
solution models	
Slag:	Slag-liqA
Salt:	Salt-liqA
(Ca, Mg):	liq-K,Ca/CO <sub>3</sub> ,SO <sub>4</sub> (-LCSO) s-K,Ca/CO <sub>3</sub> ,SO <sub>4</sub> (-SCSO) s-Ca(SO <sub>4</sub> ),Mg(SO <sub>4</sub> ) (-SCMO) liq-Ca,Mg,Na/(SO <sub>4</sub> ) (-LSUL) s-Ca,Mg,Na/SO <sub>4</sub> (-SSUL)

<sup>a</sup> The designations of the solution models are taken from the software program FACT-Win 5.1.

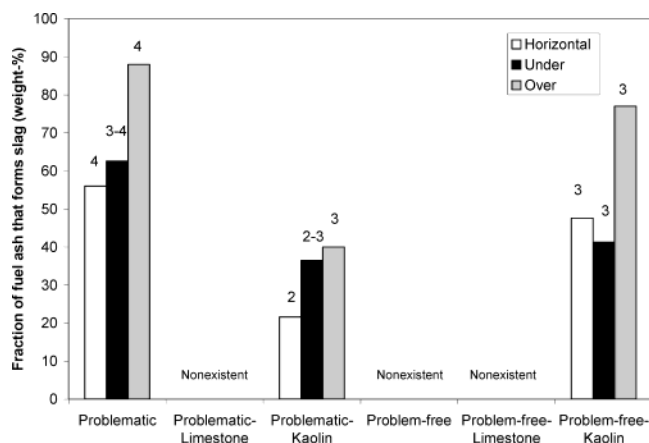
**2.5. Chemical Equilibrium Model Calculations.** To help to interpret the experimental findings, chemical equilibrium model calculations were performed using the software program FACT-Win 5.1. The program uses the method of minimization of the total Gibbs free energy of the system. Thermodynamic data were taken from the Fact-Win database<sup>12</sup> including all available stoichiometric data as well as the appropriate data and models for nonideal solid and liquid solutions. Two separate liquid phases were assumed, comprising the potentially coexisting oxide/silicate (slag) melt and alkali salt melt. In addition, all relevant binary solid and liquid solutions with Ca and Mg were included. The elements and solution models used in the calculations are shown in Table 3. Fuel compositions were used as given in Table 1. The calculations were performed using a global approach for atmospheric pressure (1 bar) and an air-to-fuel ratio ( $\lambda$ ) of 2.0 corresponding to the typical global oxidizing conditions present in the burners during operation. The calculations were carried out covering a temperature range of 800 °C to 1300 °C. From the calculations, the predicted amounts of melt and solid phases as functions of temperature could be extracted.

### 3. Results and Discussion

**3.1. Amount of Deposited Slag, Sintering-Degree, and Melting Behavior.** By continuous and extensive measurements during the experiments, the maximum combustion temperature in the region where the slag was formed (on the grate) was estimated to be about 1000–1050 °C in the over- and under-fed burner and to be about 1050–1100 °C in the horizontal-fed burner. These temperatures did not vary for the different fuels used.

**3.1.1. Effect of Additive-to-Fuel Ratio.** Due to severe slagging (melted ash) on the burner grate, the combustion experiment of problematic pellets without any additive was stopped due to a shutdown of the burner after 10 h operation. The formed slag was relatively hard, i.e., sintering degree 4 according to the classification scheme described in section 2.3. During this first experiment, almost all of the fuel ash was deposited as slag on the burner grate.

Limestone addition to the raw material/pellet had a distinct effect on the slag formation and thereby also on the operation of the burner. Less than 5 wt % of the fuel ash formed slag on the burner grate and no operational problems occurred during the experiment with a limestone addition corresponding to 0.5 wt %<sub>d.s.</sub>. The sintering degree of the formed deposit was low (sintering degree 1–2), and the initial sintering tem-



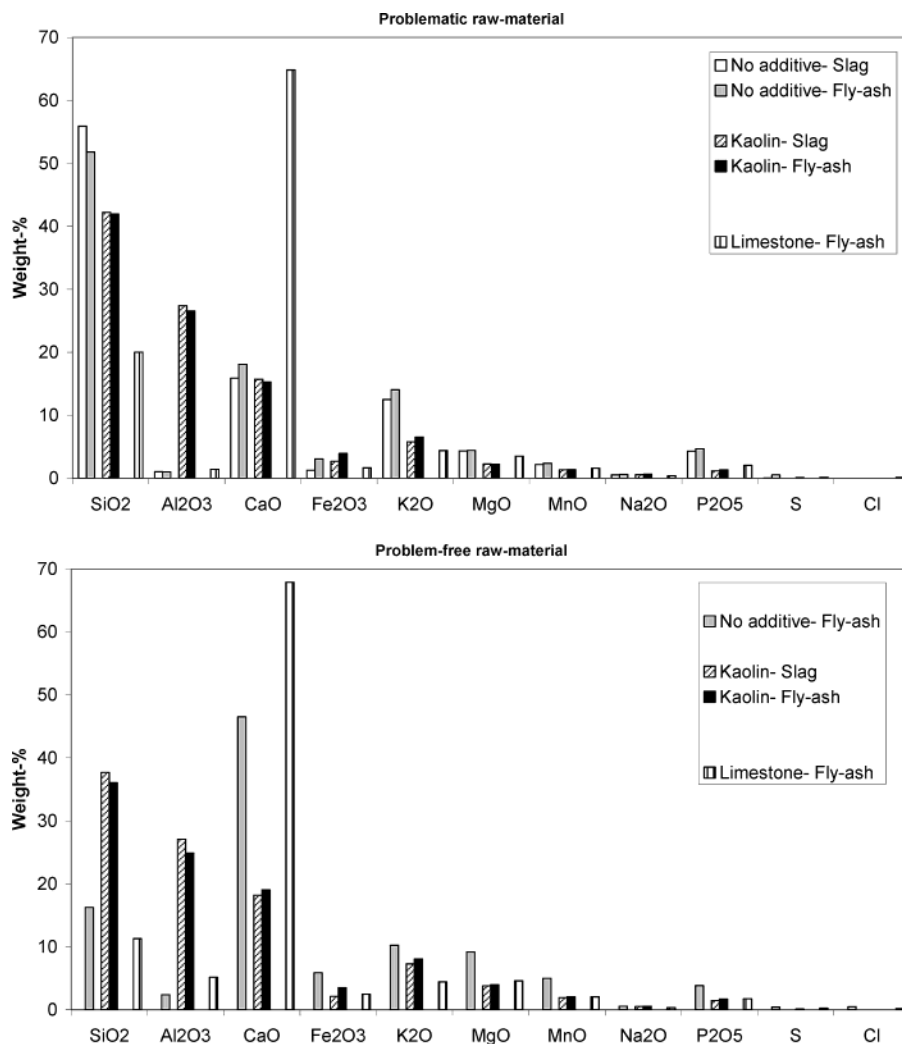
**Figure 1.** Fraction of fuel ash that forms slag (sintering category 2–4, specified above corresponding bar) for different fuels.

perature of the slag was found to be above 1050 °C. When using pellets with a lower additive-to-fuel ratio (<0.3 wt %), operational problems due to slagging were observed with an estimated sintering degree of class 3 and sintering temperature of 870 °C.

The kaolin addition also reduced the slag formation but not as efficient as the limestone addition. About 15 wt % of the fuel ash formed slag on the burner grate when pellets with a kaolin-to-fuel ratio corresponding to 0.7 wt-%<sub>d.s.</sub> was used. The sintering degree of the produced deposit was relatively low (sintering degree 2), and the initial sintering temperature of the formed slag was determined to be above 1050 °C. However, despite the low degree of sintering, this deposit was relatively dense and therefore effectively clogged the air distributor nozzles on the burner grate which gives rise to severe operational problems (burner shutdown). When using pellets with a lower additive content (<0.3 wt %), severe operational problems due to slagging occurred. For both additives, the amount of slag formed in the burner decreased with the additive content of the fuel.

**3.1.2. Combustion with "Optimal" Additive-to-Fuel Ratio.** As for the over-fed burner, the experiments using the under- and horizontal-fed burners with the problematic pellets without any additive resulted in a shutdown after 17–18 h operation due to slag formation. The effects on both slag formation and prevention of operational problems were, in general, similar in all burner types studied for the two studied additives, respectively. No slag formation was detected when using the limestone additive (additive-to-fuel ratio 0.5 wt %<sub>d.s.</sub>) and a decrease in both deposited amount as well as hardness and melt formation of the formed slag was observed when using kaolin as additive (additive-to-fuel ratio 0.4 wt %<sub>d.s.</sub>), see Figure 1. However, the experiments in all burners with kaolin as additive to the problematic pellets were interrupted due to burner shutdown after 12–13 h operation caused by deposit/slag formation on the grates. Further, kaolin, in contrast to dolomite, gives rise to deposit/slagging formation in the burners when the problem-free raw material was used, see Figure 1. The initial sintering temperatures of the formed slag were determined to be 920–940, 930–940, and 970–1000 °C, using the problematic pellet, the

(12) Bale, C. W.; Pelton, A. D. FACT-database of FACT-Win version 3.05, CRCT École Polytechnique de Montréal, Quebec, Canada, 1999.



**Figure 2.** Elemental distribution (given as oxides) of the formed slag and fly ash (bottom-ash) samples in the under-fed burner.

problematic pellet with kaolin addition, and the problem-free pellet with kaolin addition, respectively.

Most of the inorganic materials supplied as additive to the burner are found in the fly ash. This implies that approximately a doubled amount of fly ash must be handled when using additives-to-proposed ratios. However, the discussed additions of additive have not to any significant extent changed the physical characteristics of the fly ash in terms of ash disposal properties, i.e., bulk density and voidage. Ordinary ash-transport systems which commonly are used in ordinary combustion units (>50 kW) would therefore preferably be used.

### 3.2. Chemical Composition of the Formed Slag.

The results from the bulk elemental analysis (ICP-AES) of the slags and fly ashes formed in the under-fed burner are shown in Figure 2. The major elements in the slag from the pelletized problematic raw material were silicon, calcium, and potassium. When adding limestone to the different pelletized raw materials, no slag was formed; however, when adding kaolin to both the problematic and the problem-free raw material, slags rich in silicon, aluminum, calcium, and potassium was formed. The latter is also in agreement with the results presented in section 3.1.2 which showed a relatively uniform degree of sintering and initial sintering temperatures of the slags when kaolin were used in the different raw materials/pellets. Thus, the slags presum-

ably consist of different silicates. Magnesium, phosphorus, manganese, iron, and sodium were also found in all the slag samples but to a lower extent. Sulfur and chlorine were more or less totally depleted from the slag. Further, by comparing the results from the analyses of the slag with corresponding fly ash (see Figure 2), it can be seen that the distribution of the elements do not differ significantly. The enrichment of aluminum/silicon and calcium in the slag and corresponding fly ash (see Figure 2) originates, of course, from the kaolin and limestone additives, respectively.

The collected slag samples and the corresponding fly ash from the under-fed burner were further analyzed with XRD for identification of crystalline phases. The phases found in the slags and corresponding fly ashes are listed in Table 4. The following classifications have been used in describing the concentration of crystalline phases detected: dominant, >50%; sub-dominant, 20–50%; minor, 5–20%; trace, <5%.

The XRD analyses indicated a significant amorphous contribution, but also showed that the slag formed during combustion of the problematic pellet consisted mainly of the crystalline phases  $\text{SiO}_2$ ,  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ,  $\text{CaSiO}_3$ , and  $\text{Ca}_3(\text{PO}_4)_2$ . When limestone was added to the problematic pellet, more calcium-rich silicates were formed. Due to a surplus of limestone,  $\text{CaO}$  ( $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$ ) also appeared. All these systems have

**Table 4. Phases Identified in the Slag and Fly Ash<sup>a</sup>**

phase	problematic		problematic-limestone		problematic-kaolin		problem-free		problem-free-limestone		problem-free-kaolin	
	slag	fly ash	slag	fly ash	slag	fly ash	slag	fly ash	slag	fly ash	slag	fly ash
CaMgSi <sub>2</sub> O <sub>6</sub>		**										
Ca <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	**						**	*			***	
Ca <sub>3</sub> Mg(SiO <sub>4</sub> ) <sub>2</sub>							**	**	**	**	*	
CaSiO <sub>3</sub>	**											
Ca <sub>2</sub> SiO <sub>4</sub>			***	***			**	**		**		
KAlSiO <sub>4</sub>							**		*		***	**
KAlSi <sub>2</sub> O <sub>6</sub>					***	**						
CaAlSi <sub>2</sub> O <sub>8</sub>					****				**		***	
Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>		**				***		*			**	***
MgAl <sub>2</sub> Si <sub>3</sub> O <sub>10</sub>	*											
SiO <sub>2</sub>	***	***	*		**	***	*	*		*	*	***
CaO		**	**	***			**	***	***	***		
CaCO <sub>3</sub>		***	****	***			**	*	***	**		
Ca(OH) <sub>2</sub>			**					*	*	**		
MgO				**			**	**	**	*		
CaFeO <sub>2</sub>								***		***		
Al <sub>2</sub> O <sub>3</sub>						**		**				**
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	**											
Ca <sub>2</sub> P <sub>2</sub> O <sub>3</sub>												*
K <sub>3</sub> P <sub>3</sub> O <sub>9</sub>												*

<sup>a</sup> \*\*\*\*, dominant (>50 wt % of sample); \*\*\*, sub-dominant (20–50 wt % of sample); \*\*minor, (5–20 wt % of sample); \*, trace (<5 wt % of sample).

**Table 5. Phases Predicted to Form during Combustion in 1000 °C According to the Equilibrium Calculations<sup>a</sup>**

phase	problematic	problematic-limestone	problematic-kaolin	problem-free	problem-free-limestone	problem-free-kaolin
CaMgSi <sub>2</sub> O <sub>6</sub>	***					
CaSiO <sub>3</sub>	***					
Ca <sub>2</sub> SiO <sub>4</sub>		****		***	*	
KAlSi <sub>2</sub> O <sub>6</sub>			***			***
Ca <sub>3</sub> Fe <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	*					*
CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>			***			***
MgSiO <sub>3</sub>			**			
MgAl <sub>4</sub> Si <sub>5</sub> O <sub>18</sub>			*			
SiO <sub>2</sub>			***			
CaO		**		***	****	
MgO		**		***	*	
Mn <sub>3</sub> O <sub>4</sub>	*	*		*		
MgAl <sub>2</sub> O <sub>4</sub>						**
Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>		*		**	*	
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	***		**			
Ca <sub>5</sub> HO <sub>13</sub> P <sub>3</sub>		*		*		*

<sup>a</sup> \*\*\*\*, dominant (> 50 wt % of sample); \*\*\*, sub-dominant (20–50 wt % of sample); \*\*, minor (5–20 wt % of sample); \*trace (<5 wt % of sample).

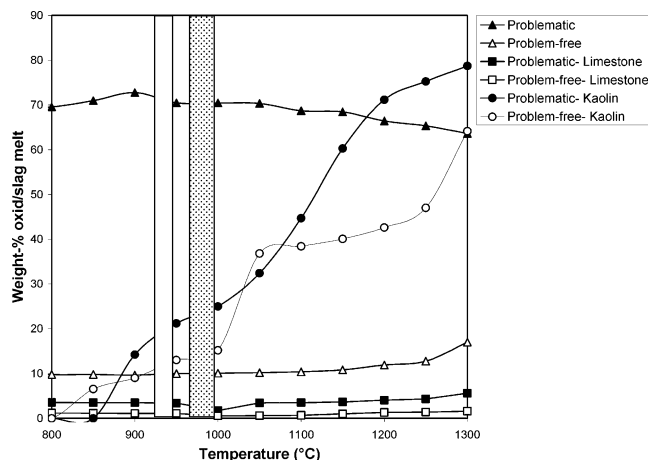
higher melting temperatures. The reason CaCO<sub>3</sub> and Ca(OH)<sub>2</sub> are detected in the sample is most probably an experimental artifact. When the combustion experiment is finished the slag is cooled to room temperature, and some of the CaO is transferred to CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>. Whitlockite (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>), which also was found, has a melting temperature above 1700 °C and therefore probably does not contribute to any sintering/slagging problems. Potassium which is detected in the elemental analysis is most probably completely included in the “glass-fraction”, and therefore no K-containing phase was detected by XRD. Thus, the effect of decreased slagging tendencies when using limestone as additive can be explained by changed melting behavior of the formed compounds within the system K<sub>2</sub>O–MgO–CaO–SiO<sub>2</sub>.

When adding kaolin to the problematic raw material, Ca–Al–K silicates are preferably formed instead of Ca–Mg silicates, see Table 4. The Ca–Al–K silicates have, in comparison to the species formed when adding limestone (e.g., CaO), lower melting temperatures and thus gives a higher fraction of melt in the actual

temperature interval (1000–1100 °C), i.e., more slag. The latter also agrees with the experience from the combustion experiments where the problematic pellets with limestone addition do not cause any problem whereas the problematic pellet with kaolin addition cause problems regarding slagging.

Also, when kaolin is introduced into the problem-free raw material, Ca–K–Al silicates are formed. These silicates have lower melting temperatures than the Ca–Mg oxides, the dominating phases formed during combustion of the pelletized problem-free raw material. This is also in agreement with the present combustion experiences.

It was also found that the identified phases in the fly ashes are roughly the same as the phases identified in the corresponding slag, see Table 4. The minor differences could be explained by the fact that the slags which are formed in the burner, in contrast to the fly ashes which are recovered in the boiler, have a longer residence time in the actual temperature and therefore form phases which are closer to their chemical equilibrium composition, see Table 5.



**Figure 3.** Predicted melting behavior of the oxide/silicate melt, expressed as wt % of the total amount of condensed phases, predicted from the equilibrium “global” calculations (lines). The gray and white rectangles represent the initial sintering temperature interval for the slag formed during combustion of problem-free pellet with kaolin (grey) and problematic pellets with and without kaolin (white), respectively.

### 3.3. Chemical Equilibrium Model Calculations.

The results from the equilibrium calculations showed that an oxide/silicate melt rich in silicon and potassium should be thermo-chemically expected to form in the temperature range 1000–1100 °C. On the basis of these calculations the amount of melt in relation to the total amount of produced condensed species could be evaluated. In Figure 3, the resulting fractions of melt (solid lines) versus temperature are shown. The experimentally determined initial sintering temperature corresponded well with the theoretical predictions where those indicated a significant increase of a fraction of melt (>20 wt %). Thus, both the theoretical and experimental results showed that melt formation of “sticky” silicates is responsible for the slagging. The results from the melt fraction calculation also showed that the fraction of melt decreased to a large extent when adding limestone and to a minor extent when adding kaolin to the problematic raw material. In addition, kaolin addition to the problem-free raw material gave a substantial increase of the fraction of melt in the actual temperature interval (1000–1100 °C). The latter also agrees well with the present experience from the combustion experiments.

The phases predicted to form in 1000 °C according to the equilibrium calculations are showed in Table 5. For

all experiments, there was a qualitative agreement between the theoretical predictions and the compounds found in XRD-analysis. When limestone was added to the problematic pellet, more calcium-rich silicates were formed and due to a surplus of limestone also CaO was formed. When kaolin was added to the problematic pellet, K–Al–Ca silicates were formed. In addition, the high temperature melting Ca–Mg oxides are transferred to more low-temperature melting Ca–Al–K silicates when kaolin is added to the problem-free raw material.

## 4. Conclusions

- By adding a limestone suspension (1–2  $\mu\text{m}$  particles in water) with an additive-to-fuel ratio of 0.5 wt %<sub>d.s.</sub>, via nozzles to the problematic stemwood raw material, the severe slagging tendency of the fuel could totally be eliminated. The reason for this was that the composition of the formed slag was changed from relatively low temperature melting silicates to more high temperature melting silicates and oxides.

- Adding a kaolin suspension to the problematic raw material resulted in a minor decrease in slagging tendency of the problematic raw material and a major increase in slagging tendency of the problem-free stemwood raw material.

- Further, kaolin addition to the problematic raw material eliminates the Ca–Mg silicates in favor of K–Al silicates which also have relatively low melting points.

- When introducing kaolin to the problem-free raw material the slagging tendency increased because high-temperature melting Ca–Mg oxides react to form more low-temperature melting Ca–Al–K silicates.

- Good agreements were generally obtained between chemical equilibrium results, the controlled sintering test results, and the actual slagging tendencies from the combustion tests in the burners.

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