

ASH CHEMISTRY AND SINTERING

Bengt-Johan Skrifvars, Rainer Backman, Mikko Hupa,
Åbo Akademi University, Combustion Chemistry Group
FIN-20520-Turku, Finland

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INTRODUCTION

The thermal behavior of a fuel ash is one important factor to consider when fireside slagging and fouling problems in steam boilers are addressed. It is well known that different types of chemical reactions and melts in deposits play an important role in the build-up of problematic fireside deposits.

Low viscous melts occur in steam boilers mainly when salt mixtures are present in the ash. Such are different mixtures of alkali and earth alkali sulfates, chlorides and carbonates. These mixtures do not melt at a certain temperature but form a melt in a temperature range which in some cases may be several hundreds of degrees. The amount of melt is crucial for the deposit build-up. For some boilers it has been found that roughly 10 - 20 weight-% melt in an ash mixture would be enough to cause extensive deposit formation, while 60 - 80 weight-% melt would already cause the ash to be so wet it would flow down a vertical tube and not cause any further deposit growth [1].

Another type of melt that causes deposits is the highly viscous silicate melt which occurs when silicon is present in the system. This type of melt causes mainly slagging problems in pulverised fuel fired boilers using coal or peat as fuel, but may occur also in fluidised bed boilers when quartz is used as the bed material. The silicate melts are problematic also because of their capability to form glassy phases which do not crystallize when the temperature decreases back below their first melting points. Viscous flow sintering of glassy silicate particles may cause extensive fouling. The amount of the formed melt and its viscosity are two important factors to consider when looking at viscous flow sintering, besides those parameters expressed in the Frenkel equation [2].

Also chemical reactions may cause hard deposits [3]. Calcium is one element which has been found very active in this sense. If it arrives in the oxide form to a surface it has been found to cause extensive deposit build-up if it reacts with $\text{SO}_2(\text{g})$ or $\text{CO}_2(\text{g})$ at the surface.

When studying these phenomena one has to take the chemistry into consideration since these above mentioned mechanisms are all strongly dependent on which elements you have present in the deposit, as which component and in which surrounding gas phase they are placed.

In this paper we present some initial thermal behavior predictions made for 10 different ashes which have been studied in a broader project. In this project both laboratory scale testing, as well as theoretical tools were used for establishing the thermal behavior of the ashes. In this paper we wanted especially to focus on the prediction of molten phases in the ash and compare these with sintering tests performed on the same ashes.

EXPERIMENTAL

10 different ashes were chosen for the tests. These are presented in Table 1.

The ashes were characterized in three different ways. Firstly, they were analysed quantitatively, secondly, they were sintering tested with a compression strength test and thirdly, they were analysed with a combined differential thermal - thermogravimetric analyser (DT/TGA). Details of these results are presented elsewhere [4].

The quantitative wet chemical analyses were re-calculated to components using stoichiometrical assumptions and thermodynamic considerations. The calculations assumed that all phosphour was present as calcium phosphate, carbonate as both potassium and calcium carbonate, rest calcium as oxide, all chlorine as potassium chloride, sulfur as both sodium and potassium sulfate, rest potassium as oxide and all silicon as quartz. Rest of analysed elements were assumed as their oxides and unanalysed elements (differences to 100% oxides) as unknown.

After this we calculated the melting behavior of the ashes using multi-component, multi-phase thermodynamic calculations and compared the results with the sintering test results we had achieved earlier in the study. In the melting behavior calculations we treated the ashes as if they would have consisted of four separate parts, one salt part consisting of the alkali sulfates, carbonates and chlorides (referred to as alkali salts in the further text), another silicate part consisting of the elements expressed as oxides, a third part consisting of calcium oxide and carbonate and a fourth part consisting of the phosphate and unknown elements.

Of these four parts, the silicates and salts were assumed to be those causing melt formation, while the calcium oxide/carbonate part would be active to react with flue gases and the inert part wouldn't affect deposit at all.

RESULTS

The results from the sintering tests are summarized in Figure 1. The results revealed significant differences in the sintering tendencies such as they were detected by the compression strength test. The temperatures at which the strength of the pellets started to increase varied from 625°C (ash #8) to above 1000°C (ash #7).

In Figure 2 the estimated amounts of different components present in the ash is shown. Focusing on the silicate and salt parts in the ash, one sees that the ashes #1 to 6 are fairly rich in silicates, while the ashes #7 to 10 are very rich in calcium oxide/carbonate with low amounts of silicates. The salt part varies significantly, from roughly 1% by weight for the ash #3 to 44% by weight for the ash #8.

Figure 3 summarises the results from the melting behavior calculations. The results are presented as the amount of melt, expressed as percentages by weight in the sample vs the temperature. The melting of the silicate part and salt part are treated and expressed separately in the figure. The calcium oxide/carbonate and the inert parts are added up to the total amount (100%).

Ash #1 reaches its first melting point, T_0 , already at 525°C. At this temperature a very small amount of alkali salt forms a melt which is approximately 1/10 of a percent of the total ash. The amount of melt stays low throughout the calculated temperature range. At 770°C the silicate part in the ash reaches its T_0 , forming immediately some 17% melt, causing the total amount of melt to increase to 19% melt in the ash. From here on the amount of melt increases very slowly with temperature to reach its maximum, 19% melt, at 1200°C. At this temperature the salt part contributes to the melt with only 3.5% by weight.

Ash #2 reaches its T_0 at 615°C. At this point the alkali salt part of the ash forms a small amount of melt. As the temperature increases to 750°C, the whole alkali salt part has become molten, the amount being 14% by weight. At 770°C the silicate part forms a 15% melt, the total amount being now 29% melt in the ash. From here on the silicate part continues to melt, ending up at 36% total melt in the ash at 1200°C.

Ash #3 forms a large amount of silicate melt at 770°C. At this point 35% of the ash is found in the molten phase. At 845°C the alkali salt part starts to contribute to the melt formation. At 895°C all the alkali salts have melted, the total amount of melt now being 55%. This amount increases still and reaches the maximum value of 65.6% melt in the ash at 1200°C.

Ash #4 forms an alkali salt melt at 625°C. At 770°C also the silicate part starts to melt, almost doubling the total amount of melt from 17% to 30%. The amount increases to about 33% at 810°C after which the increase slows down, however, still increasing the melt part to 40% which is reached at 1200°C.

Ash #5 forms also a first alkali salt melt at 625°C. The amount increases immediately to 15%. At 765°C the whole alkali salt part is molten, forming some 30% molten phase in the ash. At this same temperature the silicate part starts to melt, forming roughly 20% molten phase immediately. This increase the total amount of melt to 50% at this temperature. The amount increases still up to the maximum temperature 1200°C at which 57% of the ash has molten.

Ash #6 forms a very small amount of alkali salt melt already at 530°C. The amount stays very low (below 5%) throughout the calculated temperature range. At 780°C the silicate part starts to melt. The amount is up to some 1000°C low, but increases above 1000°C rapidly to reach its maximum of some 35% silicate melt at 1040°C. The total amount of melt is at this temperature 38% and does not exceed that number in the calculated temperature range.

The rest of the ashes, i.e. #7, 8, 9 and 10 form only alkali salt melts. Ash #7 has a T_0 of 575°C. The amount stays low to approximately 800°C and does not exceed the value of 20% in the whole calculation range. Ash #8 forms a first melt of roughly 20% at 615°C. The amount continues to increase until the temperature reaches the value of 760°C. At this point 45% of the ash is molten. After this the amount does not increase anymore. Ash #9 behaves somewhat like ash #7, i.e. a T_0 of 535°C with a low amount of melt formed, up to a temperature of roughly 750°C, where the amount starts to increase up to the maximum value of 25% which is reached at 810°C. Ash #10 forms a first melt at 870°C. At this temperature the alkali salt part melts almost completely and forms a 25% melt of the total ash.

DISCUSSION

Comparing the sintering tendencies for the ashes #2, 5, 6, and 8 with the melting behavior calculations one finds fairly good correlations between the T_{20} temperature, i.e. the temperature where 20% of the ash is molten and the sintering temperatures, T_{smt} . For the ash #2 the T_{smt} is between 700° and 750°C, the T_{20} is 770°C. For the ash #5 the T_{smt} is between 650° and 675°C, and the T_{20} is 700°C. For the ash #6 the T_{smt} is between 950° and 1050°C, and the T_{20} is 1025°C and for the ash #8 the T_{smt} is between 625° and 650°C, the T_{20} being 625°C. In all these cases the melt probably caused the strength increase in the ash pellets tested. In the case with ashes #2 and 6 it seems probable that it was the silicate melt that caused the sintering, while it for the ashes #5 and 8 seemed to be the alkali salt melt causing the sintering.

For the ash #3 the compression strength test indicates sintering to start at roughly 800°C. The melting behavior calculations suggest, however, a significant melt formation already at 770°C, i.e. the melt behavior calculations overpredict the sintering. The viscosity of the formed melt may explain the temperature difference found when comparing the T_{20} to the T_{smt} . If we assume that the formed melt had a high viscosity, the time for the sintering caused by that glassy phase would have been longer than that for a low viscous glassy phase, indicating that the sintering measurements were not done long enough. In these tests 4 hours were used as the standardized sintering time. No viscosity measurements were, however, done at this stage.

For the ash #1 the melting behavior calculations suggest a molten phase below 20% from 770°C throughout the calculated temperature range. Some sintering was detected beyond 900°C. Since most of the formed melt for the ash #1 throughout the calculated temperature range was a silicate melt the viscosity of that may again explain the sintering. No viscosity calculations were however done.

For the ashes #7, 9, and 10 the melting behavior calculations predict melts up to roughly 20% of the total ash from 800°C for the ash #9, 850°C for the ash #7, and 880°C for the ash #10. For the ashes #9 and 10 a fairly good correlation can be seen between the T_{20} and the T_{smt} but for the ash #7 the sintering temperature and the melting behavior calculation does not correlate at all. In this case no sintering was detected in the tested conditions. Obviously the component estimations presented in Fig. 2 fail in this case. The ash #7 contains fairly large amounts of analysed carbonate (expressed as CO_2 in Tab. 1). The melts predicted for this ash was all alkali salt melts, with potassium carbonate as the main component. If we assume that no potassium carbonate is present in the ash (all analysed CO_2 as calcium carbonate instead), the alkali salt part would decrease to 1/10 of its amount and hence, no large amount of melt could form.

For ash #4 the melt behavior calculations do not correlate well with the sintering measurements. The alkali salt part of the ash reaches its complete melting temperature T_{100} at 820°C, at which also most of the silicate melt to be formed is present. At this point roughly 35% of the ash should be molten. The sintering, detected by the compression strength test, does not, however, indicate any significant strength increase until 950°C. No clear explanation could be found for this behavior.

CONCLUSIONS

Silicate and salt melts may cause extensive deposit formation in steam boilers. The formation of these kind of melts can today be calculated with fairly acceptable accuracy, using multi-component, multi-phase thermodynamic equilibrium calculation. Good knowledge of which components are present in the ash and accurate thermodynamic data is, however, required.

Of ten ashes tested in laboratory conditions and predicted for their melting behavior, for six ashes the melt behavior calculations correlated well with the measured behavior. For the ashes #5, 8, 9, and 10 the alkali salts formed the major part of the melt while it for the ashes #2 and 6 seemed to be the silicate melt that caused the strength increase.

In two cases, for the ashes #1 and #3 the melt behavior calculations predicted a somewhat lower temperature for T_{20} than for T_{smt} . In these cases the calculations predicted a viscous silicate melt to be formed as the major phase. A possible cause for the higher T_{smt} may have been a high viscosity in the silicate melt, causing so slow sintering that the compression strength test didn't have time to detect it.

In the rest of the cases (two ashes) the melt prediction calculations seemed to fail to predict the sintering behavior detected by the compression strength test. A possible reason to this failure is errors in the assumed components used in the calculations.

REFERENCES

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Table 1. The ash analyses of the studied fuels, expressed as weight-% of their corresponding oxides.

#	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	CaO	MgO	Na ₂ O	K ₂ O	SO ₂	CO ₂	Cl
1	65.7	1.7	1.4	5.0	2.7	1.8	0.3	4.6	1.4	0.0	0.2
2	56.3	0.5	0.6	1.9	6.3	1.4	0.2	12.6	2.9	1.3	2.1
3	48.8	6.4	1.9	3.0	3.9	5.5	0.8	18.9	3.5	3.1	0.0
4	44.1	5.1	2.3	2.1	6.7	3.6	0.3	16.0	5.2	1.9	1.8
5	34.2	0.4	0.5	2.1	9.1	2.0	0.1	24.7	2.3	6.1	3.2
6	34.0	4.7	4.4	3.0	17.3	11.4	0.4	17.1	1.2	0.5	0.5
7	7.3	1.5	1.3	4.8	44.8	5.8	0.8	11.3	1.5	5.2	0.0
8	3.3	0.3	0.3	7.6	27.7	3.1	0.7	28.4	1.9	22.3	4.4
9	0.6	0.3	0.3	6.0	35.1	10.4	2.3	13.6	2.0	27.6	0.3
10	0.6	0.1	0.7	10.7	28.8	4.4	0.2	22.5	5.9	23.5	0.2

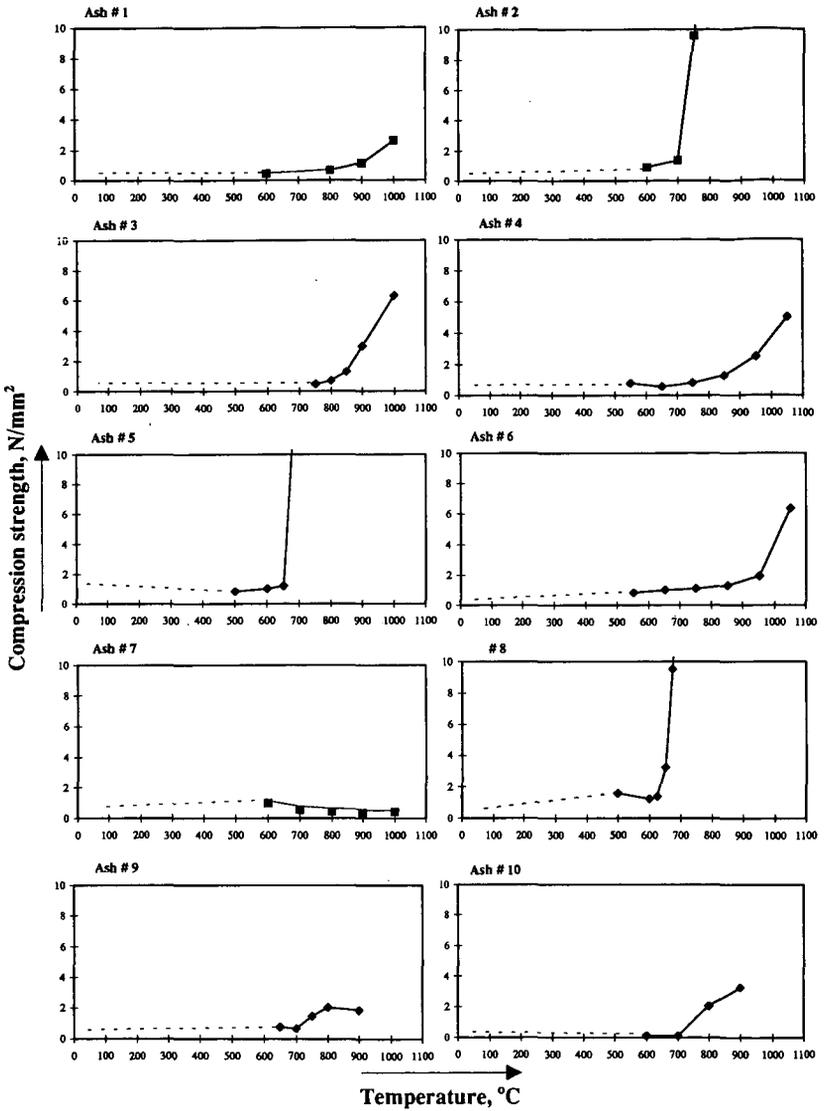


Figure 1. Sintering tendency for ten ashes, tested with the compression strength sintering test. 0-tests indicated in the left corner of each figure. Sintering time 4h, dry air atmosphere.

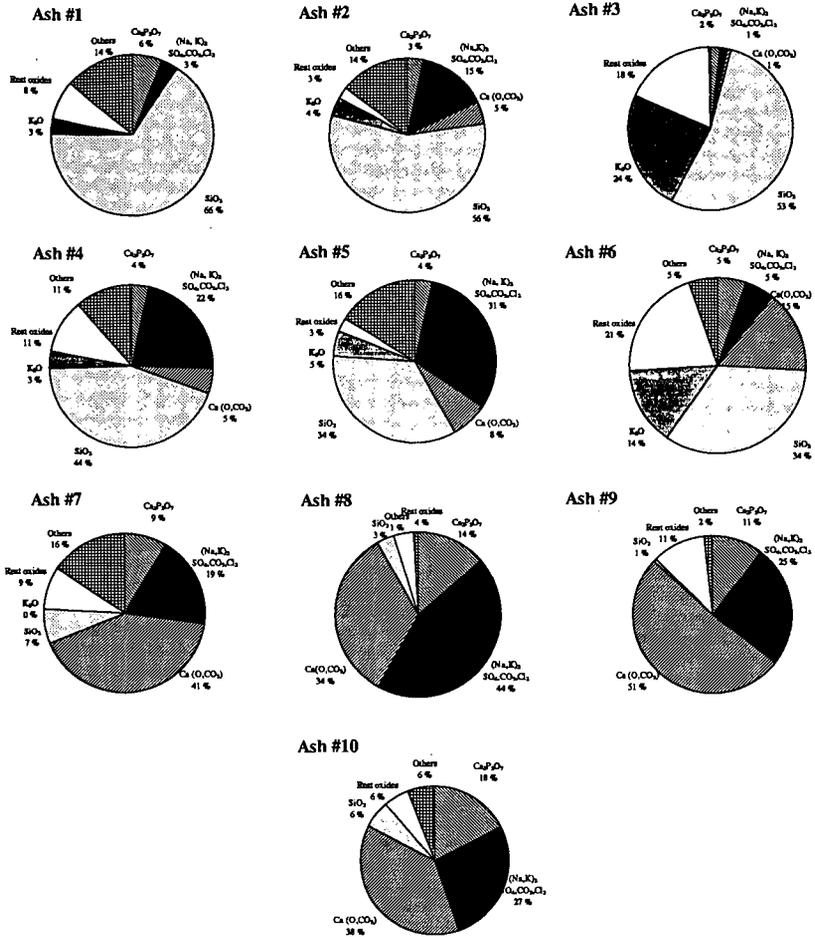


Figure 2. Stoichiometrically estimated amounts of different components (weight-%) present in the 10 ashes, presented in Table 1. The calculations assume that all phosphour is present as $\text{Ca}_3\text{P}_2\text{O}_8$, carbonate as both K_2CO_3 and CaCO_3 , rest calcium as CaO , all chlorine as KCl , sulfur as both Na_2SO_4 and K_2SO_4 , rest potassium as K_2O , all silicate as SiO_2 , rest analysed elements as oxides and un-analysed elements as others.

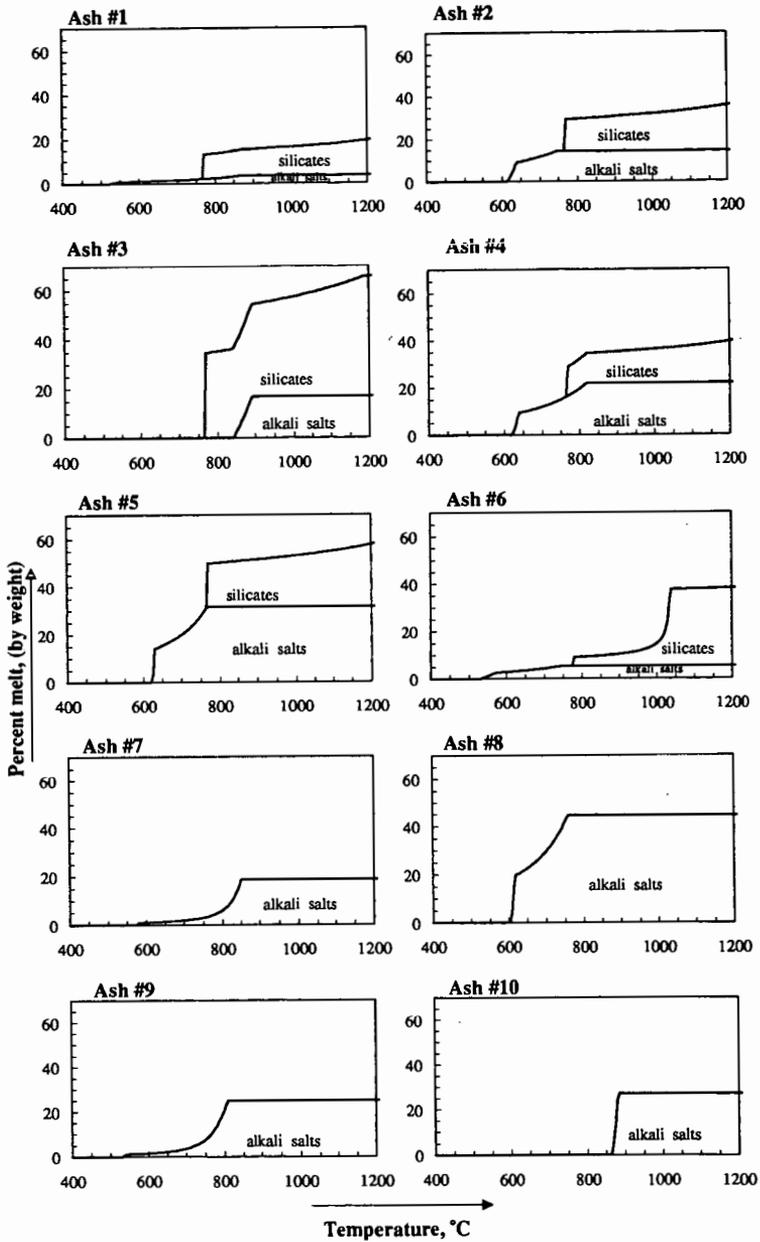


Figure 3. The melting behavior calculations, based on the components presented in Figure 2.