

THERMODYNAMIC AND KINETIC STUDY ON EMISSION CONTROL IN GLASS MELTING

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Abstract

Aggressive fluxes or gaseous species, that slip through flue gas filters, complicate the process control and maintenance of the complex filters behind industrial glass melting tanks. Partly due to a lack of accurate thermodynamic data and kinetic analyses of condensation phenomena, the process control is often based on experience. The two projects presented in this paper focus on condensation phenomena in Na-O-H-S and Na-O-H-B containing flue gases. It can be shown that the important phases in sulfur containing flue gas are Na₂SO₄, Na₂S₂O₇ and NaHSO₄. Aggressive fluxes form at low water partial pressures between 400°C and 250°C. In boron containing flue gas, the most important species are NaBO₂, condensing between 320°C and 160°C, and H₃BO₃, condensing at temperatures lower than 90°C. The kinetic experiments can be supported by thermodynamic calculations made with the help of Factsage®.

Keywords: Emission control, flue gas, condensate formation, boron emission

Introduction

In the glass industry, fossil fuels are used to melt glass at about 1400°C continuously. The fossil fuels combust with oxygen forming CO₂, H₂O and SO₂. Other emissions during glass melting occur due to flying batch particles and evaporation from the melt. As the laws for environmental protection are getting stricter, primary measures of emission control are no longer sufficient. Flue gas filters are used by many producers as an effective tool to reduce the emissions.

Species evaporating from glass melts are mostly alkali metals for soda-lime-silica

glasses and boron from boro-silica glasses. The evaporation process of boron and sodium species out of the glass melt was already studied by various researchers (Ehrig, 1978; Wenzel and Sanders, 1982; Conradt and Scholze, 1986; Beerkens, 2001). The following reactions (1-4) are of capital importance for sodium and boron evaporation.



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Sodium at the surface of the glass melt reacts with water in the atmosphere forming NaOH. With increasing amount of water in the atmosphere and sodium in the melt, the evaporation increases (CRCT Therm Fact Inc. & GTT Technologies, 2010).

Boron can either react with water in the atmosphere over the melt forming HBO_2 and H_3BO_3 or evaporate as NaBO_2 directly. The amount of evaporated boron from the melt is mainly influenced by the composition of the melt and the conditions in the atmosphere over the melt. The evaporation is enhanced with increasing amount of water in the atmosphere, especially when the ratio of the fractions of sodium and boron is $x_{\text{Na}_2\text{O}}/x_{\text{B}_2\text{O}_3} < 1$ (Wenzel and Sanders, 1982; Beerkens, 2001). Also, the evaporation of boron is increased with a glass melt composition close to the evaporating species of NBO_2 .

Notwithstanding the evaporation process was intensively studied, the occurrences during flue gas cleaning are not clarified yet. Although the flue gas filters are widely used, the process control is still mainly based on empirical data and experience. Problems due to aggressive fluxes, for example in case of sodium sulfates in the flue gas, and slip-through of gaseous boron species, cause a reduction in the life-time of filters and problems in reaching the demanded level of flue gas cleaning.

The aim of the presented projects is the clarification of thermodynamic and kinetic conditions in the Na-O-H-S and Na-O-H-B systems. This will help to detect and avoid the conditions enhancing the formation of aggressive fluxes. This paper will give a summary of the results found in the Na-O-H-S system by Neumann (Neumann *et al.*, 2011) and an introduction to primary results found in the Na-O-H-B system.

Materials and Methods

To clarify the thermodynamic behaviour of phases in the Na-O-H-S system, a DTA/TG (SETARAM SETSYS 18) with a supersonic coupled mass-spectrometer (MS) (BALZER) was used. The mass-spectrometer permits measurements up to 1024 amu (atomic mass unit). To investigate the thermal decomposition occurring in this system in a temperature range from 25°C up to 1000°C with different heating rates of 2 to 5 K/min, commercially available $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (Fluka) was used. The substance was analysed under different oxygen partial pressures (in air and He-atmospheres).

Samples of both the Na-O-H-S and Na-O-H-B systems, were analysed under kinetic conditions in a specially designed experimental setup, shown schematically in Figure 1. 20 mg glass in a platinum crucible was heated in a high temperature two-zone

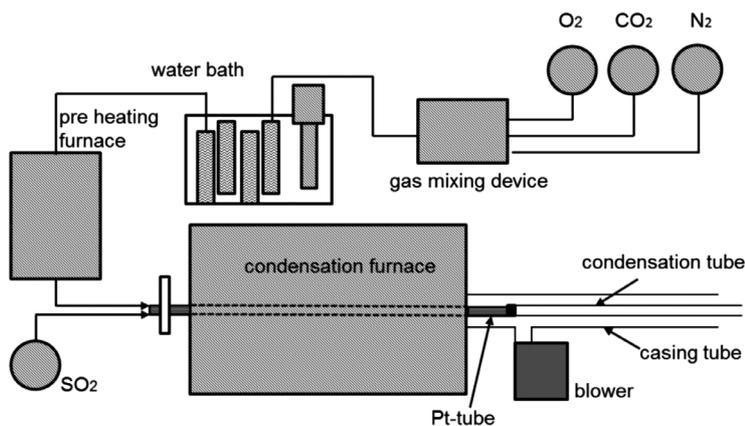


Figure 1. Schematic diagram of the experimental setup used to observe condensation dependent on the flue gas composition and temperature

platinum tubed furnace ($T_{\max} = 1650^{\circ}\text{C}$; ThermAix). With a gas mixing device (Flow SMS system by Bronkhorst) a synthetic flue gas composed of N_2 , O_2 , CO_2 and SO_2 was produced. Flowing through a water bath at defined temperatures, various partial pressures of H_2O can be regulated. In a pre-heating furnace, the gas was heated to a temperature close to the furnace temperature to assure that the conditions were close to those in industrial melting processes. The synthetic flue gas flows over the melt in the furnace taking evaporating substances with it. In the following condensation line, consisting of a double walled glass tube, a heat profile was created by a hot air blower, reaching from 40°C to 300°C . Various condensates form due to different temperature ranges and could be

observed directly along the line. The formed condensates were analysed by XRD measurements.

In this section, you are requested to reconsider the use of the Present tense. If this section aims to tell the experiment activities that you DID in the research, the use of Past tense is a better choice.

Results and Discussion

Sulfur Containing Flue Gas

The results of the DTA/TG + MS measurements of commercially available $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ in synthetic air and He-atmosphere up to a temperature of 1000°C are shown in Figure 2 and 3.

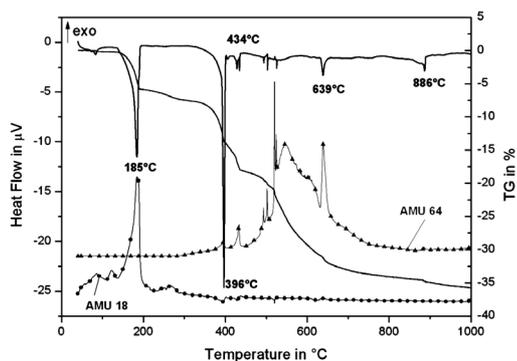


Figure 2. Result of the DTA/TG measurement of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ in He-atmosphere. AMU 18 (-○-) is the mass spectrometer signal of H_2O and AMU 64 (-▲-) the signal for SO_x . The sample was heated up to 1000°C with a heating rate of 5 K/min

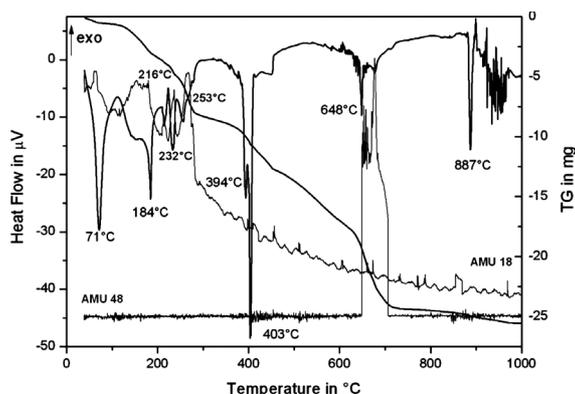


Figure 3. Result of the DTA/TG measurement of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ in synthetic air. AMU 18 is the mass spectrometer signal of H_2O and AMU 64 the signal for SO_x . The sample was heated up to 1000°C with a heating rate of 5 K/min

In Figure 2, the measurement under inert gas atmosphere, the dotted curve presents the amu 18 for H_2O ; the curve with the triangular symbols shows the amu 64 for SO_x . The endothermic peak and the peak of the amu 18 curve at a temperature of 185°C correlate to a complete loss of physically bonded water in the sample. The endothermic peak at 396°C shows the melting point of an eutectic phase consisting of 0.4% $\text{Na}_2\text{S}_2\text{O}_7$ and 0.1% Na_2SO_4 (in relation to the initial sample weight). Besides, the peak overlaps another one, which should be found at 403°C , corresponding to the melting point of sodium pyrosulfate ($\text{Na}_2\text{S}_2\text{O}_7$). At 886°C , the melting point of sodium sulfate (Na_2SO_4) can be detected. At temperatures over 400°C , the mass loss of SO_3 begins. Two smaller peaks at 434°C and 639°C , correlating with peaks in the amu 64 signal, represent the melting of different mixed phases between $\text{Na}_2\text{S}_2\text{O}_7$ and Na_2SO_4 .

As seen in Figure 3, the main reactions under synthetic air are identical with those under He-atmosphere. However, due to the different oxygen partial pressure, more different phases form, especially in the temperature range up to 400°C . Contrary to the measurement in He-atmosphere, the loss of physically bonded water is split to different

peaks. The aggregate state of the sample is changing several times from solid to liquid and back, forming different mixtures of NaHSO_4 and $\text{Na}_2\text{S}_2\text{O}_7$. At 184°C , a mixture of NaHSO_4 and 25% $\text{Na}_2\text{S}_2\text{O}_7$ melts. Again, the eutectic point at 394°C can be detected. The peak at 403°C indicates the melting point of $\text{Na}_2\text{S}_2\text{O}_7$. The mass loss of SO_3 is shifted to temperatures over 600°C .

The two thermograms indicate that the oxygen partial pressure has a great influence on the system. With increasing partial pressure, the decomposition point of sodium pyrosulfate is shifted from 300°C to 600°C . Several liquid mixed phases are formed between approximately 100°C and 400°C . The range, in which liquid phases occur, can easily be shown by comparing the mass loss of SO_3 between the measurement under synthetic air and He-atmosphere. The mass loss of SO_3 is used as an indicator for the reaction from NaHSO_4 to Na_2SO_4 and the different mixed phases that occur. Figure 4 shows the difference of the mass loss of SO_3 during heating under He-atmosphere and synthetic air. The grey marked region indicates the for the flue gas cleaning relevant range, in which liquid condensates can occur.

To verify the results, condensation was

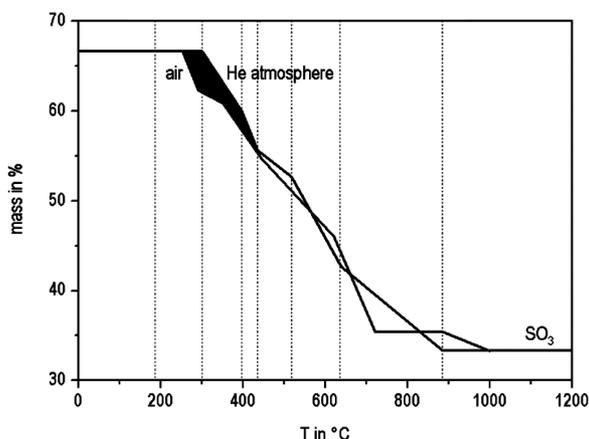


Figure 4. Comparison of the mass losses of SO_3 during the DTA/TG measurement in He-atmosphere and synthetic air showing the temperature range where the occurrence of liquid condensates is possible (marked in grey)

analyzed under various kinetic conditions in the specially designed furnace. Figure 5 shows an exemplary result of an experiment with 7.4% water and 2% oxygen in the synthetic flue gas. The liquid condensate, which formed during the experiment overall lasting for 50 h, crystallized at last.

The condensate between 400°C and 300°C was identified as Na_2SO_4 according to the XRD result; the condensate between 300°C and 250°C consists of $\text{Na}_2\text{S}_2\text{O}_7$ and the mixed phase $\text{Na}_3\text{H}(\text{SO}_4)_2$. The condensate at temperatures lower than 250°C was identified as NaHSO_4 and $\text{Na}_3\text{H}(\text{SO}_4)_2$.

The kinetic experiments show that liquid condensates occur in a temperature range between 400°C and 250°C dependent on the water and oxygen partial pressure. With decreasing water partial pressure (at relative humidity smaller than 13%), condensation of liquid phases occurred. At a relative humidity above 13%, no liquid condensates could be observed.

For more detailed information, please find the work published earlier by Neumann (Neumann *et al.*, 2011).

Boron Containing Flue Gas

To identify relevant phases occurring in

boron containing flue gas, thermodynamic calculations with Factsage® were made (CRCT Therm Fact Inc. and GTT Technologies, 2010). As mentioned earlier, various researchers have suggested that HBO_2 is the main species evaporating from boron containing glasses in sodium free, and NaBO_2 is the main evaporating species from sodium rich glasses. Hence, these phases were used as the foundation for the thermodynamic calculations. The composition of the synthetic flue gas used for the calculations should be similar to industrial conditions. Therefore, a composition of 18 mol-% O_2 , 3mol-% H_2O , 18 mol-% CO_2 and 60 mol-% N_2 was used. According to the gas flow in industrial filter systems, temperature ranges are seen from hot to cold temperatures in the following explanations.

Figure 6 shows the phases supposed to be stable in a system containing H_2O , O_2 , N_2 , CO_2 and 0.1 mol-% HBO_2 evaporating from the melt. According to the calculation, gaseous H_3BO_3 and $(\text{HBO}_2)_3$ are formed with decreasing temperature. Starting at temperatures around 200°C, solid HBO_2 forms.

With the addition of 0.1 mol-% NaBO_2 evaporating from the melt, the calculation suggests different phases. Figure 7 shows the predicted phases in a flue gas containing

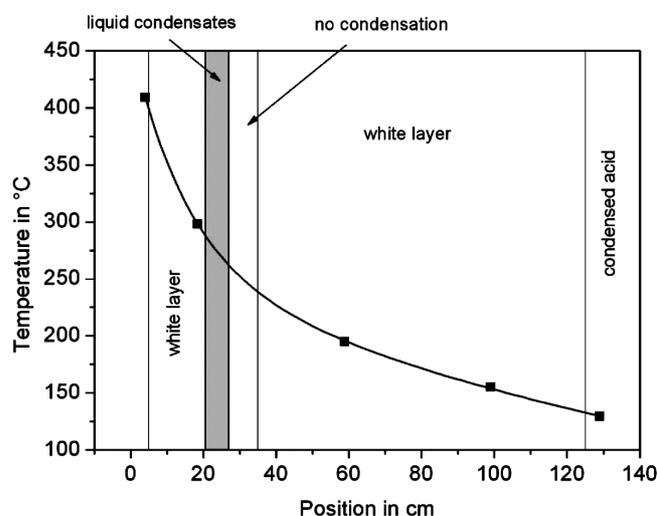


Figure 5. Temperature ranges of formed condensates dependent on their position in the condensation tube after 17 h runtime with 7.4 % H_2O , 79% N_2 , 16% CO_2 , 2% O_2 , and 0.2% SO_2

HBO_2 and NaBO_2 . According to the calculation, gaseous NaBO_2 changes to a solid phase around 1000°C . Solid NaBO_2 is stable between 1000°C to 180°C . At 180°C , a peak of gaseous H_3BO_3 can be found. In industrial processes, a sudden increase of gaseous species due to back-reactions of already precipitated filter dust can often be observed. The thermodynamic data suggest that gaseous H_3BO_3 is formed before solid HBO_2 forms at temperatures lower than 180°C .

For kinetic observations in the condensation furnace, two glass samples were chosen to verify the thermodynamic calculations. The experiments were performed using sodium free (6 mass-% B_2O_3) and sodium rich (2 mass-% B_2O_3 , 8 mass-% Na_2O) glass.

Figure 8 shows the temperature ranges of formed condensates using the sodium free glass. Between 320°C and 220°C , a light layer is formed. In a temperature range from 220°C to 90°C , no condensation occurs. At temperatures lower than 90°C , a thick layer forms.

In Figure 9, the condensates formed during an experiment with the sodium rich glass is shown. Over a wide temperature range from 320°C to 160°C , a thick layer

forms. Between 160°C and 90°C , no condensation occurs. At temperatures lower than 90°C , only light condensation can be observed.

The formed condensates were identified by XRD-measurements. For sodium free glasses, the condensate between 90°C and 80°C consists of H_3BO_3 . For sodium rich glasses, the condensates between 320°C and 160°C consist of NaBO_2 and $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. The condensates in the temperature ranges with only light condensation could not be analyzed for both glasses due to the small amount of formed condensates.

Gaseous species are stable over a wide temperature range. The results found in the kinetic experiment are comparable with the calculation results. It was shown that the thermodynamically predicted phases are found during the kinetic experiments. The calculations suggest that condensation is minimal between 250°C and 100°C for sodium rich melts due to formation of H_3BO_3 . For sodium free environments, gaseous H_3BO_3 and $(\text{HBO}_2)_3$ are stable until 200°C . However, a distinction also exists. At low temperatures, H_3BO_3 forms instead of HBO_2 by the calculation suggested. It probably reacts due to hydrophobic behavior. Possibly,

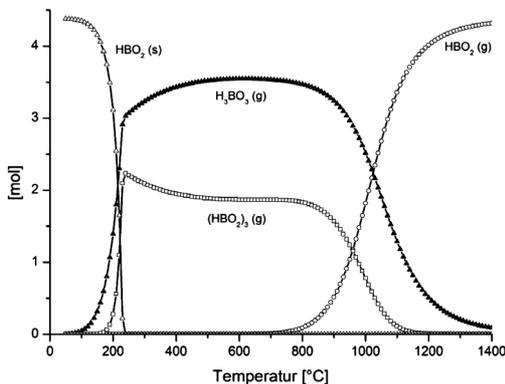


Figure 6. Calculated phases in a fuel gas containing 18 mol-% O_2 , 3 mol-% H_2O , 18 mol-% CO_2 and 60 mol-% N_2 and 0.1 mol-% HBO_2

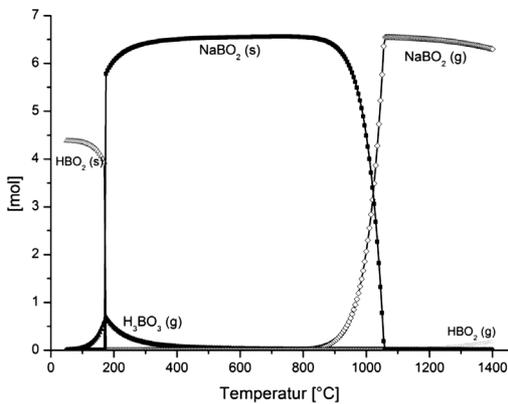


Figure 7. Calculated phases in a fuel gas containing 18 mol-% O_2 , 3 mol-% H_2O , 18 mol-% CO_2 60 mol-% N_2 , 0.1 mol-% HBO_2 and 0.1 mol-% NaBO_2

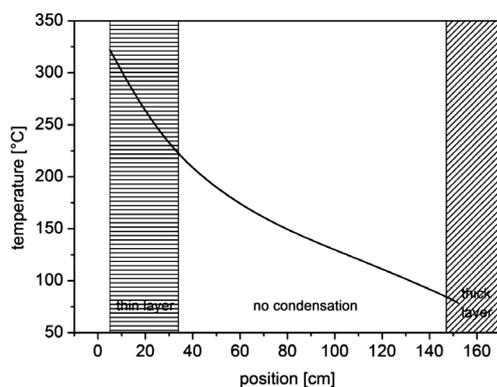


Figure 8. Temperature ranges of formed condensates using sodium free glass dependent on their position in the condensation tube after 24 h runtime with 19.9 % H₂O, 70 % N₂, 20 % CO₂, and 10 % O₂

the condensates in the low temperature region for sodium rich glass consist of H₃BO₃, while the condensate in a high temperature range for sodium free glass, due to traces of sodium inside, consists of NaBO₂.

Conclusions

The knowledge gained through combining thermodynamic calculations and kinetic experiments can assist to prevent conditions that enhance the formation of aggressive fluxes and help to understand occurrences in boron containing systems. The Na-O-H-S system is well analyzed; for boron containing flue gases more experiments will be made. Especially, the back-reaction of already precipitated filter dust will be analyzed in detail. Furthermore, thermodynamic and kinetics in a boron and sulfur containing flue gas are of great interest for industrial processes.

Acknowledgments

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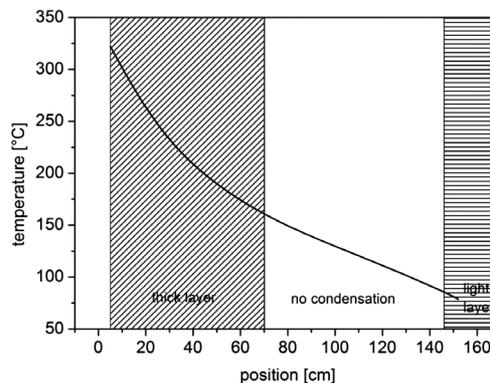


Figure 9. Temperature ranges of formed condensates using sodium rich glass dependent on their position in the condensation tube after 24 h runtime with 19.9% H₂O, 70% N₂, 20% CO₂, and 10% O₂

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