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Thermal behaviour of arsenic oxides (As_2O_5 and As_2O_3) and the influence of reducing agents (glucose and activated carbon)

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Abstract

In this paper the thermal behaviour of pure arsenic oxides (As_2O_5.aq and As_2O_3) and the influence of the presence of reducing agents (glucose or activated carbon) on the thermal behaviour of the arsenic oxides are studied through thermogravimetric (TG) analysis.

The TG experiments with pure As_2O_5.aq reveal that the reduction reaction $As_2O_5 \rightarrow As_2O_3 + O_2$ does not take place at temperatures lower than 500 °C. At higher temperatures decomposition is observed. Pure As_2O_3, however, is already released at temperatures as low as 200 °C. This release is driven by temperature dependent vapour pressures.

Comparing these results with earlier observations concerning the thermal behaviour of chromated copper arsenate (CCA) treated wood, suggests that wood, char and pyrolysis vapours form a reducing environment that influences the thermal behaviour of arsenic oxides. Therefore, the influence of the presence of reducing agents on the thermal behaviour of As_2O_5.aq is studied. First, TG experiments are carried out with mixtures of As_2O_5 and glucose. The TG and DTG curves of the mixture are not a simple superposition of the curves of the two pure constituents. The interaction between As_2O_5.aq and glucose results in a faster decomposition of arsenic pentoxide. This effect is more pronounced if the purge gas nitrogen is mixed with oxygen. Second, TG experiments are performed with mixtures of As_2O_5 and activated carbon. The presence of activated carbon also promotes the volatilisation of arsenic for temperatures higher than 300 °C, probably through its reducing action.

Extrapolation of the thermal behaviour of these model compounds to the real situation of pyrolysis of CCA treated wood confirms the statement that the reduction of pentavalent arsenic to trivalent arsenic is favoured by the reducing environment, created by the presence of wood, char and pyrolysis vapours.

Keywords: Arsenic oxides; Thermogravimetric analysis; Glucose; Activated carbon; Release

1. Introduction

A study has been set up by the authors to design a low-temperature pyrolysis facility for chromated copper arsenate (CCA) treated wood waste such that the major part of the metals are contained in a concentrated solid product stream, and the pyrolysis gases are used to their maximum potential with respect to energy recuperation [1,2].

A set of experimental and theoretical studies has been carried out by the authors in order to gain more insight in the metal (Cr, Cu and As) behaviour during the pyrolysis process [3–11]. Since arsenic is identified as the problem compound with respect to metal release during pyrolysis, the aim is to identify the mechanism of arsenic release. Knowledge of this mechanism may help to control and prevent arsenic release. However, the current literature [12–16] clearly shows that the mechanism of metal, and in particular arsenic, volatilisation during the thermal decomposition of CCA treated wood is not yet completely understood. Sandelin and Backman [17] studied the equilibrium chemistry involved when CCA treated wood is burned. The high temperature chemistry of burning impregnated wood was studied by utilising an equilibrium model based upon minimising the Gibbs free energy of a hypothetical combustion system. They revealed that partial pressures of arsenic-containing compounds dominate in the temperature range from 500 to 1600 °C.

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At temperatures between 500 and 1150 °C, As_4O_6(g) is the dominating species, but at higher temperatures AsO(g) takes over. The following explanation was given: arsenic pentoxide is stable at low temperatures but "forms" gaseous As_4O_6 at about 580 °C. They concluded that chromium and copper in impregnated wood are unlikely to volatilise at common combustion temperatures. At 1200 °C only 0.05% of the total chromium and 0.51% of the copper was found in the gas phase. Arsenic was more volatile, existing 86.89% in the gas phase at the same temperature. Supplementary calculations showed that magnesium, copper and chromium compounds may prevent arsenic from volatilising. In addition, reducing conditions within the char particle may affect the tendency of the metals to vaporise. Conclusions with respect to low-temperature chemistry were not given.

In order to gain more insight in the volatilisation mechanism of arsenic during pyrolysis of CCA treated wood, the thermal behaviour of arsenic model compounds (arsenic oxides) is studied through thermogravimetric (TG) analysis. TG experiments are performed with arsenic pentoxide and arsenic trioxide, but also with mixtures of arsenic pentoxide and glucose or activated carbon, in order to study the influence of a reducing environment on the thermal behaviour of arsenic pentoxide. TG experiments are carried out in both a nitrogen atmosphere and a mixed nitrogen–oxygen atmosphere.

This paper is organised as follows. In the first section a summary of a literature review with respect to the thermal behaviour of arsenic pentoxide and arsenic trioxide is given. In Section 3 the materials and methods are described. Then, the results of the three parts (1) thermal behaviour of arsenic oxides, (2) influence of the presence of glucose and (3) influence of the presence of activated carbon, are presented and discussed and finally, the most important conclusions are summarised.

2. Literature review: thermal behaviour of arsenic oxides

2.1. Arsenic pentoxide

In the current literature the decomposition temperature of As_2O_5 is not clearly defined. An overview of the different data with respect to As_2O_5 decomposition and/or evaporation is presented in Table 1. The decomposition temperature could be defined as the temperature at which traces of O_2 and/or As_2O_3 are released. Another definition could be the temperature at which the total pressure of arsenic sesquioxide (As_4O_6) and oxygen reaches 1 atm.

Furthermore, evaporation processes of As_2O_5 are described in the literature [18,25,26] in different ways. Data are found for the dissociative evaporation of As_2O_5, according to the reaction:

$$2As_2O_5(s) \rightarrow As_4O_6(g) + 2O_2(g) \qquad (1)$$

Table 1
Overview of literature data with respect to As_2O_5 decomposition and/or evaporation

As_2O_5 decomposition and/or evaporation	Source
$T_{decomposition} = 327\,°C$	[18–21]
$T_{decomposition} = 315\,°C$	[20,22,23]
As_2O_5 existence until 435–450 °C	[24]
As_2O_5 existence until 400 °C	[24]
At 193 °C: $2As_2O_5{\cdot}3H_2O \rightarrow 2As_2O_5 + 3H_2O$ At 246 °C: $As_2O_5 \rightarrow As_2O_3 + O_2$	[24]
$T < 400\,°C$: no decomposition of As_2O_5 in air or in vacuo	[24]
$T_{decomposition} = 740–750\,°C$	[25]

as well as for the non-dissociative evaporation of As_2O_5, according to the reaction:

$$2As_2O_5(s) \rightarrow As_4O_{10}(g) \qquad (2)$$

followed by dissociation in the gas phase, according to

$$As_4O_{(10-y)}(g) \rightarrow As_4O_{(9-y)}(g) + 0.5O_2(g) \qquad (3)$$

A correlation for the dissociation pressure of arsenic pentoxide in the temperature range of 537–740 °C is presented by Polukarov et al. [25]. The dissociation pressure of arsenic pentoxide can be calculated in the temperature range of 20–327 °C using thermodynamic data published by Barin [18]. Barten and Cordfunke [26] described the non-dissociative evaporation reaction and derived a correlation to calculate the arsenic oxide vapour pressure in the temperature range 592–736 °C. The available data show a gap for the temperature range between 327 and 573 °C.

2.2. Arsenic trioxide

In the current literature no consistent data exist with regard to the existence of either a melting and boiling point, or a sublimation point for As_2O_3. Table 2 gives an overview of the different values found in the literature. Arsenolite and claudetite are two naturally occurring arsenic trioxides (As_2O_3 or As_4O_6); arsenolite is allotropically transformed to claudetite at −33 °C [18]. For As_2O_3 vapour pressure data have been determined experimentally or are calculated from equilibrium data (equilibrium solid or liquid–vapour), according to the reaction:

$$2As_2O_3(s\,\text{or}\,l) \rightarrow As_4O_6(g) \qquad (4)$$

In Fig. 1 [27] vapour pressures corresponding to five different sources are plotted [18,22,28–30]. The values of the

Table 2
Melting temperature (T_m), boiling temperature (T_b) and sublimation temperature (T_s) of arsenic trioxide (As_2O_3 or As_4O_6) at atmospheric pressure

	T_m (°C)	T_b (°C)	T_s (°C)
As_2O_3	312.8 [28], 315 [22]	457.2 [28]	
Arsenolite	278 [18]		193 [22]
Claudetite	193 [22], 312 [18]	457.2 [22], 459 [18]	315 [22]

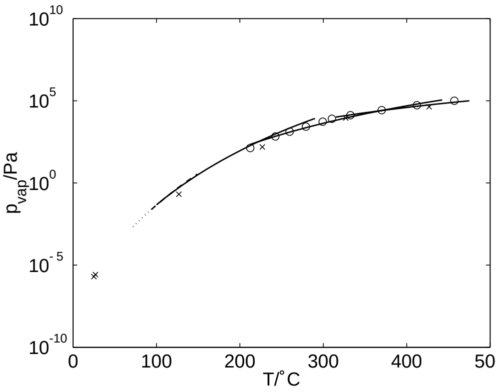

Fig. 1. Arsenic trioxide vapour pressure as a function of temperature according to different sources: solid line for The Chemical Rubber Co. [22], dotted line for Murray and Pottie [29], dashed line for Behrens and Rosenblatt [30], crosses for Barin [18] and circles for Perry and Chilton [28].

different sources are in good agreement. It can be concluded that the arsenic trioxide vapour pressure is well known in the temperature range between 20 and 457 °C.

3. Experimental

3.1. Samples

3.1.1. Arsenic oxides

Arsenic pentoxide hydrate (As_2O_5.aq, aq being 2 up to 3 mol H_2O) from purum quality was purchased from Fluka Chemika. XRD analysis shows that the arsenic pentoxide hydrate corresponds to the molecular formula $3As_2O_5{\cdot}5H_2O$ (*23-1112). XRD analysis had to be performed very fast due to the hygroscopic nature of the compound. Arsenic trioxide (As_2O_3) from pro analysis quality was purchased from Riedel–de Haen. The XRD spectrum of the arsenic trioxide compound corresponds very well to the spectrum of arsenolite (*36-1490) (As_2O_3). Both arsenic pentoxide and arsenic trioxide are white powders (grain size not specified).

3.1.2. Glucose

Anhydrous D(+)-glucose ($C_6H_{12}O_6$) from puriss quality was purchased from Fluka Chemika. The XRD spectrum of anhydrous D(+)-glucose agrees with its reference (*24-1964) and does not show extra crystalline phases. Glucose is a white sugar-like powder.

3.1.3. Activated charcoal

Activated charcoal (C) powder from spruce wood with puriss quality was purchased from Fluka Chemika. The XRD spectrum of activated carbon resembles the spectrum of pure carbon (*26-1080). The activated charcoal is a black powder with 30% of the particles being larger than 50 μm and 5% of the particles being larger than 150 μm.

3.1.4. Mixtures

TG experiments were performed with mixtures of As_2O_5.aq and glucose and of As_2O_5.aq and activated charcoal. Since As_2O_5.aq is hygroscopic the preparation of the mixtures had to be performed in a controlled atmosphere, being either a balance purged with dry air or an inert (N_2) chamber containing a balance. The mixtures were prepared by adding the reducing agent to the arsenic oxide and stirring the mixture with a small metal spoon. The mixtures had an As_2O_5.aq/glucose ratio or an As_2O_5.aq/activated carbon ratio of 1.162. It is assumed that the mixtures were perfectly mixed, which will be nearly the case for the As_2O_5.aq–activated charcoal mixture, but maybe less for the As_2O_5.aq–glucose mixture.

3.2. Thermogravimetric analysis

TG experiments were carried out using a TA Instruments TGA 951-2000. To analyse the gas stream, resulting from the decomposition of the sample, the TG apparatus was on-line coupled to a mass spectrometer (MS, FISONS Instruments, Thermolab) which is able to measure components up to mass 300. In this study the sample, approximately 30 mg in weight, was introduced into a quartz sample pan and heated to a preset temperature following a preset temperature profile using nitrogen (to have an inert atmosphere) or dry air as purge gas. Only when gas analysis was carried out, helium was used as purge gas. In order to ensure inert working conditions, the TG apparatus has been modified as described elsewhere [32]. Moreover, the installation was flushed with nitrogen for 1 h (in the case of coupled TG–MS experiments for 2 h) before starting the temperature rise. The apparatus provides for the continuous measurement of sample weight as a function of temperature and provision is made for an electronic differentiation of the weight signal to give the rate of weight loss.

Since TG experiments were performed with arsenic oxides, a sampling train for arsenic was coupled to the outlet of the TG apparatus in order to prevent the release of arsenic in the laboratory room. The sampling train consists of a cooling tube, a filter section containing an alkali impregnated cellulose ester membrane filter with backup pad and an impinger containing 50 ml NaOH 0.1 N. In order to have a substantial bubbling in the impinger, a higher purge gas flow rate (257 ml/min) was used in these TG experiments. Coupled TG–MS experiments were performed with a helium flow rate of 70 ml/min. Experiments with this sampling train have shown that no arsenic breakthrough occurs through this sampling train [10].

For the mixture of As_2O_5.aq and glucose a high resolution thermogravimetric experiment (using TA Instruments HiRes 2950 TGA) was carried out. The sample, approximately 6.7 mg in weight, was introduced into a platinum sample pan and heated to 800 °C applying a downward flow of helium (100 ml/min) to keep the volatiles away from the electronics and a horizontal purge flow of nitrogen

(257 ml/min). Characteristic to HR-TG experiments is that the heating rate is not specified in advance but automatically adjusted to the rate of weight loss. As long as a mass reduction is recorded, the temperature is kept nearly constant (very small heating rate dependent on the value preset for the resolution). As soon as the sample weight remains constant heating of the sample is allowed to progress faster.

3.3. Experimental programme

First, TG experiments were carried out with the pure arsenic oxides: As_2O_5.aq and As_2O_3. For As_2O_5.aq a TG–MS experiment was also performed in order to examine whether oxygen was released.

Second, the influence of the presence of glucose on the thermal behaviour of As_2O_5.aq was studied. Therefore, a comparison was made between TG curves obtained for pure As_2O_5.aq, pure glucose and a mixture of As_2O_5.aq and glucose. Furthermore, TG experiments with mixtures of As_2O_5.aq and glucose were performed in a nitrogen atmosphere and mixed nitrogen–oxygen atmospheres containing 5 or 10% oxygen to examine the influence of the presence of oxygen. A HR-TG experiment was also carried out with a mixture of As_2O_5.aq and glucose in a nitrogen atmosphere.

Third, the influence of the presence of activated charcoal on the thermal behaviour of As_2O_5.aq was studied in a nitrogen atmosphere.

4. Results and discussion

4.1. Thermal behaviour of arsenic oxides [27]

4.1.1. Arsenic pentoxide

TG analysis of arsenic pentoxide (As_2O_5.aq) results in the TG curve, DTG curve and MS spectra presented in Fig. 2. The sample was heated to 500 °C with an isothermal part of 10 min at 220 °C in a helium atmosphere. The outlet of the TG apparatus was coupled to the mass spectrometer (MS) for gas analysis.

The TG curve in Fig. 2 shows that the total mass loss at 500 °C is less than 12%. Furthermore, comparison of the DTG curve and the MS spectra reveals that both DTG peaks (at 231 °C and at 348 °C) coincide with the MS peaks for H_2O. The mass loss of almost 12% can thus be attributed to the release of H_2O ($3As_2O_5{\cdot}5H_2O$ contains 1.67 mol of H_2O per mol of As_2O_5, corresponding to 11.5% H_2O). For O_2, on the other hand, an MS peak is not visible. It can thus be concluded that no O_2 is released at temperatures

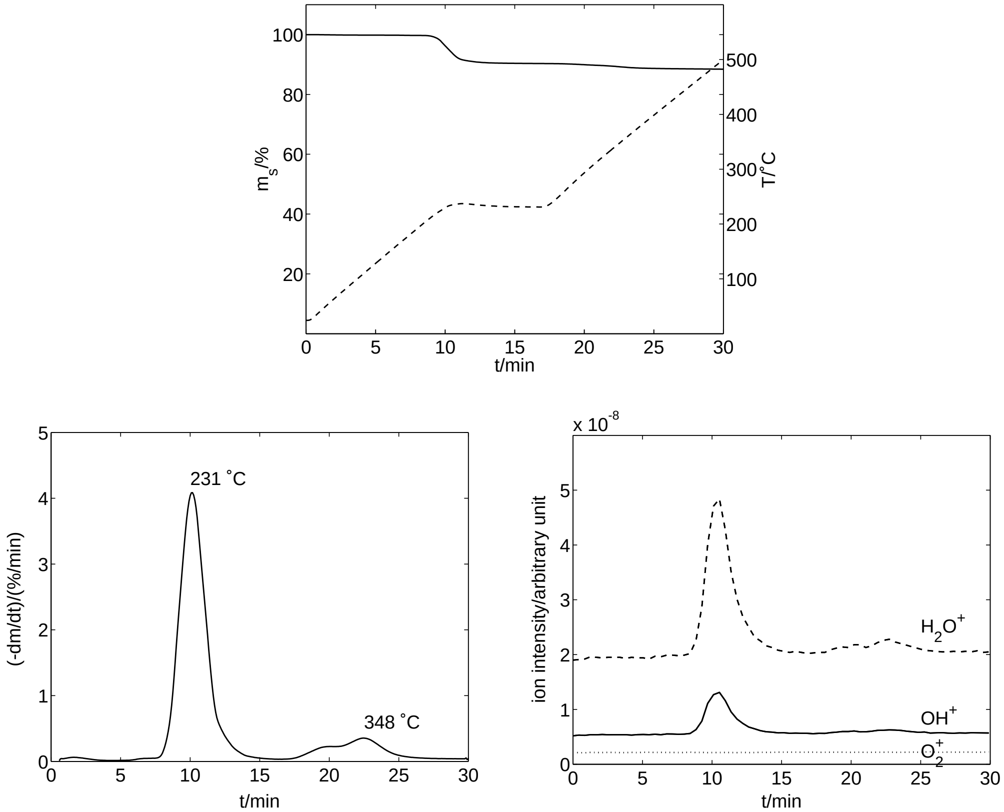

Fig. 2. Thermal behaviour of arsenic pentoxide (As_2O_5.aq) in helium atmosphere (temperature profile: heating at 20 °C/min to 500 °C with an isothermal part for 10 min at 220 °C): (a) TG curve (solid line) and temperature profile (dashed line); (b) DTG curve; (c) MS spectra for OH^+ ($m/z = 17$, solid line), H_2O^+ ($m/z = 18$, dashed line), $O_2{}^+$ ($m/z = 32$, dotted line).

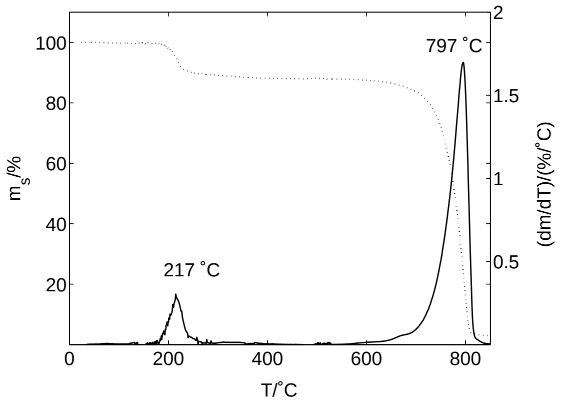

Fig. 3. Thermal behaviour (dotted line for TG curve and solid line for DTG curve) of arsenic pentoxide (As_2O_5.aq) in nitrogen atmosphere (temperature profile: heating at 10 °C/min to 850 °C).

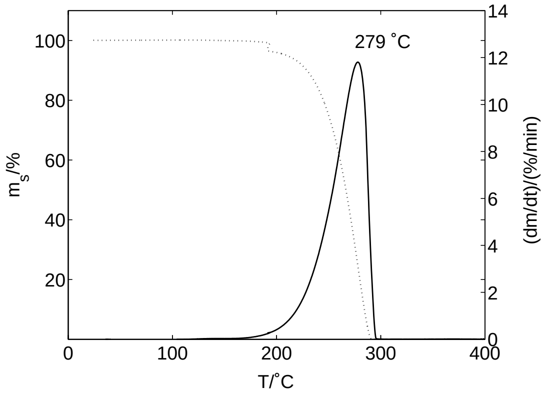

Fig. 4. Thermal behaviour (dotted line for TG curve and solid line for DTG curve) of arsenic trioxide (As_2O_3) in nitrogen atmosphere (temperature profile: heating at 5 °C/min to 500 °C with an isothermal part of 10 min at 200 °C).

lower than 500 °C, which means that the reduction reaction $As_2O_5 \rightarrow As_2O_3 + O_2$ does not take place and trivalent As is not formed when pure As_2O_5.aq is heated to 500 °C.

To examine whether As_2O_5 decomposes at higher temperatures, TG analysis of As_2O_5.aq was performed in a nitrogen atmosphere while heating from room temperature to 850 °C at 10 °C/min. The resultant TG and DTG curves are presented in Fig. 3. From these curves it is clear that decomposition takes place at temperatures higher than 600 °C, leading to arsenic release. This high value for the decomposition temperature differs substantially from most reported values (see Table 1). This discrepancy can be explained by the criteria used to define the decomposition starting and the specificity of the applied procedure.

4.1.2. Arsenic trioxide

Besides the thermal behaviour of arsenic pentoxide (As_2O_5.aq) the thermal behaviour of arsenic trioxide (As_2O_3) has been studied through TG analysis. First, TG analysis of As_2O_3 was performed in a nitrogen atmosphere (the same results were obtained in a dry air atmosphere) by heating the sample at 5 °C/min to 500 °C with an isothermal part of 10 min at 200 °C. The resultant TG and DTG curves are presented in Fig. 4. These curves show that arsenic is already released at temperatures as low as 200 °C. The abrupt start of sublimation around 200 °C with a very marked inflection between 350 and 450 °C was also reported by Duval [24].

To check whether this release is caused by high values of the vapour pressure, TG analysis of As_2O_3 was carried out at different constant temperatures (170, 180 and 190 °C) in a dry air atmosphere (the same results were obtained in a nitrogen atmosphere). The sample was heated to the preset temperature at 10 °C/min and held at that temperature for 60 min. The corresponding TG and DTG curves are presented in Fig. 5. A linear decrease of mass at constant temperature with the slope increasing at higher temperatures is observed (see TG curve). The DTG curve gives rise to the same observation: an almost constant $-\mathrm{d}m/\mathrm{d}t$ for the isothermal parts with a higher value for higher temperatures. Therefore, it can be concluded that the release of As_2O_3 is driven by a vapour pressure controlled volatilisation process; the higher the temperature, the faster the release.

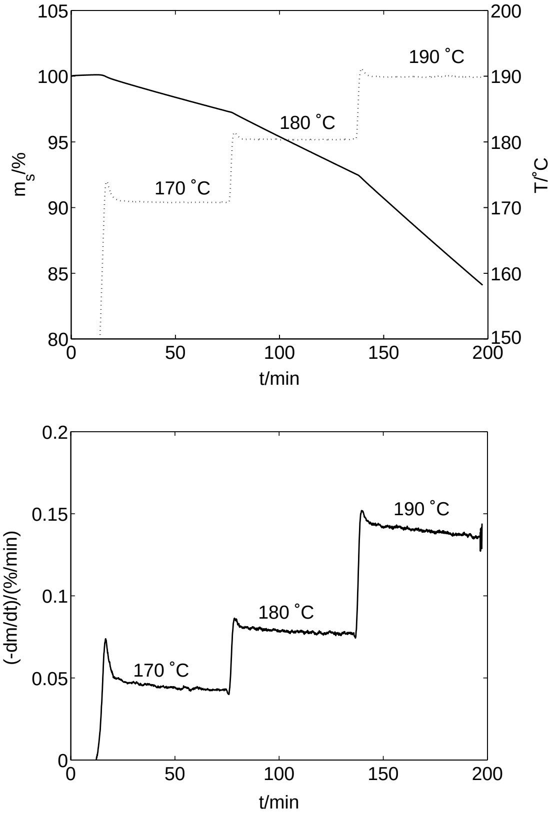

Fig. 5. Thermal behaviour of arsenic trioxide (As_2O_3) in dry air atmosphere (temperature profile: heating at 10 °C/min to 170 °C, isothermal part for 60 min, heating at 10 °C/min to 180 °C, isothermal part for 60 min, heating at 10 °C/min to 190 °C, isothermal part for 60 min): top, TG curve (solid line for TG curve, dotted line for temperature profile); bottom, DTG curve.

4.1.3. Comparison of the results of the thermal studies of CCA treated wood and arsenic model compounds

Pure As_2O_5.aq does not decompose (or reduce) nor volatilise at temperatures lower than 500 °C. On the other hand, during pyrolysis of CCA treated wood arsenic is already released at a temperature of 320 °C [4]. Moreover, in the pyrolysis residue resulting from pyrolysis at 350 °C for 20 min trivalent arsenic is found [5]. Originally, arsenic is present in pentavalent state in the CCA solution (As_2O_5), as well as in the CCA treated wood ($CrAsO_4$). This means that arsenic is partly reduced to the trivalent state during pyrolysis at temperatures lower than 400 °C. Since pure As_2O_5.aq does not decompose (or reduce) nor volatilise at temperatures lower than 500 °C, it can be concluded that the presence of wood, char and pyrolysis vapours may influence the thermal behaviour of arsenic oxides.

4.2. Influence of the presence of glucose

Wood consists of three major compounds: hemicellulose, cellulose and lignin. Since glucose is one of the constituents of the polysaccharide hemicellulose, which is the wood compound that decomposes first when wood is heated, the influence of the presence of glucose on the thermal behaviour of As_2O_5.aq has been studied. Therefore, TG analyses of a mixture of glucose and As_2O_5.aq were carried out in both nitrogen atmosphere and mixed nitrogen–oxygen atmosphere.

4.2.1. TG study in nitrogen atmosphere

First, to have a reference, TG analysis of pure glucose was performed in a nitrogen atmosphere by heating the sample at 10 °C/min to 900 °C. The resultant TG and DTG curves are presented in Fig. 6 (dashed line), together with the TG and DTG curves of pure As_2O_5.aq (dotted line). The latter was also obtained in a nitrogen atmosphere by heating the sample at 10 °C/min to 900 °C. To compare the thermal behaviour of the mixture of glucose and As_2O_5.aq with the thermal behaviour of the pure constituents, the TG and DTG curves obtained for the mixture are also plotted in Fig. 6 (solid line). Again, this experiment was performed in a nitrogen atmosphere by heating the sample at 10 °C/min to 900 °C.

Fig. 6 shows that both pure glucose and pure As_2O_5.aq are decomposed into two distinctive steps, characterised by two well-separated DTG peaks. The TG and DTG curves of the mixture are not a simple superposition of the curves of the two pure constituents. An interaction between both compounds is clearly visible. This interaction can be translated in a faster decomposition of the mixture compared to the superposition of the individual decompositions. As a result the TG curve as well as the DTG peaks of the mixture are shifted to lower temperatures. The mixture starts to decompose at temperatures far below the initial decomposition temperatures of the pure compounds. Moreover, the number of DTG peaks is higher which was first thought to be due to the granular structure of the mixture. A second experiment with the same conditions (not shown in Fig. 6) indicates that the reproducibility of the DTG peaks is high. A third experiment, introducing an isothermal part at 300 °C (not shown in Fig. 6), gives rise to a linear mass reduction at constant temperature, indicating a vapour pressure controlled volatilisation process. The measured amount of solid residue (dark grey-black) remaining in the crucible at the end of the TG experiment with the mixture is smaller than the amount that would be expected without interaction (4.9% versus 7.5%).

The faster decomposition of As_2O_5.aq in the presence of glucose can be easily explained for temperatures higher than the initial decomposition temperature of pure glucose. Once glucose starts to decompose, reducing species are formed. These reducing species promote the reduction of As_2O_5.aq to As_2O_3 [33,34], which is volatile, and O_2, which may accelerate the further decomposition of glucose. However, the faster decomposition of the mixture at temperatures lower than the initial decomposition temperature of glucose cannot be explained by this mechanism.

A possible explanation for the interaction between glucose and As_2O_5.aq at lower temperatures could be the occurrence of an oxidation–reduction reaction, which manifests itself through the transfer of electrons [35,36]. Through electron

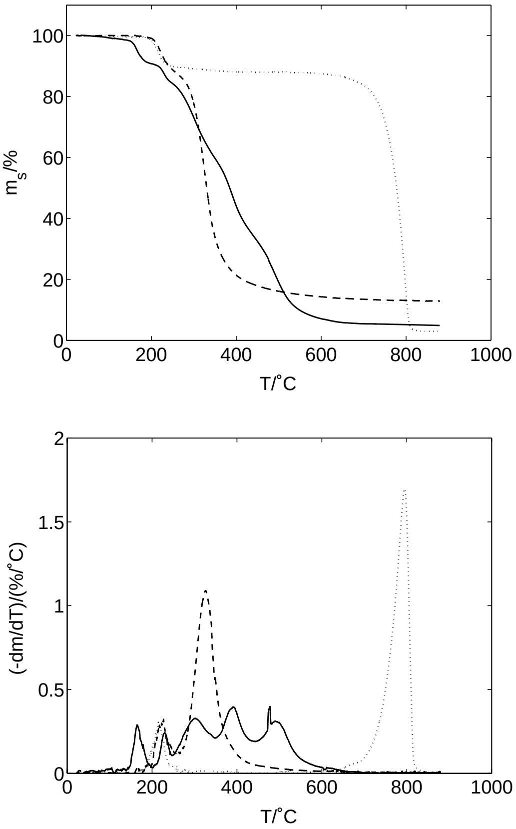

Fig. 6. Thermal behaviour of glucose (dashed line), arsenic pentoxide (As_2O_5.aq) (dotted line) and a mixture of glucose and As_2O_5.aq with As_2O_5.aq/glucose = 1.162 (solid line) in nitrogen atmosphere (temperature profile: heating at 10 °C/min to 900 °C): top, TG curve; bottom, DTG curve.

transfer As_2O_5.aq can be reduced and the aldehyde functional group of glucose can be oxidised to an acid functional group, transforming glucose into gluconic acid. Reduction of As_2O_5.aq may result in the formation of As_2O_3 which is volatile at low temperatures. Moreover, the presence of acid/water (H^+ ions from As_2O_5.aq or H_3AsO_4) has a catalytic effect on the decomposition of glucose. Gluconic acid is volatile and can be easily oxidised with the formation of CO_2. Once these reactions are initiated, they progress consecutively and accelerate each other.

However, this oxidation–reduction reaction is not the only mechanism taking place since formation of As_2O_3 would lead directly to the release of volatile compounds. Probably (complex) compounds are formed between arsenic and organic species. The reaction of an acid (As_2O_5.aq or H_3AsO_4) with an alcohol (primary OH group of glucose) may deliver an ester (arsenate ester) and water. Arsenate esters are known to be formed through the reaction of glucose with arsenate [37–40]. The decomposition of these arsenate esters may result in multiple DTG peaks.

The interaction of glucose and As_2O_5.aq is probably a combination of the aforementioned effects: mutual acceleration of the decomposition reactions, oxidation–reduction reactions and the formation and decomposition of arsenate esters.

The influence of the heating rate on the multiple peak DTG curve of the mixture of glucose and As_2O_5.aq has been studied by performing a HR-TG experiment in nitrogen atmosphere. For temperatures lower than 500 °C lower heating rates shift the TG curve to lower temperatures while the opposite is true for temperatures higher than 500 °C. The heating rate may thus have an influence on the rate of the mechanisms mentioned above.

4.2.2. *TG study in mixed nitrogen–oxygen atmosphere*

In order to study the influence of the presence of oxygen on the thermal behaviour of a mixture of glucose and As_2O_5.aq, TG analyses were performed in mixed nitrogen–oxygen atmospheres. Nitrogen and synthetic dry air (80% N_2 + 20% O_2) were mixed in such amounts that oxygen concentrations of, respectively, 5 and 10% were used in the purge gas. The resultant TG and DTG curves are presented in Fig. 7 together with the curve obtained in a pure nitrogen atmosphere.

From Fig. 7 it is clear that the presence of oxygen accelerates the decomposition of the mixture of glucose and As_2O_5.aq and reduces the amount of solid residue to nihil. Multiple DTG peaks are observed for each of the three purge gas compositions. Besides for the first DTG peak, the DTG peak temperatures are of the same order of magnitude for the three purge gas concentrations considered.

It can be concluded that oxygen concentrations of, respectively, 5 and 10% in the purge gas are sufficient to accelerate the decomposition of the mixture, but insufficient to reverse the reaction $As_2O_5\text{.aq} \rightarrow As_2O_3 + O_2 + H_2O$. Probably the presence of oxygen accelerates the decomposition of glucose by partial oxidation and consequently the decomposition of the mixture of glucose and As_2O_5.aq through the above-mentioned mechanisms. It is known that As_2O_5 can be formed by reacting As_2O_3 with O_2 under high pressure (120–130 atm) and high temperature (400–480 °C) [31,41]. For these conditions, the reaction is said to be reversible [31]. However, such high pressures are not applied here.

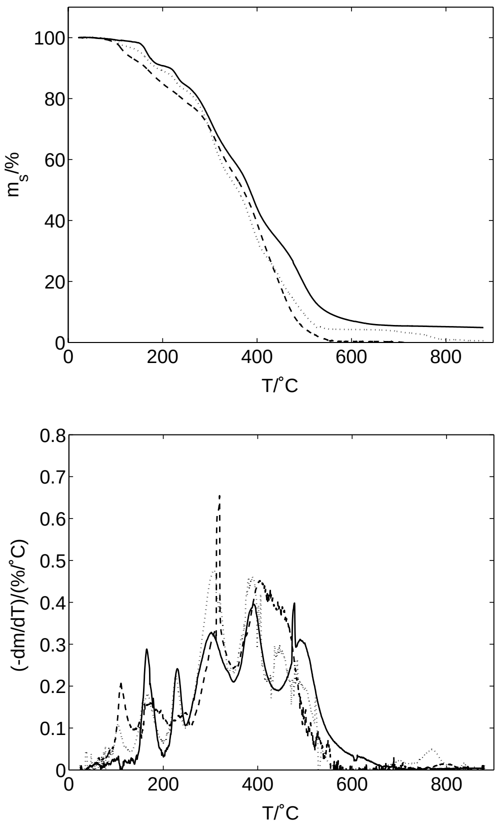

Fig. 7. Thermal behaviour of a mixture of glucose and As_2O_5.aq with As_2O_5.aq/glucose = 1.162 in different atmospheres: pure nitrogen (solid line), nitrogen with 5% oxygen (dotted line) and nitrogen with 10% oxygen (dashed line) (temperature profile: heating at 10 °C/min to 900 °C): top, TG curve; bottom, DTG curve.

4.3. *Influence of the presence of activated carbon*

In order to study the influence of the presence of activated carbon on the thermal behaviour of As_2O_5.aq, TG analysis was carried out with a mixture of activated carbon and As_2O_5.aq with As_2O_5.aq/activated carbon = 1.162. The sample was heated at 10 °C/min to 900 °C in a nitrogen atmosphere. The resultant TG and DTG curves are presented in Fig. 8 (dashed line). For comparison the TG and DTG curves of pure As_2O_5.aq (solid line) and a mixture of glucose and As_2O_5.aq (dotted line) in nitrogen atmosphere are plotted in the same figure.

Fig. 8 shows that activated carbon accelerates the decomposition of As_2O_5.aq in an inert atmosphere. The initial decomposition (probably attributed to the release of water) even starts at lower temperatures than in the case of

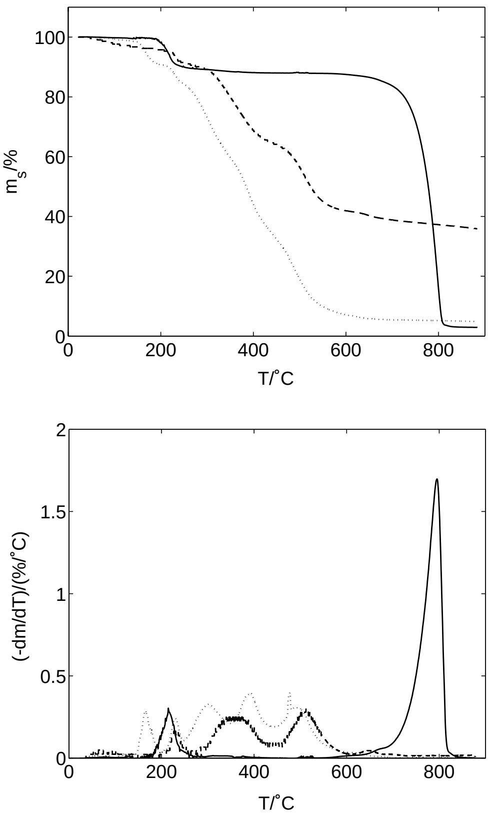

Fig. 8. Thermal behaviour of As_2O_5.aq (solid line), a mixture of glucose and As_2O_5.aq with As_2O_5.aq/glucose = 1.162 (dotted line) and a mixture of activated carbon and As_2O_5.aq with As_2O_5.aq/activated carbon = 1.162 (dashed line) in nitrogen atmosphere (temperature profile: heating at 10 °C/min to 900 °C): top, TG curve; bottom, DTG curve.

the mixture of glucose and As_2O_5.aq, but is spread over a broader temperature range. The presence of activated carbon clearly promotes the volatilisation of arsenic for temperatures higher than 300 °C, probably through its reducing action. Since the measured mass of the solid residue (black) is only 36% at 900 °C, some of the carbon (originally 46.3% in mass) is released, probably in oxidised form (CO or CO_2). Reduction of As_2O_3 by carbon with the formation of CO_2 is known to take place easily at temperatures between 650 and 700 °C [31]. However, at these high temperatures As_2O_3 is expected to be already released (boiling point at 1 atm is 457 °C). On the other hand, activated carbon acts as a catalyst in the oxidation of As_2O_3 to As_2O_5 in the presence of oxygen [31].

5. Conclusions

First, the thermal behaviour of pure arsenic oxides (As_2O_5.aq and As_2O_3) has been studied. Pure arsenic pentoxide As_2O_5.aq does not decompose (nor volatilise) at temperatures lower than 500 °C. Release of water (between 200 and 400 °C) results in the formation of anhydrous As_2O_5. Only at higher temperatures (>600 °C) decomposition of As_2O_5 takes place, leading to arsenic release. Pure arsenic trioxide (As_2O_3), on the other hand, already volatilises at temperatures as low as 200 °C. This release is driven by a vapour pressure controlled volatilisation process: the higher the temperature, the faster the release.

From the comparison of the results of the thermal studies of CCA treated wood and pure arsenic oxides it can be concluded that the reduction of pentavalent arsenic to trivalent arsenic is favoured by a reducing environment, created by the presence of wood, char and pyrolysis vapours. Therefore, the influence of the presence of glucose and activated carbon on the thermal behaviour of arsenic pentoxide has been studied.

From the TG study of the mixture of glucose and As_2O_5.aq, it is obvious that the thermal behaviour of As_2O_5.aq is highly influenced by the presence of glucose, both in a nitrogen atmosphere and in a mixed nitrogen–oxygen atmosphere. The presence of glucose gives rise to a faster decomposition, the effect being more pronounced the higher the oxygen concentration in the purge gas is. The interaction of glucose and As_2O_5.aq is probably a combination of three effects: mutual acceleration of the decomposition reactions, oxidation–reduction reactions and the formation and decomposition of arsenate esters. As a result, the DTG curve of the mixture shows multiple peaks which are shifted to lower temperatures. It can be concluded that oxygen concentrations of, respectively, 5 and 10% in the purge gas are sufficient to accelerate the decomposition of both As_2O_5.aq and glucose, but insufficient to reverse the reaction $As_2O_5.aq \rightarrow As_2O_3 + O_2 + H_2O$.

The thermal decomposition of hydrated chromium arsenate, studied earlier by the authors [9,27], also revealed a multiple peak DTG curve, but with ill-defined peak temperatures. Due to the synthesis process of the hydrated chromium arsenate compound traces of glucose were present. The interaction of glucose and the arsenic compound may cause the reduction of pentavalent arsenic to trivalent arsenic and the corresponding release of volatiles.

The thermal behaviour of As_2O_5.aq is also highly influenced by the presence of activated carbon. The presence of activated carbon promotes the volatilisation of arsenic for temperatures higher than 300 °C, probably through its reducing action.

Both reducing agents, glucose and activated carbon, influence the thermal behaviour of As_2O_5.aq, giving rise to arsenic volatilisation at lower temperatures compared to the case with pure As_2O_5.aq. Extrapolation of the thermal behaviour of these model compounds to the real situation of pyrolysis of CCA treated wood confirms the statement that the reduction of pentavalent arsenic to trivalent arsenic is favoured by the reducing environment, created by the presence of wood, char and pyrolysis vapours. Therefore, the most important conclusion is that zero arsenic release during pyrolysis of CCA treated wood seems to be impossible since the reduction reaction ($As_2O_5 \rightarrow As_2O_3 + O_2$) cannot be avoided in the reducing environment. Once the trivalent arsenic oxide is formed, it is released, obeying a temperature controlled solid–vapour equilibrium.

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