



Thermal behaviour of arsenic trioxide adsorbed on activated carbon

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ABSTRACT

The thermal stability and desorption of arsenic trioxide (As_2O_3) adsorbed on activated carbon (AC) was investigated as this phenomenon is expected to influence the arsenic release during low temperature pyrolysis of chromated copper arsenate (CCA) wood waste. Firstly, a thermogravimetric (TG) experiment with arsenolite, an allotropic form of As_2O_3 , was performed. The sample starts to sublime at temperatures lower than 200°C with a sublimation peak temperature of 271°C . Subsequently, TG experiments with samples of As_2O_3 adsorbed on AC revealed that only very little (max. 6 ± 3 wt%) As_2O_3 was volatilised at temperatures below 280°C , while still $41.6 (\pm 5)$ wt% of the original arsenic concentration was retained at 440°C and $28.5 (\pm 3)$ wt% at 600°C . The major arsenic volatilisation occurred between 300°C and 500°C . The kinetic parameters of desorption, activation energy of desorption (E_d) and pre-exponential factor (A), were determined by fitting an Arrhenius model to the experimental data, resulting in $E_d = 69$ kJ/mol, $A = 1.21 \times 10^4 \text{ s}^{-1}$. It can be concluded that the adsorption of As_2O_3 on AC can contribute to the thermal stabilisation of As_2O_3 . Consequently, during low temperature pyrolysis of CCA wood arsenic release may be prevented by adsorption of As_2O_3 on the coal-type product formed during the thermal decomposition of the wood.

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1. Introduction

For many years, wood has been preserved with chromated copper arsenate (CCA). Recently CCA wood waste has been classified as hazardous waste, and disposal has become a growing problem [1]. Low temperature pyrolysis, identified as a promising disposal solution [2], combines the recuperation of energy and materials, thanks to the agglomeration of heavy metals. The agglomerates of metals and minerals can be separated from the carbon product by a centrifugal separation of the solid product, hereby concentrating the heavy metals for recycling or disposal. The main concern in thermal processes is controlling the release of volatile arsenic compounds.

Arsenic pentoxide, originally present in the CCA solution used to impregnate the wood, is already reduced at temperatures lower than 330°C to the less thermally stable arsenic trioxide (As_2O_3) [3,4]. Furthermore, small amounts of As_2O_3 are already present in the CCA wood due to weathering [5]. These phenomena justify the interest in the thermal stability of As_2O_3 , and the processes controlling its volatilisation, when studying low temperature pyrolysis of CCA wood.

Earlier research has suggested the formation of more stable arsenic compounds (without additives) as a mechanism to

reduce arsenic volatilisation [6]. However, this mechanism is inconclusive in preventing the arsenic volatilisation, since still major arsenic losses have been reported [4,7]. Furthermore, Kitamura and Katayama [8] explained the difference between arsenic retention in ash, obtained from burning CCA wood, and arsenic retention in charcoal, obtained from CCA wood pyrolysis, to be due to the adsorption of arsenic on char. Adsorption on char may thus have a significant influence on the release of arsenic during thermochemical conversion of CCA wood.

This paper will focus on thermal desorption of As_2O_3 that was adsorbed on activated carbon (AC), as this process influences the thermal stability of As_2O_3 and thus arsenic volatilisation. These desorption phenomena could certainly play a role during low temperature pyrolysis of CCA wood: during pyrolysis, wood is converted into a char product which has similar properties as AC. As_2O_3 present in CCA wood can be adsorbed and stabilised on the partially pyrolysed wood, and As_2O_3 that still vaporises can be caught and stabilised by above lying wood layers.

Since online detection of arsenic in the gas phase is problematic, it was opted to acquire arsenic emission data indirectly via the continuous monitoring of weight loss during thermogravimetric (TG) analysis, combined with offline As analysis of samples collected in the TG apparatus and the sampling train. TG analysis is performed for both the pure components and the adsorbed samples. The outline of this paper is as follows: first a summary of the literature with respect to thermal properties of As_2O_3 and adsorption/desorption

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of As_2O_3 is given. In the next part the materials and methods are described followed by the results of the TG experiments. Finally, the most important conclusions are summarised.

2. Materials and methods

2.1. Sample preparation

Arsenic trioxide from pro analysis quality was purchased from Riedel-de Haen, and was earlier identified as arsenolite [9].

The activated carbon samples loaded with As_2O_3 were prepared by adsorption of As_2O_3 from an aqueous solution on AC, hereby ensuring an intense interaction between both components. First, a 1.0 wt% stock solution of As_2O_3 was prepared by adding a known amount of As_2O_3 to a flask of 50 ml, containing 40 ml of ultra-pure milli-Q water (Millipore, Bedford, MA, USA). The As_2O_3 was allowed to dissolve for 24 h, after which the solution was diluted to volume with milli-Q water. Subsequently, 10 ml of stock solution was added to 2 g of AC (from spruce wood, puriss quality, Fluka Chemika) and the mixture was stirred for 2 h to ensure that adsorption equilibrium was reached. Finally the samples were dried at 105 °C till constant weight.

Since dissolution of As_2O_3 in water proceeds very slowly and the solubility is limited to 1.2–3.7 g/100 ml (20 °C) [10], the As_2O_3 in the stock solution was not completely dissolved. For the AC + As_2O_3 sample preparation, the As_2O_3 stock solution was allowed to settle down and only the upper, clear part of the solution was used. Consequently, the arsenic concentration in the AC + As_2O_3 sample could not be easily calculated. Therefore, the sample (As_2O_3 + AC) was analysed by inductively coupled plasma-mass spectrometry (ICP-MS), after digestion, resulting in an As_2O_3 load of 40.7 (± 1.3) mg As_2O_3 /g AC which corresponds to 31.0 (± 0.9) mg As/g AC.

2.2. Thermogravimetric analysis

The thermogravimetric analysis experiments were carried out on a TA instruments TGA 951-2000 which has an easily accessible gas outlet. In order to ensure inert working conditions, the apparatus was modified as described elsewhere [11]. The sample, approximately 30 mg in weight, was introduced into a quartz sample pan and the whole apparatus was flushed for 1 h with nitrogen. The heating of the sample was executed according to a preset temperature profile. The weight and temperature of the sample were monitored and recorded continuously. Furthermore, the data of the AC + As_2O_3 samples were filtered using a high pass/low pass filter and the derivative of weight as a function of temperature was calculated off-line.

Since TG experiments were performed with toxic As_2O_3 , a sampling train was connected to the outlet of the apparatus in order to prevent arsenic release in the lab. This ensures safe working conditions and allows to calculate and control mass balances. 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 of 0.1N. To ensure sufficient bubbling in the last impinger, the nitrogen flow of the TG apparatus was set at 120 ml/min, which is relatively high. Earlier experiments have shown that no arsenic breakthrough occurs through this sampling train [12].

At the end of each experiment the whole sampling train was disassembled. All glassware was rinsed with 1N NaOH, and two times with milli-Q water. These solutions, together with the filter and backup pad were collected for later determination of arsenic content.

2.3. Digestion and solution analysis

Arsenic concentrations in various samples were determined by ICP-MS. To minimise the background level of arsenic, all glassware was soaked overnight in an acid bath (2% HNO_3) and washed with milli-Q water. As a first step, the AC + As_2O_3 samples and corresponding blanks were dissolved by a “total destruction” procedure: approximately 100 mg of a sample was weighed and transferred into a Teflon beaker. After adding 5 ml of HNO_3 (suprapur, Fluka) the beaker was covered and placed on a heating plate. After 30 min of boiling the lid was removed to allow part of the volume to evaporate. Subsequently, 3 ml of HClO_4 was added, and the mixture boiled with lid for another 60 min. Finally the mixture was transferred to a 100 ml volumetric flask and diluted with milli-Q water to volume. Filter samples were dissolved according to the same procedure.

These solutions, as well as the solutions obtained in the sampling train, were diluted another 2 to 100 times dependent on the expected arsenic concentration in the sample, hereby minimising matrix effects during ICP-MS measurements. Known amounts of HNO_3 were added every dilution step in order to have equal final acid concentrations in all solutions.

The ICP-MS measurements were carried out on an X series ICP-MS (thermo electron, detection limit: 0.2 ppb) equipped with an auto sampler ASX-510 (Cetac) and software to correct for instrumental drift and spectral interferences. Blanks and arsenic standards (50–250 ppb), based on a 1000 ppm arsenic solution, were used to calibrate the apparatus. The internal standards used were Te (50 ppb), In (50 ppb), Ga (100 ppb) and Be (500 ppb).

3. Results and discussion

As a first step, the thermal behaviour of the pure reagents was investigated in order to compare these results with the results of As_2O_3 + AC. Therefore, TG experiments with pure As_2O_3 and pure AC were performed.

3.1. Thermal behaviour of arsenic trioxide

Solid As_2O_3 naturally occurs in three different forms: amorphous As_2O_3 , arsenolite which is typically obtained from the vapour phase or from solutions, and claudetite (I, II), being the thermodynamic more stable polytropes at room temperature and ambient pressure. The claudetite phases are monoclinic and have a structure very similar to orpiment (As_2S_3). Arsenolite is a cubic molecular crystal composed of As_4O_6 dimers [13–17].

A summary of melting, boiling and sublimation temperatures for As_2O_3 , arsenolite and claudetite, retrieved from the literature is presented in Table 1. Especially for the sublimation temperature of arsenolite, different literature sources are inconsistent with a spread of more than 140 °C. On the other hand, there seems to be some kind of consensus on the different melting and boiling temperatures (with one exception for the melting temperature of claudetite).

Because of these inconsistent data on the thermal properties of As_2O_3 (arsenolite), own TG experiments were performed. The TG profile of As_2O_3 (arsenolite) together with its derivative (DTG curve) is presented in Fig. 1. The sample was heated till 450 °C at a rate of 5 °C/min with an isothermal part of 10 min at 110 °C, to allow evaporation of water. As can be seen from the TG and DTG curves, no water was present and the mass loss of the sample took place between 170 °C and 280 °C. The derivative of the TG profile shows a narrow peak at 271 °C.

Earlier research reported a vapour pressure dependent mass loss of arsenolite with a maximum rate at 279 °C, identified as the sublimation peak of As_2O_3 [9]. Others reported similar profiles, with the

Table 1
Melting (T_m), boiling (T_b) and sublimation (T_s) temperatures for As_2O_3 , arsenolite and claudetite.

| | T_m (°C) | T_b (°C) | T_s (°C) |
|------------|--|----------------------|-----------------------------|
| As_2O_3 | 312.8 [18], 315 [19,20] | 457.2 [18] | |
| Arsenolite | 278 [21], 274 [13], 275 [22], 275–315 [23] | | 193 [19], 135 [22], 278 [3] |
| Claudetite | 193 [19], 312 [21], 314 [13], 313 [22] | 457.2 [19], 459 [21] | 315 [19] |

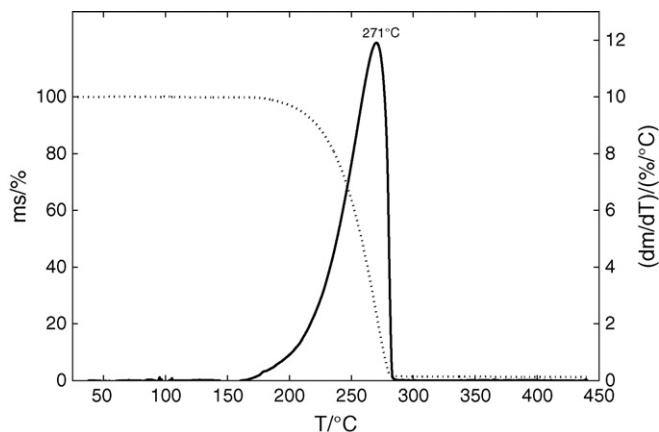


Fig. 1. Thermal behaviour (dotted line for TG curve and solid line for DTG curve) of arsenic trioxide (As_2O_3) in nitrogen atmosphere (temperature profile: heating at 5 °C/min to 450 °C with an isothermal part of 10 min at 110 °C).

sublimation of As_2O_3 starting around 200 °C and a marked inflection at temperatures between 350 °C and 450 °C [26].

The observed mass loss is most probably caused by sublimation of arsenolite, since melting and subsequent evaporation from the liquid phase would deliver a smooth TG profile only if melting occurs at temperatures lower than 200 °C. However, no reference was found reporting melting of arsenolite at temperatures lower than 200 °C. Furthermore, a transition of metastable arsenolite to claudetite, which is catalysed by water, and occurs at 180 °C [24], is not likely to have occurred since this transition is reported to proceed very slowly [23,25]. The temperature at the narrow peak, being 271 °C, is therefore identified as the sublimation peak temperature at given experimental conditions.

3.2. Thermal behaviour of activated carbon

The TG analysis of activated carbon results in the TG curve, and its derivative (DTG curve), presented in Fig. 2. The Y-axis in Fig. 2 is

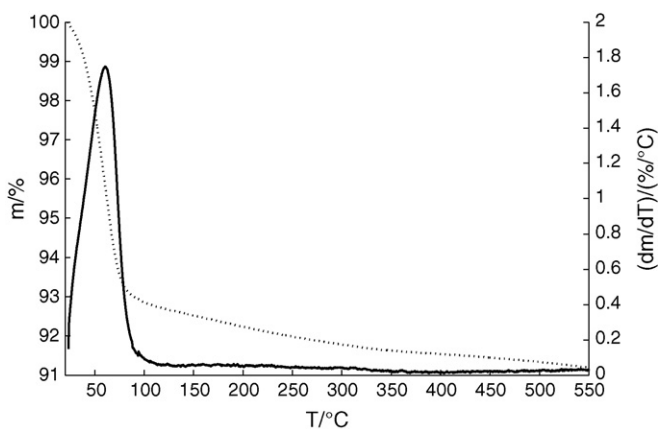


Fig. 2. Thermal behaviour (dotted line for TG curve and solid line for DTG curve) of activated carbon (AC) in nitrogen atmosphere (temperature profile: heating at 5 °C/min to 550 °C).

limited to the range 90–100 wt%, to present the effects more clearly. At the initial stage, there is a mass reduction of about 7 wt%, mainly due to the evaporation of water. Despite the predrying of the samples at 115 °C, there is still a significant amount of water evaporating at temperatures lower than 115 °C. This water most probably originated from moisture adsorbed on the sample during filling of the TG apparatus. At temperatures higher than 150 °C, there were no pronounced peaks in the DTG curve and only 0.5% reduction in mass was recorded between 150 °C and 550 °C.

3.3. Thermal behaviour of arsenic trioxide adsorbed on activated carbon

In order to investigate the desorption behaviour of As_2O_3 , adsorbed on AC, and the influence of adsorption of As_2O_3 on its thermal stability, a TG experiment was set up. The temperature profile had an isothermal part of 10 min at 115 °C, and the heating rate was set to 5 °C/min. To obtain a clear picture of the behaviour of the adsorbed As_2O_3 and the interaction AC– As_2O_3 , the TG curve of AC was subtracted from the curve of the mixture of AC + As_2O_3 . Furthermore, the TG curve is set to 100 wt% after the isothermal part at 115 °C in order to exclude free adsorbed water from the total mass. Hereby the mass loss in the TG curve is narrowed to the volatilisation of As_2O_3 and more intense adsorbed water. The obtained TG curve, together with its derivative (DTG curve) is presented in Fig. 3. The Y-axis in Fig. 3 is limited to the range 95–100% to make the effects clearly visible.

The DTG curve shows a broad peak between 290 °C and 500 °C with a maximum at 405 °C. The broadness of the peak, compared to the narrow and distinctive volatilisation peak of pure arsenolite, suggests a slower volatilisation process. The two smaller peaks at 199 °C and 238 °C contribute to a lesser extent (1.2% weight reduction) to the total mass loss (5% weight reduction).

To determine the origin of the different peaks a sample was heated till 280 °C and the arsenic concentration in the solid residue and the various fractions of the sampling train was measured by ICP-MS. The results are summarised in Table 2. Still 96.3 (±3) wt%

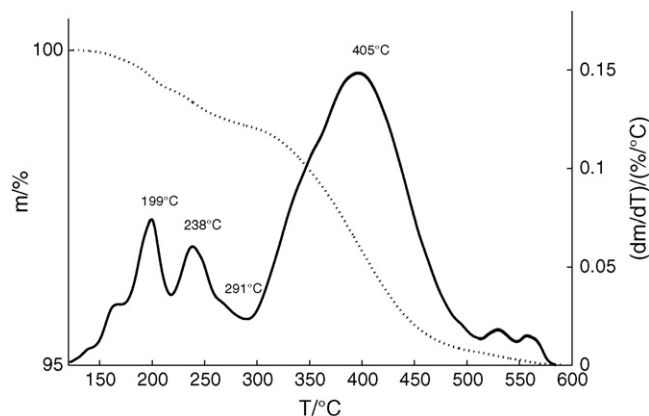


Fig. 3. Thermal behaviour (dotted line for TG curve and solid line for DTG curve) of arsenic trioxide (As_2O_3) adsorbed on activated carbon (AC) in nitrogen atmosphere (temperature profile: heating at 5 °C/min to 600 °C with an isothermal part of 10 min at 115 °C) after subtraction of the profile of pure activated carbon and filtering of noise.

Table 2

Absolute amounts of arsenic (mg) and relative amounts of arsenic (wt%) in the various fractions, together with the total mass balance, for a sample heated till 280 °C.

| Various fractions | Amount of As (mg) | Relative amount (wt%) |
|--------------------|---|-----------------------|
| Original sample | $1.64 \pm 5.0 \times 10^{-2}$ | 100 |
| Solid residue | $1.58 \pm 7.0 \times 10^{-2}$ | 96.3 |
| Quartz tube | $9.1 \times 10^{-2} \pm 1.0 \times 10^{-3}$ | 5.6 |
| Cooler | $6.6 \times 10^{-3} \pm 3.0 \times 10^{-4}$ | 0.40 |
| Filter | $4.7 \times 10^{-4} \pm 9.0 \times 10^{-5}$ | 0.029 |
| Impinger | $2.1 \times 10^{-4} \pm 4.0 \times 10^{-5}$ | 0.013 |
| Total mass balance | | 102.4 ± 3.0 |

Table 3

Absolute amounts of arsenic (mg) and relative amounts of arsenic (wt%) in the various fractions, for a sample heated till 440 °C.

| Various fractions | Amount of As (mg) | Relative amount (wt%) |
|----------------------------------|---|-----------------------|
| Original sample | $1.74 \pm 5.3 \times 10^{-2}$ | 100 |
| Solid residue | $0.72 \pm 3.6 \times 10^{-2}$ | 41.6 |
| Quartz tube, cooler and impinger | $0.98 \pm 4.0 \times 10^{-3}$ | 56.6 |
| Filter | $3.6 \times 10^{-4} \pm 6.7 \times 10^{-5}$ | 0.021 |
| Total mass balance | | 98.3 ± 5.0 |

of the original arsenic content was present in the sample, indicating that only 3.7 wt% arsenic may have evaporated at temperatures lower than 280 °C

In addition, an arsenic mass balance has been calculated from the arsenic content in the various fractions of the sampling train and the solid residue. The total mass balance (102.4%) falls within the range of the experimental error (97–103%) indicating that no significant arsenic breakthrough occurred. Furthermore, Table 2 shows that most of the arsenic that did evaporate deposited already in the quartz tube. The amount of arsenic caught in the last part of the sampling train, the impinger, is almost negligible (0.013%) which, together with the mass balance in the range 97–103%, confirms the proper functioning of the sampling train.

Since the mass balance was slightly higher than 100% it has been opted to assume that maximum 6 (±3) wt%, the total amount of arsenic caught in the sampling train, was evaporated at temperatures lower than 280 °C, which represents a more conservative value. This corresponds to 0.24% total mass reduction attributed to arsenic on the TG curve compared with 1.2% total mass reduction at 280 °C. It was therefore concluded that two smaller peaks at 199 °C and 238 °C originate mostly from evaporation of water strongly associated with As₂O₃ and AC. The sample preparation phase, during which the arsenic trioxide was dissolved in water and contacted with AC, is identified as a possible source of the associated water.

The origin of the major broad peak between 290 °C and 500 °C was investigated by analysing the residue of a sample heated till 440 °C and the residue of the original sample (that was heated till 600 °C). The results are presented in Tables 3 and 4, respectively. The arsenic concentration in the various parts of the sampling train

Table 4

Absolute amounts of arsenic (mg) and relative amounts of arsenic (wt%) in the various fractions, together with the total mass balance, for a sample heated till 600 °C.

| Various fractions | Amount of As (mg) | Relative amount (wt%) |
|---------------------|---|-----------------------|
| Original sample | $1.22 \pm 4.0 \times 10^{-2}$ | 100 |
| Solid residue | $0.35 \pm 1.0 \times 10^{-2}$ | 28.5 |
| Quartz tube | $0.85 \pm 2.0 \times 10^{-2}$ | 70.0 |
| Cooler and impinger | $4.50 \pm 1.5 \times 10^{-2}$ | 3.7 |
| Filter | $3.0 \times 10^{-3} \pm 1.0 \times 10^{-3}$ | 0.23 |
| Total mass balance | | 102.5 ± 3.0 |

and the mass balance are also included, however, analysis of arsenic concentrations for some parts of the sampling train were merged together. Both mass balances are in the range of the experimental error which once again proves the proper working of the sampling train.

For the sample heated till 440 °C, still 41.6 (±5) wt% of the original arsenic content was present. The amount of arsenic that volatilised therefore accounts for a total mass loss of 2.3 (±0.2) wt% of the original sample. The total mass loss of the whole sample between 280 °C and 440 °C recorded, by the TG profile amounts to 3.0 wt%. It can, therefore, be concluded that the main part of mass reduction between 280 °C and 440 °C is caused by volatilisation of arsenic.

For the sample heated till 600 °C, still 28.5 (±3) wt% of the original arsenic content was present in the residue. The amount of arsenic that volatilised therefore accounts for a mass loss of 2.9 (±0.1) wt% of the original sample. The mass loss of the whole sample between 280 °C and 600 °C recorded by the TG profile amounts to 3.8 wt%. Detailed analysis reveals that between 440 °C and 600 °C, 13.1 (±5) wt% (41.6%–28.5%) of the original arsenic content was volatilised accounting for a mass loss of 0.6 (±0.2)% (2.9%–2.1%). The total mass loss of the whole sample in the same temperature range is 0.8% (3.8%–3.0%). It can therefore be concluded that the mass loss between 440 °C and 600 °C is almost entirely caused by volatilisation of arsenic trioxide. Based on these results the broad peak between 290 °C and 500 °C is mainly assigned to the volatilisation of arsenic trioxide.

When the TG profiles of pure arsenic trioxide and arsenic trioxide adsorbed on activated carbon and the additional analysis of the residues are taken in account, it can be concluded that the thermal stability of arsenic trioxide was significantly improved by adsorption on activated carbon. This gives a good perspective to better control arsenic volatilisation during pyrolysis of CCA-treated wood.

TG experiments with As₂O₃ adsorbed on wood have been performed too, in order to gain more insight in the stabilising effect of As₂O₃ adsorption on wood. Since the volatilisation peak of As₂O₃ coincides with the broader volatilisation peak of wood, it is impossible to distinguish both decomposition peaks (even with HR-TG [27]).

To gain deeper insight in the thermal stability of As₂O₃ adsorbed on AC, an attempt was made to model the kinetics of Arsenic release by looking at the combined process of desorption and volatilisation. For this purpose, the major DTG peak was isolated, and to eliminate interference with other peaks, only the temperature range between 315 °C and 470 °C was retained. Furthermore, it has been assumed that only arsenic trioxide volatilises in this temperature range. This was, however, not exactly the case and therefore the figures obtained must be regarded as a good first estimate.

The desorption rate (wt%/s), *S*, for the temperature range 315–470 °C was calculated from the DTG curve (which represents the continuous registration of the derivative of the mass loss of the sample). Additionally, the mass ratio (As₂O₃/AC, wt%), *MR*, as a function of temperature was calculated from the DTG curve. After the determination of the reaction order *n*, the rate coefficient (1/s), *k*, could be determined by following formula

$$S = k[MR]^n \quad (1)$$

Because the temperature dependency of the rate coefficient, *k*, is best described by an Arrhenius behaviour [28], the reaction order, *n*, was specifically chosen to deliver the best possible fit between the data and an expected Arrhenius behaviour of the rate coefficient, *k*. Therefore various values of *n* were taken to calculate *k* values as a function of temperature. Subsequently, an Arrhenius behaviour was fitted to these *k* values and a correlation coefficient was obtained. The reaction order that resulted in the best possible fit was retained for further calculations.

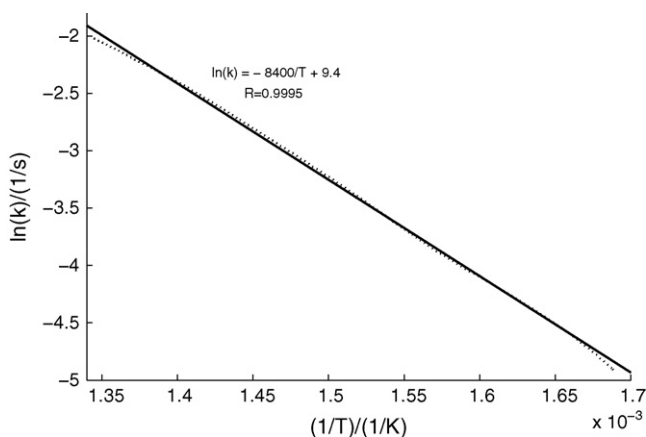


Fig. 4. Plot of $\ln(k)$ vs. $1/T$ ($\times 10^{-3}$): dashed line for experimental data and solid line for the fitted Arrhenius behaviour.

Based on the fitted curve of the rate coefficient, k , as a function of temperature, the Arrhenius parameters could be determined by following formula

$$\ln k = \ln A - \frac{E_d}{RT} \quad (2)$$

With A being the pre-exponential factor ($1/s$), R the gas constant ($J/molK$), T the absolute temperature (K) and E_d the activation energy of desorption (kJ/mol), which depends on the strength of the interaction between adsorbent and adsorbate [28].

The experimental data together with the fitted Arrhenius behaviour are presented in Fig. 4.

A "pseudo reaction order" of 1.2 resulted in the best possible fit ($R^2 = 0.99$) with the experimental data. This reaction order of 1.2 may result from the fact that besides arsenic trioxide, also small amounts of water may evaporate in the given temperature range. As temperature rises above $440^\circ C$, the mass loss is almost entirely dedicated to arsenic volatilisation which explains the lower desorption rate at higher temperatures/lower mass ratios. From the fitted line the Arrhenius parameters could be derived.

$$E_d = 69 \text{ kJ/mol}$$

$$A = 1.21 \times 10^4 \text{ s}^{-1}$$

E_d values for arsenic trioxide (activation energy of desorption) are poorly documented in literature, but can be derived from E_a values (activation energy of adsorption) together with heat of adsorption (ΔH_a).

$$E_d = E_a + \Delta H_a \quad (3)$$

However, both E_a and ΔH_a exhibit a wide range of values.

The magnitude of the activation energy of desorption suggests a strong physical bonding or a combination of physisorption and chemisorption between adsorbate and adsorbent [28].

4. Conclusions

In this paper, the thermal stability of arsenic trioxide, adsorbed on activated carbon, was investigated. The sublimation of arsenolite was found to be not well documented in the literature and therefore a TG analysis of arsenolite was performed. The sample already starts to sublime at $170^\circ C$ with a sublimation peak temperature of $271^\circ C$. At around $280^\circ C$, the whole sample was sublimated. Mass and heat transfer limitations could only have had little influence on this result since a relatively high purge gas flow rate and low sample masses were used.

The experiments with samples of $As_2O_3 + AC$ show an interesting effect that could prevent As_2O_3 from volatilisation during heating. The DTG curve shows a broad volatilisation peak between $300^\circ C$ and $500^\circ C$ with a maximum at $405^\circ C$. Very little (max. $6 \pm 3 \text{ wt}\%$) As_2O_3 was volatilised at temperatures below $280^\circ C$. Furthermore, still $41.6 (\pm 5) \text{ wt}\%$ of the original arsenic content was retained at $440^\circ C$ and $28.5 (\pm 3) \text{ wt}\%$ at $600^\circ C$. The adsorption of As_2O_3 on AC clearly has a beneficial effect on the thermal stability of As_2O_3 . The kinetic parameters of the desorption process were determined: $E_d = 69 \text{ kJ/mol}$, $A = 1.21 \times 10^4 \text{ s}^{-1}$ with the activation energy being in the upper range of physisorption.

These results suggest that arsenic adsorption on AC may play an important role in the pyrolysis of CCA-treated wood. On the one hand, adsorption may prevent the volatilisation of arsenic trioxide and on the other hand, adsorption may facilitate the formation of agglomerates of As_2O_3 with wood minerals, giving rise to thermally more stable micro-structures. Furthermore, in a fixed bed or moving bed reactor, small fractions of As_2O_3 that volatilise at the bottom of the pyrolysis reactor can be re-adsorbed by above lying wood or partially pyrolysed wood layers, giving rise to thermally more stable adsorbed As_2O_3 .

References

- [1] H.M. Solo-Gabriele, T.G. Townsend, J. Schert, Environmental impacts of CCA treated wood: a summary from seven years of study focusing on the US Florida environment, in: Presented at the 34th Annual IRG Meeting, Brisbane, Australia, 2003.
- [2] L. Helsen, E. Van den Bulck, Review of disposal technologies for chromated copper arsenate (CCA) treated wood waste, with detailed analyses of the thermochemical conversion processes, Environ. Pollut. 134 (2005) 301–314.
- [3] L. Helsen, E. Van den Bulck, M.K. Van Bael, J. Mullens, Arsenic release during pyrolysis of CCA treated wood waste: current state of knowledge, J. Anal. Appl. Pyrolysis 68 (2003) 613–633.
- [4] T. Kakitani, T. Hata, T. Kajimoto, Y. Imamura, Two possible pathways for the release of arsenic during pyrolysis of chromated copper arsenate (CCA)-treated wood, J. Hazard. Mater. 113 (2004) 247–252.
- [5] B.I. Khan, H.M. Solo-Gabriele, B.K. Dubey, Arsenic speciation of solvent-extracted leachate from new and weathered CCA-treated wood, Environ. Sci. Technol. 38 (2004) 4527–4534.
- [6] J. Wang, A. Tomita, A chemistry on the volatility of some trace elements during coal combustion and pyrolysis, Energy Fuels 17 (2003) 954–960.
- [7] K. Lundholm, D. Boström, A. Nordin, A. Shchukarev, Fate of Cu, Cr and As during combustion of impregnated wood with and without peat additive, Environ. Sci. Technol. 41 (2007) 6534–6540.
- [8] T. Kitamura, H. Katayama, Behavior of copper, chromium and arsenic during carbonisation of CCA treated wood, J. Jpn. Wood Res. Soc. 46 (2000) 587–595.
- [9] L. Helsen, E. Van den Bulck, M.K. Van Bael, G. Vanhoyland, J. Mullens, Thermal behaviour of arsenic oxides (As_2O_5 and As_2O_3) and the influence of reducing agents (glucose and activated carbon), Thermochim. Acta 414 (2004) 145–153.
- [10] ICSC, International Chemical Safety Cards data base (n.d.) Retrieved on 10 July, 2007 from <http://www.inchem.org/pages/icsc.html>.
- [11] J. Mullens, A. Vos, R. Carleer, J. Yperman, L.C. Van Poucke, The decomposition of copper oxalate to metallic copper is well suited for checking the inert working conditions of thermal analysis equipment, Thermochim. Acta 207 (1992) 337–339.
- [12] L. Helsen, E. Van den Bulck, H. Cooreman, C. Vandecasteele, Development of a sampling train for arsenic in pyrolysis vapours resulting from pyrolysis of arsenic containing wood waste, J. Environ. Monit. 5 (2003) 758–765.
- [13] F. Wells, Structural Inorganic Chemistry, 5th ed., Clarendon press, Oxford, 1984.
- [14] F. Pertlik, Strukturverfeinerung von Kubischem As_2O_3 (Arsenolith) mit Einkristalldaten, Czech. J. Phys. B 28 (1978) 170.
- [15] K.A. Becker, H. Karger, I.N. Stranski, Über die Stabilitätsbereiche der monoklinen Arsenikphasen Claudetit I und Claudetit II, Z. Phys. Chemie Neue Folge 44 (1965) 1.
- [16] F. Pertlik, Die Kristallstruktur der monoklinen Form von As_2O_3 (Claudetit II), Monat. Chem. 106 (1975) 755.
- [17] F. Pertlik, Verfeinerung der Kristallstruktur des Minerals Claudetit, As_2O_3 ("Claudetit I"), Monat. Chem. 109 (1978) 277.
- [18] R.H. Perry, C.H. Chilton, Chemical Engineers' Handbook, 5th ed., McGraw-Hill, New York, 1973.
- [19] R.C. Weast, CRC Handbook of Chemistry and Physics, The Chemical Rubber Co., Ohio, 1970.
- [20] R.H. Perry, C.H. Chilton, Chemical Engineers Handbook, 7th ed., McGraw-Hill, New York, 1997.

- [21] Barin, Thermochemical Data of Pure Substances, VCH Verlags-gesellschaft GmbH, Weinheim, 1989.
- [22] K. Ogusu, Y. Hosokawa, S. Maeda, M. Minakata, H. Li, Photo-oxidation of As_2Se_3 , Ag- As_2Se_3 , and Cu- As_2Se_3 chalcogenide films, *J. Non-Cryst. Solids* 351 (2005) 3132–3138.
- [23] E.R. Rushton, F. Daniels, The vapor pressure of arsenic trioxide, *J. Am. Chem. Soc.* 48 (1926) 384–389.
- [24] K.A. Becker, K. Plieth, I.N. Stranski, The polymorphic modifications of arsenic trioxide, *Prog. Inorg. Chem.* 4 (1962) 1.
- [25] J.H. Schulman, W.C. Schumb, The polymorphism of arsenious oxide, *J. Am. Chem. Soc.* 65 (1943) 878–883.
- [26] C. Duval, *Inorganic Thermogravimetric Analysis*, 2nd and revised version, Elsevier, Amsterdam, 1963, p. 425.
- [27] L. Helsen, E. Van den Bulck, J. Mullens, Low-temperature pyrolysis of CCA-treated wood: thermogravimetric analysis, *J. Anal. Appl. Pyrolysis* 52 (1999) 65–86.
- [28] P. Atkins, J. De Paula, *Physical Chemistry*, Oxford university press, New York, 2002, pp. 977–1012.