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Development of design criteria for integrated treatment technologies for thermal processing of end-of-life CCA-treated timber products – Volume 2

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3 CHARACTERISATION OF CONDENSED VOLATILES

In this section we describe experiments that were carried out to provide a detailed characterisation of the fate of arsenic that has been volatilised during combustion. Because negligible amounts of chromium and copper are volatilised under the conditions we studied, these elements are not considered here.

3.1 Experimental Regimes Investigated

Two sets of experiments were conducted to investigate the behaviour of volatilised arsenic as a function of gas temperature. Arsenic was volatilised on its own in the form of As_2O_3 and through the combustion of CCA-treated timber. The gas temperatures explored were as follows:

As_2O_3 volatilisation

- 315°C
- 600°C

CCA-treated timber combustion

- 600°C
- 810°C

Different temperatures were chosen for the two sets of experiments to give comparable concentrations of arsenic in the gas phase. At the same temperature, arsenic volatilisation occurs much more rapidly from As_2O_3 than from CCA-treated timber combustion.

3.2 Apparatus

The two main design considerations for this experimental apparatus were to ensure that the temperature of combustion/volatilisation could be accurately controlled and that any particulate generated from condensing volatiles could be sampled representatively. The first design constraint was satisfied through the construction of a precisely controlled gas heater. The second design constraint was satisfied by allowing enough space between the location at which combustion/volatilisation takes place and the sampling location for laminar flow to fully develop. The resulting experimental apparatus is shown in Figure 36.

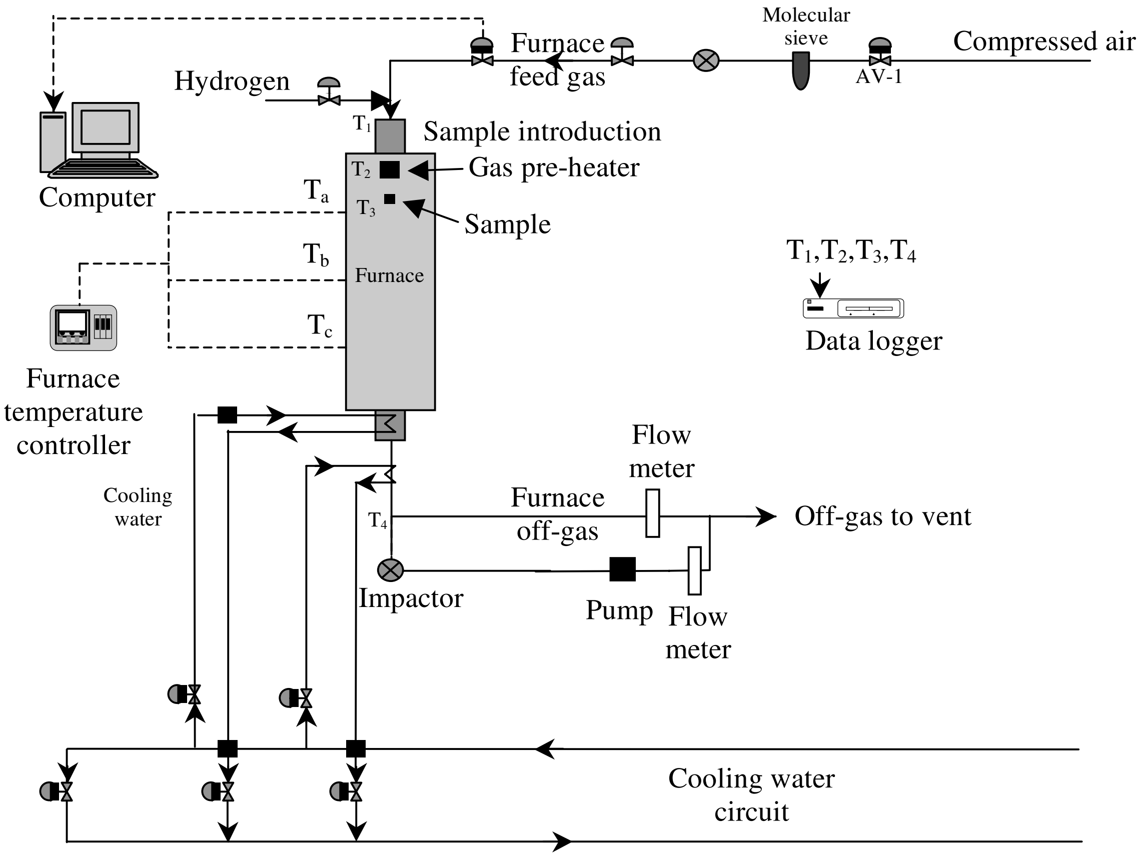

Figure 36: *Experimental apparatus for generation and study of volatilised arsenic.*

The apparatus can be divided into three sections as follows:

1. Gas pre-mixing and heating
2. Sample introduction
3. Particulate sampling

3.2.1 Gas pre-mixing and heating

3.2.1.1 Heating reaction

Gas heating in the experimental apparatus is accomplished using the following exothermic reaction:

$$2H_2 + O_2 \xrightarrow{PdCatalyst} 2H_2O \qquad \Delta H = -285.9\,kJ/mol$$

Using this reaction, a range of gas temperatures can be generated by varying the amount of hydrogen that is mixed with air as shown in Figure 37. It is important to note that as the original concentration of hydrogen increases, the concentration of oxygen in the resulting hot gas decreases and the water vapour concentration in the hot gas increases. This means that the oxygen concentration in the gas for combustion used in different temperature experiments will be different, but it was concluded in the previous study (Stewart *et al.,* 2004) that combustion of a wood sample in 10% O_2 produces essentially the same extent of arsenic volatilisation as combustion in 21% O_2.

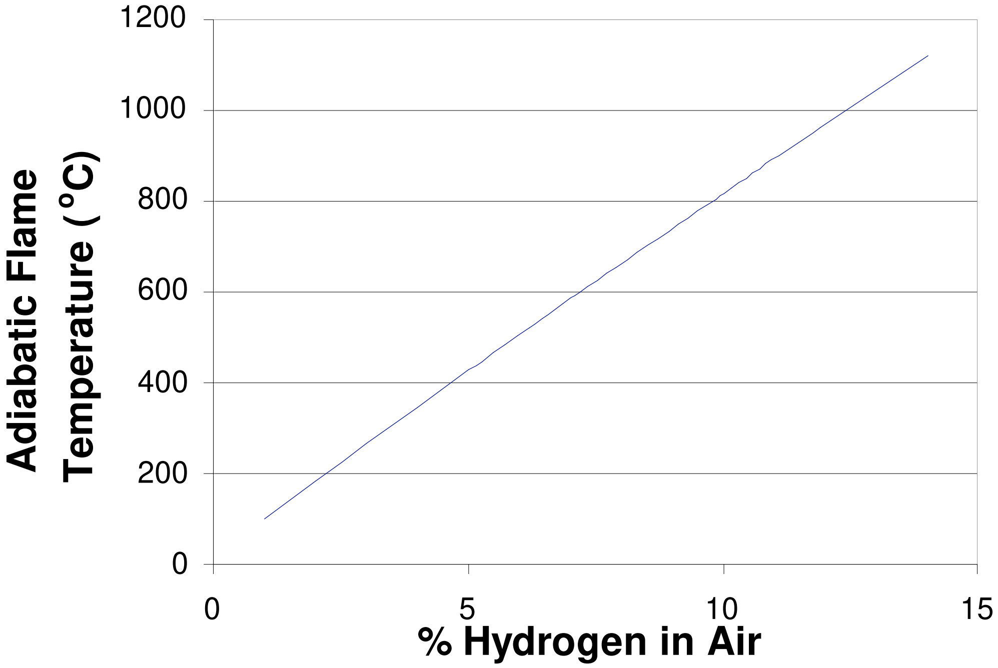

Figure 37: *Adiabatic flame temperature for hydrogen in air*

3.2.1.2 Gas pre-heater

The gas pre-heater is shown in Figure 38. The catalytic combustion of hydrogen takes place inside the top of the furnace in an annulus made up of concentric 50 mm OD Alsint (99% Al_2O_3) and 25 mm OD Pythagoras (60% Al_2O_3) ceramic tubes. The catalyst is 0.5% palladium supported on alumina pellets and is approximately 150 mm deep to ensure complete reaction of the hydrogen. The purpose of these concentric tubes is to allow room for both the gas heater and sample introduction and will be discussed further in Section 3.2.2. There are two reasons for the placement of the catalyst inside the furnace. The first reason is that the reaction between hydrogen and oxygen does not occur on the catalyst below approximately 40°C. The second reason is that the furnace is very well insulated to prevent heat loss.

The air and hydrogen mixture enters into the furnace in eight 1/16” capillary tubes. The purpose of these tubes is to evenly distribute the hydrogen/air mixture over the catalyst while at the same time ensuring that the speed of the gas mixture is high enough to prevent flashback from the combustor.

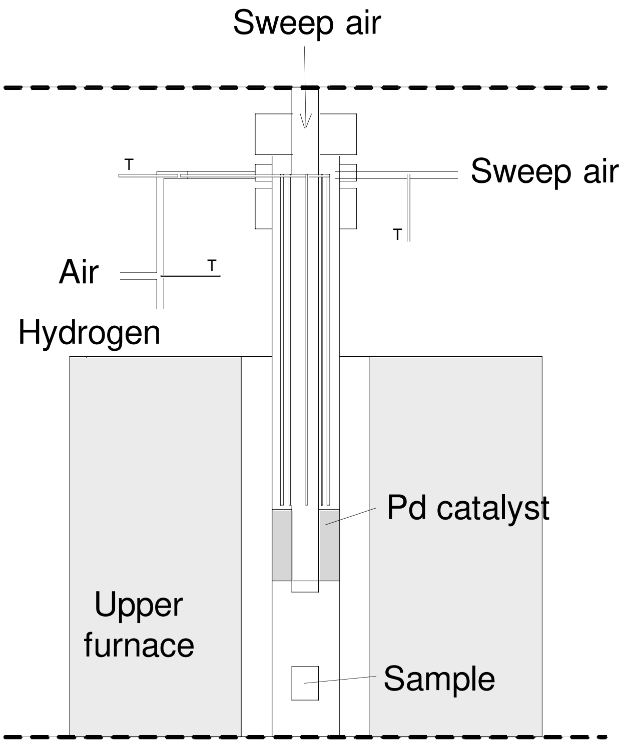

Figure 38: *Detail of the gas pre-heater*

3.2.1.3 Gas mixing

Mass flow controllers are used to mix 16 slpm of air and a variable amount of hydrogen for the gas pre-heater. A sweep flow of air (1.5 slpm) is also passed through both the sample introduction section of the apparatus and through the upper section of the annulus to ensure that both the hydrogen fed and the volatiles generated during combustion do not diffuse into these sections of the apparatus. The temperature and composition of the gas for combustion results from mixing the gas from the pre-heater with the sweep air and is summarized in Table 13.

Table 13: *Gas flows and temperatures for preheating and combustion*

Temperature at sample (°C)	Gas for pre-heater		Total sweep gas (slpm)	Gas for combustion	
	Air (slpm)	H_2 (slpm)		O_2 concentration	H_2O concentration
315	16.0	0.9	3.0	18.6%	2.4%
600	16.0	1.85	3.0	16.1%	4.9%
810	16.0	2.55	3.0	14.3%	6.7%

3.2.2 Sample Introduction

Two sample introduction systems were designed to enable weight and temperature measurements of the wood sample during combustion. Samples of As_2O_3 were volatilised using the temperature measurement introduction system.

3.2.2.1 Weight measurement

The sample introduction system required for measurement of the weight of the burning sample is shown in Figure 39. The design requirement for this section was the ability to immediately transfer the sample from the cool section of the rig to the hot section of the rig while maintaining a sealed rig. This ensured that combustion took place at the desired temperature without allowing gases to escape into the laboratory.

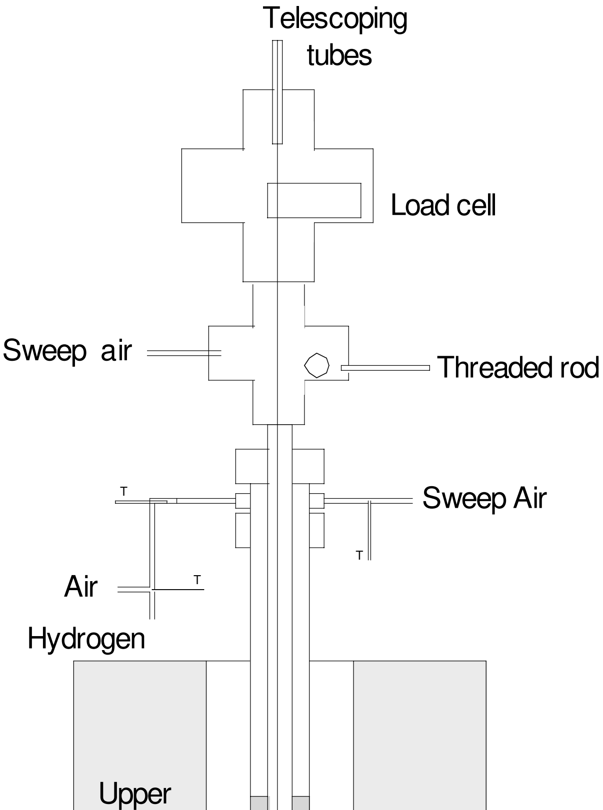

Figure 39: *Sample introduction system for weight measurement.*

The sample introduction system was constructed from Varian vacuum fittings chosen because they are lightweight, easily removable and re-sealable, and provide the necessary extra room within the apparatus. The vacuum fittings are joined together by a clamp and O-ring system ensuring that the apparatus does not leak when operational.

A 50mm lightweight aluminium vacuum cross fitting is located on top of the apparatus to house the load cell used for the mass measurement (Transducer Techniques GSO series 10g precision load cell, accurate to 0.05g). A 38mm cross is fitted below this and is used to hold the sample in a cool location before it is lowered into the combustion zone. The crosses are connected to a 25mm 60% alumina Pythagoras ceramic tube which descends axially through a 50mm 99% alumina Alsint ceramic tube into the top of the furnace. The annular space between these tubes holds the catalyst used for the gas pre-heating, as described above.

A sample basket, constructed of inconel mesh, hangs on a 0.1 mm chromel wire through the 25mm tube. The wire has a bead which when engaged in the load cell transfers the weight of the sample basket and contents to the load cell for measurement. An extension of the wire is attached to telescoping tubes fitted to the top of the upper aluminium cross fitting. Extending and retracting the telescoping tubes raises and lowers both the bead and the sample basket so that the load cell can be engaged or disengaged as needed. The resulting configuration allows room for both the sample to be dropped into the hot section of the rig through the 25 tube and the gas for combustion to be preheated in the annulus formed by the 25 and 50 mm tubes. Combustion of the sample takes place in the 50mm tube, which continues through the furnace and is attached to the gas sampling system (see Section 3.2.3.1).

Sample introduction is accomplished in a four step process which ensures that the rig stays sealed during the actual combustion. The rig is opened at the lower aluminium cross and the sample is placed inside where it rests at close to ambient temperature. The rig is then resealed and the telescoping tube is raised to bring the inconel mesh basket up inside the 25mm tube. This stabilises the basket and removes the weight from the load cell to prevent damage incurred when the wooden sample drops into the basket. A threaded rod is then used to push the sample out of the 38 aluminium cross fitting and into the 25mm ceramic tube. Once the sample has landed in the basket, the telescoping tube is lowered, bringing the sample into the hot zone and transferring the weight of the sample and basket onto the load cell.

3.2.2.2 Temperature measurement

The sample introduction system required for the temperature measurement of the burning particle is shown in Figure 40. The system was again designed to ensure that the sample could be lowered into the hot section of the rig quickly to ensure that combustion takes place at the desired temperature.

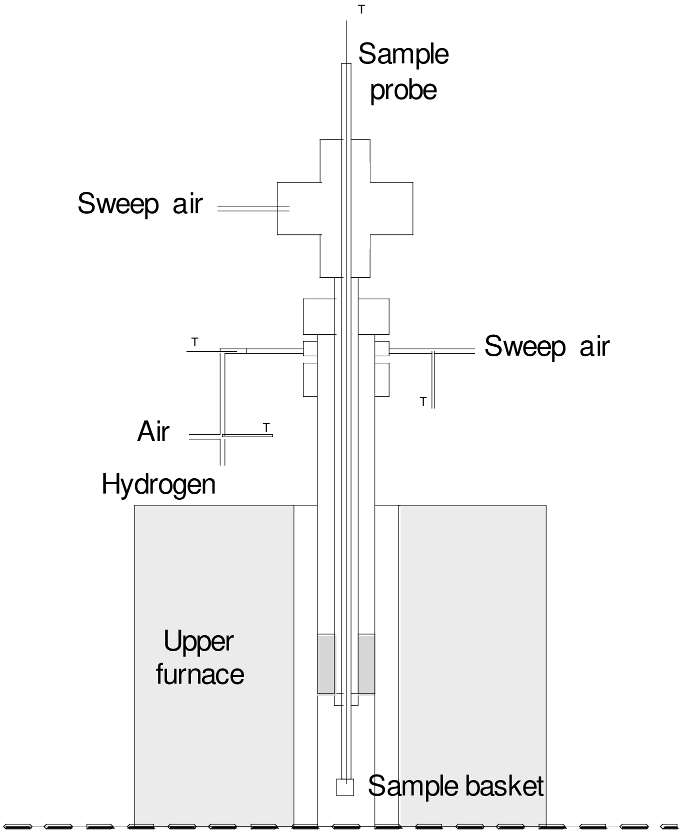

Figure 40: *Sample introduction system for temperature measurement*

The sample basket is attached to a ¼” stainless steel tube which can be raised and lowered through a fitting on the aluminium cross. A type K bare-bead thermocouple descends through the stainless steel tube to the sample basket where it can be embedded in the wooden sample. The stainless steel tube can be raised and lowered through the 25mm ceramic tube by adjusting a fitting on the top of the aluminium cross and can easily be removed entirely from the apparatus via a clamp and O-ring attachment. This allows for easy loading of the sample. The sample sits up inside the aluminium cross until the temperature of the gas for combustion has reached equilibrium at which point the stainless steel tube is lowered and the sample enters the hot zone.

For the As_2O_3 experiments, the As_2O_3 powder is placed in a pure alumina crucible which fits into the sample basket. The crucible is deep enough to ensure that the powder is not entrained in the flowing gas.

3.2.3 Particle sampling

The particle sampling method constructed as part of the experimental apparatus (Figure 41) has been designed to capture a representative sample of the particles present in the combustion gas. This part of the apparatus can be divided into two parts: the sampling probe and the particle collection.

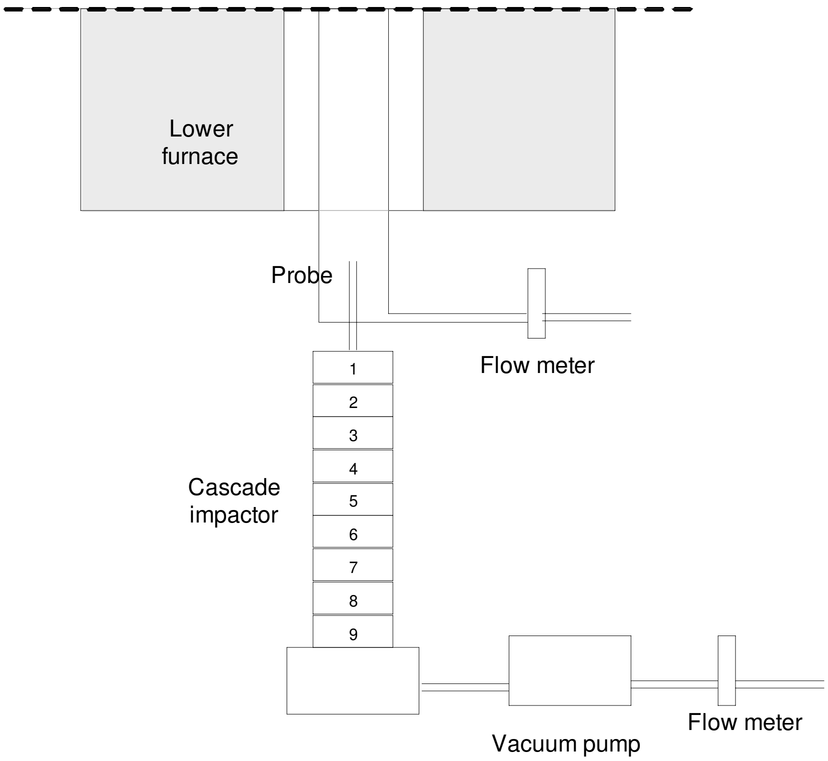

Figure 41: *Particle sampling system*

3.2.3.1 The sampling probe

The sampling probe itself is quite simple but the theory behind its design is a bit more complex. It consists of a 200 mm length of 3/8” (19mm) stainless steel tubing that extends into the 50mm ceramic tube. The tube walls where the gas enters the probe have been thinned to less than 0.5 mm thickness to ensure minimal disturbance of flow at the nozzle entrance.

The efficiency with which a particle is collected by a sampling probe is a function of the Stokes number and the ratio of the velocity of the gas in the sampling probe to the velocity of the gas in the surrounding area, provided that the sampling probe has thin walls (Belyaev and Levin, 1974). The Stokes number is defined as follows:

$$St = \frac{(\rho_p - \rho_g) d_p^{\,2} u}{18 \mu D} \qquad \textit{Equation 2}$$

where $_p$ and $_g$ are the densities of the particle and the surrounding gas, d_p is the diameter of the particle, u is the velocity of the gas, is the viscosity of the gas and D is the diameter of the probe. What this means is that the collection efficiency of a specific size of particle depends on how well the particles follow streamlines in the gas (Stokes number) and how much these streamlines are bent approaching the nozzle entrance (velocity ratio). Particles with a Stokes number less than 0.05 tend to follow streamlines quite closely which in the case of As_2O_3 particles correlates to a diameter up to approximately 7 m. The size distribution of particles collected through a narrow nozzle at high relative velocity will show a bias towards smaller particles that can follow the streamlines into the nozzle and the size distribution of particles collected through a wide nozzle at low relative velocities will show a bias to larger particles that do not follow the streamlines leading away from the nozzle.

The sampling flow rate requirement for the particle collection as dictated by the particle sampling method is 1 slpm. The sampling probe diameter chosen for the experiments was 6 mm. This corresponds to a ratio of the velocity of the gas in the probe to the surrounding gas of 0.8. The particle size distribution collected through this probe shows a bias towards particles with diameters greater than 7 m with the bias increasing with increasing diameter. The size distribution of arsenic particles was expected to be sub-micron so this bias would not affect the results.

3.2.3.2 Particle Collection

A cascade impactor is used to separate the sampled particles into groups based on particle size. An impactor operates on similar principles as discussed in the sampling probe section. The ability of a particle to follow a streamline depends on its size, mass and velocity. The principle behind impaction involves separating particles of equal velocity by how much of a bend in the streamline they can follow and hence separates them by size/mass. The velocity of the gas and particles is increased through a constriction in flow diameter and then the flow is forced to bend around a disk placed perpendicular to the direction of flow. The narrowness of the constriction and the proximity of the disk to the constriction create a size cutpoint above which the particles will not follow the bend but will instead impact onto a removable substrate placed over the disk. A cascade impactor consists of a number of impactor plates in series with decreasing cutpoints. The uppermost stage of the cascade impactor ‘impacts’ out the largest particles and each subsequent stage traps increasingly smaller particles.

The cascade impactor used in these experiments is a PIXE International 9 stage cascade impactor with cutpoints of 16, 8, 4, 2, 1, 0.5, 0.25, 0.12, and 0.06 m followed by a final filter. The largest cutpoint stage, or the first stage that the combustion gas reaches, is called stage 1 and the subsequent stages are 2 through 9. The cutpoints refer to the aerodynamic diameters of the particles. The actual diameter of the particle is related to the aerodynamic diameter through the following expression valid for spherical particles:

$$d_{actual} = d_{aerodynamic}\left(\frac{\rho_{water}}{\rho_{As_2O_3}}\right)^{1/2} \qquad \textit{Equation 3}$$

The aerodynamic and actual cutpoints of the stages are summarized in Table 14.

Table 14: *Summary of the cutpoints of the cascade impactor*

Stage	Aerodynamic cutpoint (m)	Actual cutpoint (m)
1	16	8
2	8	4
3	4	2
4	2	1
5	1	0.5
6	0.5	0.25
7	0.25	0.12
8	0.12	0.06
9	0.06	0.03

Removable polycarbonate and aluminium impactor substrates measuring 25 mm in diameter were used for particle collection depending on the further analysis required of the sample (discussed further in section 3.3).

The impactor was wrapped with heating tape and insulated. A temperature of 40°C was maintained to ensure that water vapour did not condense inside the impactor during the experimental runs.

3.3 Analytical procedures

3.3.1 Sample preparation

The same CCA-treated pole sample was used as in the work described in the studies of arsenic volatilisation (Section 2). The small block samples needed for the present studies were cut from the middle of the pole cross-section to ensure that the samples contained As, Cr, and Cu in constant ratios and reasonably constant amounts.

3.3.1.1 Weight measurements

The size of the wood sample used for weight measurements was dictated by the method of sample introduction as described in Section 3.2.2.1. All dimensions of the sample had to be smaller than the inside diameter of the 25mm ceramic tube to ensure that it would pass freely through the tube. The samples consisted of wooden cubes with a face length of 10 mm, weighing between 0.2 and 0.4 grams.

3.3.1.2 Temperature measurements

For these experiments, sample loading into the sample basket takes place outside the rig (see Section 3.2.2.2) so a larger sample could be used. The larger sample size was necessary to increase the amount of arsenic volatilised to help with particle analysis. Samples were cut to resemble thick matchsticks with a square face approximately 1 cm in length and an overall length of approximately 5 cm. Sample mass ranged from 1-2 grams.

3.3.2 *Particle capture*

Particles were sampled using the particle collection system described in Section 3.2.3.2. The furnace and the hydrogen and air mass flow controllers were turned on and the temperature in the apparatus was allowed to reach equilibrium. Prior to sampling, the vacuum pump was turned on so that the temperature of the sampling line and impactor could also reach steady state. Once steady state was reached, the sample was dropped into the furnace. The vacuum pump was turned off after three minutes of sampling.

3.3.3 *Particle characterization from As_2O_3 volatilisation*

Particles were collected on 25mm diameter polycarbonate impactor substrates. These substrates were removed from the impactor, mounted on aluminium disks and sputter coated with a thin layer of gold for SEM analysis. SEM analysis was conducted on a Philips SEM505 machine located at the Electron Microscope Unit at the University of Sydney.

3.3.3.1 XRD Analysis

XRD analysis was used to identify the form of arsenic present on the impactor substrates. A Siemens XRD-5000 X-ray diffractometer was used to record X-ray diffraction spectra from aluminium impactor substrates over the angular 2 range of 10–45º.

3.3.3.2 Analyses of the particles on impactor stage 9

Experiments were conducted to determine whether the particles present on stage 9 of the impactor were formed in the gas phase or whether they grew directly on the impactor substrate. Seven pieces of aluminium foil were attached to a 25 mm diameter aluminium impactor substrate. The substrates were labelled 1-6 with the 7th substrate used as a control. Over the course of six volatilisation runs, the substrate with the corresponding number to the run was removed after that run and replaced with a fresh substrate. The 7th substrate was replaced after each run. Pictures of the particles were taken using the SEM and the particles were sized using a program called Scion Image which measured the area of each particle in the picture.

3.3.4 *Particle characterization from the combustion of CCA-treated timber*

Preliminary experiments were conducted in the same manner as the characterization of the particles from As_2O_3 volatilisation. However, the large quantities of soot captured made the identification of particulate arsenic impossible in the analysis of the SEM pictures so a different method was used.

The particles were captured on 25 mm diameter aluminium impactor substrates. These substrates were removed from the cascade impactor and placed in a plasma asher for 5-6 hours to remove the top layer of soot. The substrates were then coated with a thin layer of gold and analysed using the SEM.

3.3.5 Mass distributions of arsenic in the particulate phase

The particles were captured on polycarbonate impactor substrates. Each substrate was digested with 3.3 mL of reagent grade 70% Nitric Acid (HNO_3) and 6.7 mL of reagent grade 70% Perchloric Acid ($HClO_4$). The Milestone™ Ethos SEL microwave solvent extraction labstation was employed to digest samples. The heating procedure consisted of heating the sample to 200ºC in 30 minutes and retaining at 200ºC for 15 minutes for the completion of the digestion. Afterwards, the sample was transferred into a volumetric flask and diluted to 200 ml for elemental analysis using a Varian Vista AX CCD Simultaneous Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) machine.

The mass of arsenic on each impactor stage was calculated using the concentrations measured by ICP-AES. While ICP-AES is a very sensitive method for arsenic detection, the sample preparation method diluted significantly the already small amount of arsenic present on the impactor stages. This meant that only the stages with larger amounts of arsenic recorded values above the limit of detection (0.05 ppm). Impactor stages that had a mass of arsenic below the limit of detection for this method were assigned a mass of arsenic of 0 on the mass distributions.

3.4 Results and Discussion

In this section we present the results obtained from the experiments designed to characterize the particles present in the gas after the combustion of CCA-treated timber. We will first discuss the results of the weight and temperature measurements of the burning particles followed by consideration of the physical characteristics and composition of the particles. We conclude with a discussion of the size distribution of particles condensed from volatilised arsenic and draw conclusions on the mechanisms of particle formation.

3.4.1 Mass and Temperature Measurements

The mass of a CCA-treated timber 0.3 g cubic sample burned at 500ºC was measured using the load cell and is shown in Figure 42. There is an initial period of unsteady weight immediately after introduction of the sample. The sample weight appears to remain constant initially but this is followed by accelerating weight loss. The period of rapid weight loss ends abruptly as combustion finishes. The combustion time appears to be in the range of 95 seconds.

Figure 43 shows the temperature profiles of two rectangular prism shaped samples with initial weights of 1.62g and 2.55g respectively burned at 600°C. The thermocouple for temperature measurement is embedded into the wooden sample before the sample is introduced into the hot section of the furnace.

Figure 43 highlights five stages in the combustion process. The first stage consists of the initial warming of the sample. The second stage is a plateau in the temperature record at 100°C corresponding to the evaporation of the water content of the wood. The third stage involves the rapid heating of the particle and shows that the temperature of combustion is roughly 300°C above the gas temperature. The fourth stage consists of a plateau where the majority of the combustion takes place. After combustion, the sample cools down to the surrounding gas temperature in the fifth stage.

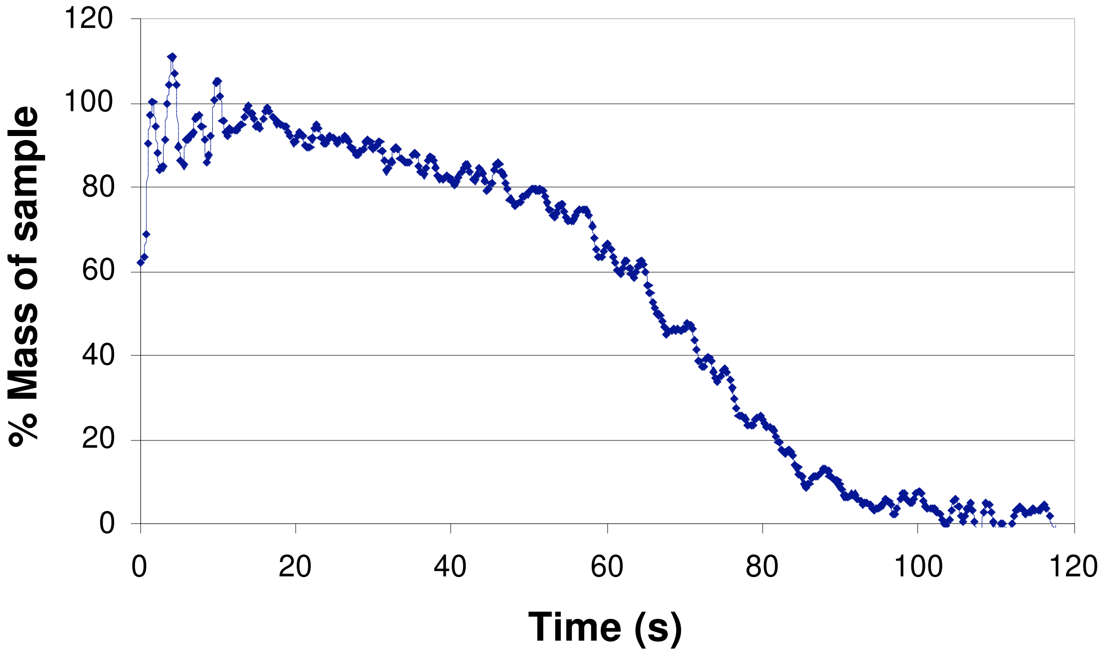

Figure 42: *Mass of a cubic 0.3g burning sample of CCA-treated timber at 500ºC*

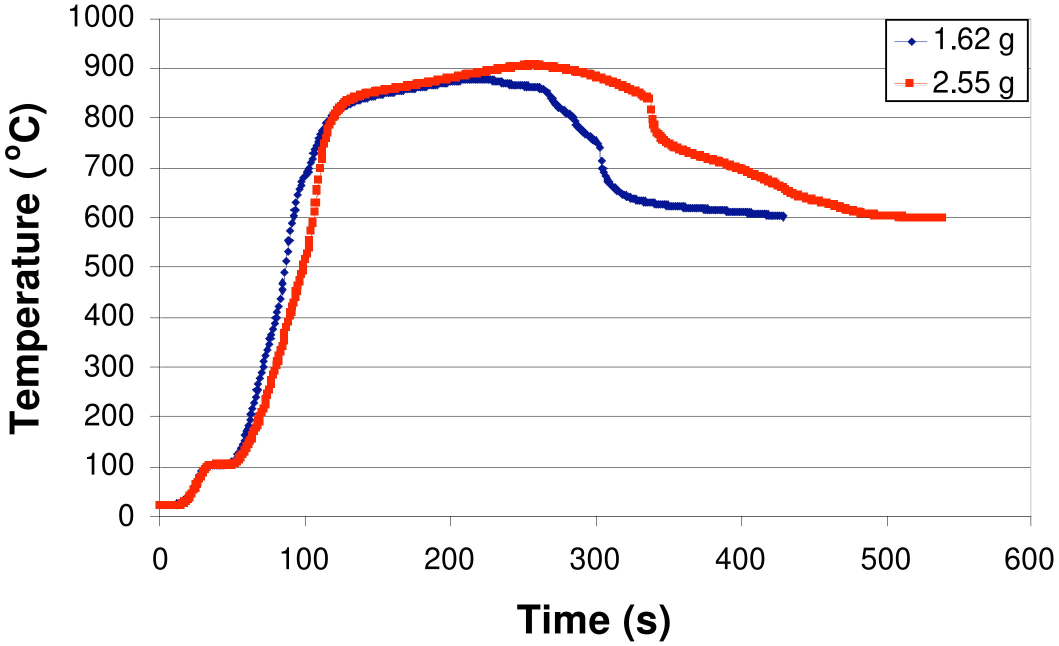

Figure 43: *Temperature of a two rectangular prism CCA-treated timber sample burned at 600°C, as measured by a thermocouple buried inside the sample*

Comparing the results of the mass and temperature experiments, the first stage shown in the temperature measurement coincides with the initial period in Figure 42 where no mass loss is observed. A gradual increase in the weight loss observed in Figure 42 coincides with stages 2 and 3 in Figure 43 and the region of greatest weight loss occurs during the combustion in stage 4. Cooling (stage 5) occurs when there is no more weight loss of the sample, or in other words, combustion is complete.

The temperature of the wood combustion is well above the temperature at which unbound As_2O_3 and As_2O_5 would volatilise. From the results discussed in our previous report Stewart *et al.*, 2004), we would expect that approximately 60% of the arsenic remains in the ash after combustion at this temperature.

3.4.2 Physical description of the collected particles

The particulate generated during experiments was collected on a cascade impactor as described in 3.3.2. Preliminary analyses of impactor substrates from CCA-treated timber combustion showed large piles of fine particles such as is shown in Figure 44 – note the bright length at the base of the image corresponds to a dimension of 10μm.

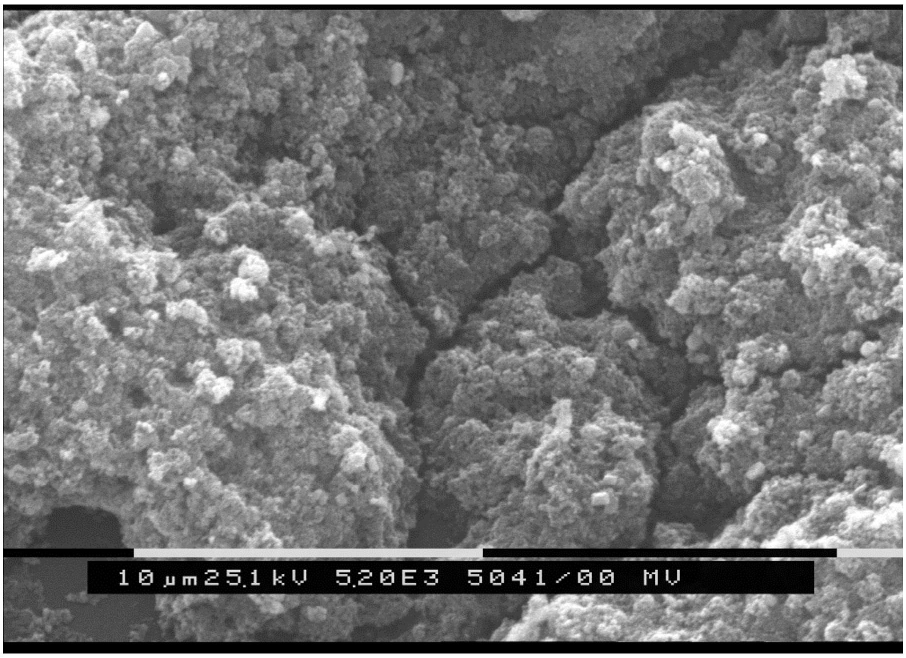

Figure 44*: SEM image of stage 6 of the cascade impactor after combustion of CCA-treated timber.*

EDS analysis confirmed the presence of arsenic on the impactor stages, but it was impossible to differentiate visually between arsenic and soot especially since the vast majority of the particulate is actually soot. Therefore, two approaches were taken in order to learn more from the SEM analysis of particles generated during the experiments.

The first approach involved volatilising As_2O_3 on its own. This provided a simple system in which to investigate the behaviour of volatilised arsenic oxide as it nucleates and condenses. Analyses of the resulting particles gave a basis for comparison with the combustion of CCA-treated timber where the arsenic would de-volatilise in a much more complicated system. The second approach involved reacting away some of the soot off of the impactor substrates from CCA-treated timber combustion to see what remained. Arsenic is the second most common element of the particulate and hence would be much more visible without soot, the most common element.

3.4.2.1 As_2O_3 volatilisation

For both the experiments conducted at 315°C and 600°C, polycarbonate impactor substrates from each stage of the cascade impactor were analysed using SEM and the resulting images are presented below.

As_2O_3 volatilisation at 600ºC

Figure 45 gives an overview of the particles present on stages 1 through 9. The morphologies of the particles on the impactor stages were found to be repeatable with the exception of stage 1 as will be discussed below.

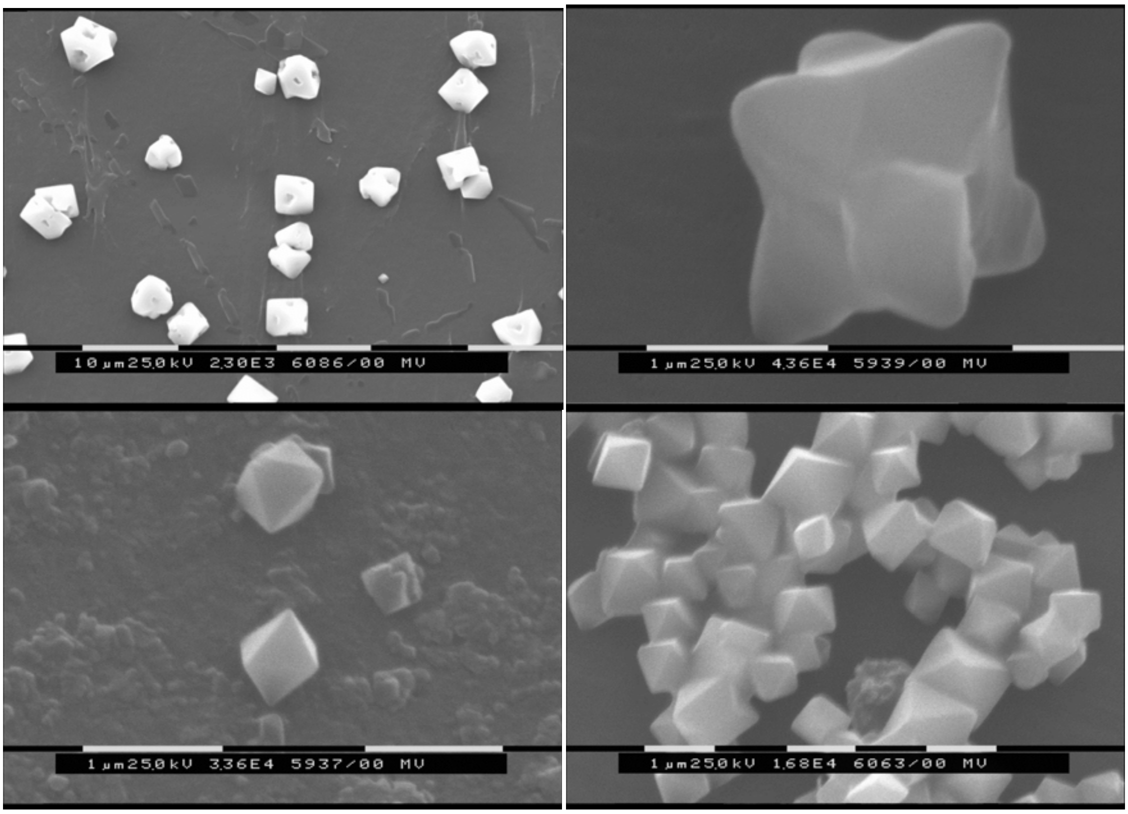

Figure 45: *Clockwise from top left: particles from stage 1; a particle from stage 4; particles from stage 5; particles from stage 6*

The first thing that can be seen clearly from these pictures is that the arsenic forms crystals as it makes the transition from gas to solid phase. Experiments were conducted at vapour pressures that lead to sublimation/desublimation rather than transition through a liquid phase as they were designed to reflect vapour pressures that would occur during the combustion of CCA-treated timber. XRD analysis has identified these crystals as As_2O_3 (see Figure 46).

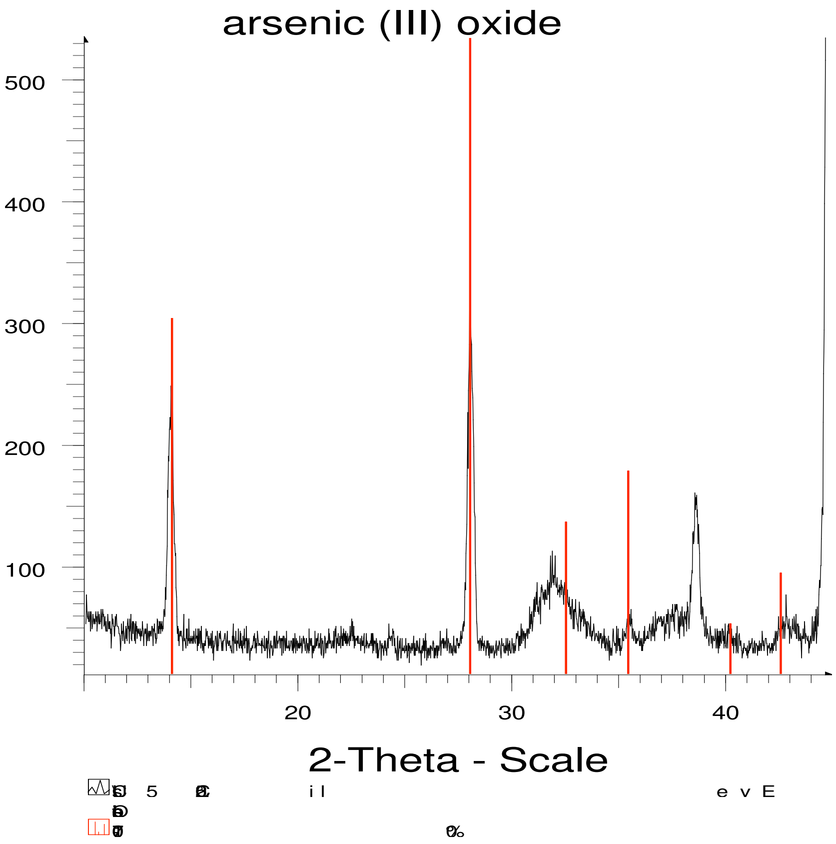

Figure 46: *XRD analysis of the crystals present at stage 5 showing the correspondence of observed peaks to the peaks associated with* As_2O_3*. Some interference from the aluminium sample holder is seen after 2-Theta = 30.*

There were three basic types of crystal shape found and some stages had very few or no particles. Stages 8 and 9 typically had no particles. Octahedral crystals were found between stages 5 and 7 with the majority of the particles being found on stage 5. Most particles on stages 3 and 4 have six elongated spikes in a similar arrangement to the particle shown in Figure 45 (top right). Stage 2 typically has few particles, but they are of a similar shape to the particles observed on Stage 1.

The majority of the particles observed were found on the 1st and 5th impactor stages with a marked difference in particle morphology and the way in which the particles are grouped between these two stages.

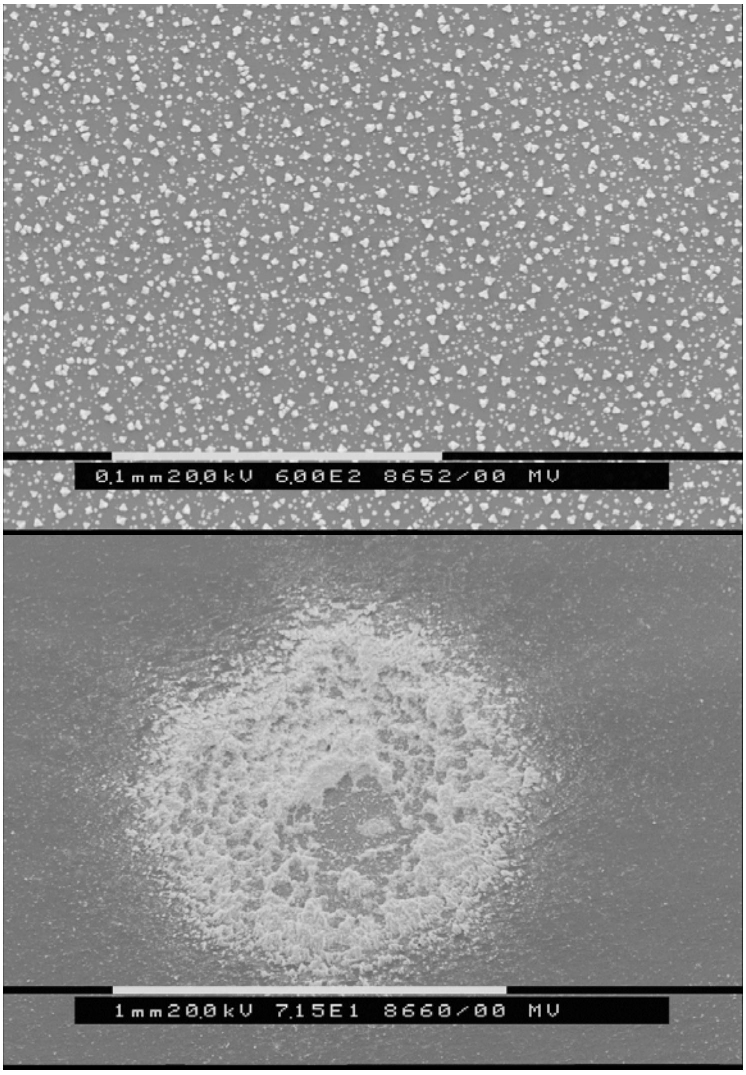

Figure 47: *Distant view of the particles present on stage 1 (top) and stage 5 (bottom)*

Figure 47 shows that the particles on stage 5 are grouped as a pile present directly underneath the nozzle entrance to the stage. This pile is actually visible to the naked eye when the impactor is disassembled after a run. In contrast, the particles present on stage 1 are not visible until the substrate is placed under the electron microscope. There is a slight tendency for the particles to be concentrated in the centre beneath the nozzle but the particles are actually found in a single layer across most of the substrate.

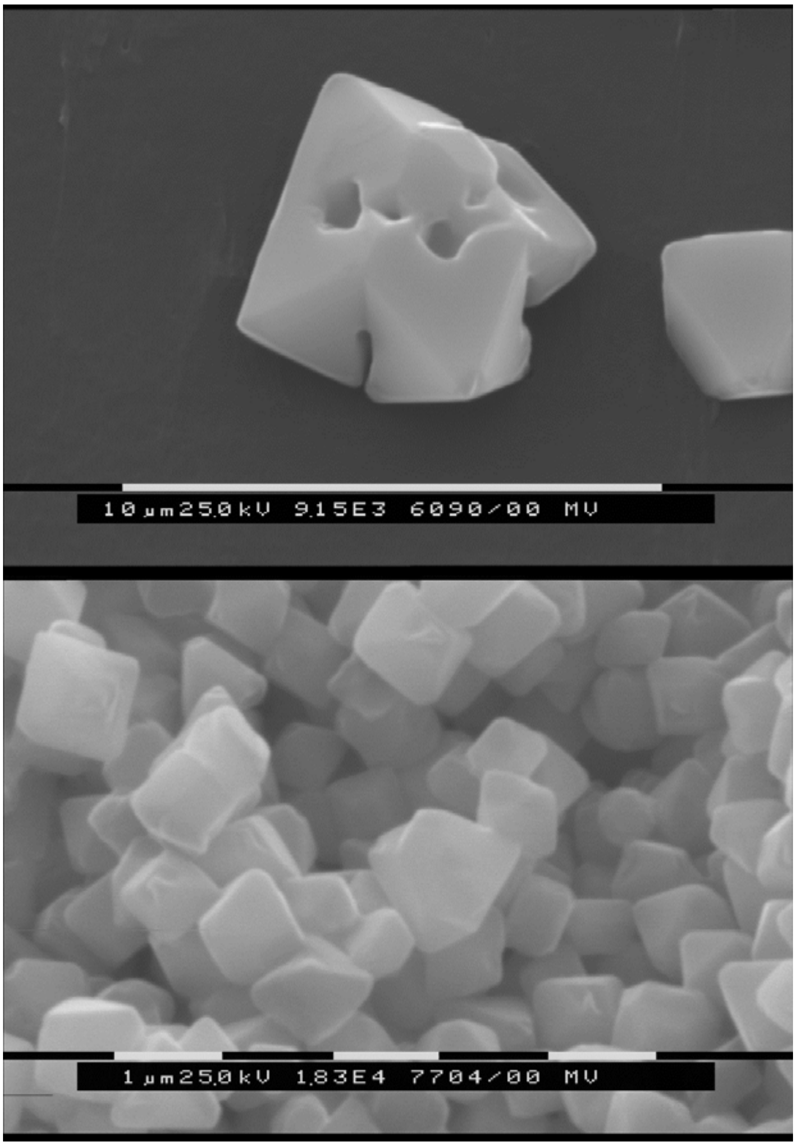

Figure 48: *Close-up view of the particles present on stage 1 (top) and stage 5 (bottom)*

The particles present on stage 5 are consistently octahedral in shape as shown in Figure 48. Also shown in Figure 48 is a close-up of one of the types of particles commonly seen on stage 1. The particles found on stage 1 exhibit less consistent behaviour than the particles found on the other impactor stages. Smaller particles on this stage tend to resemble truncated octahedrons. Larger particles tend to exhibit holes and often bear some resemblance to tetrahedrons or truncated octahedrons.

Volatilisation at 315°C

Particles were only observed on stages 1 and 2 from the lower temperature volatilisation of As_2O_3. They were similar in morphology to those found on stage 1 from the volatilisation of As_2O_3 at 600°C and are shown in Figure 49. Stage 1 had significantly more particles than stage 2.

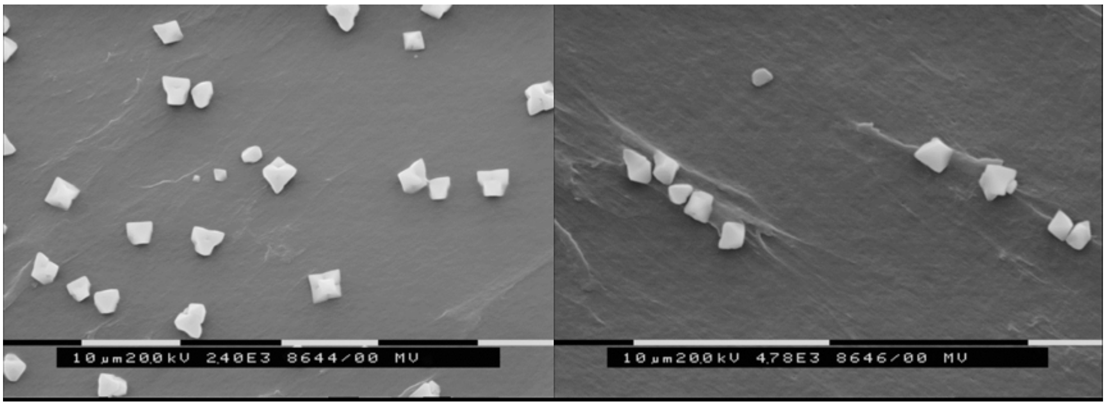

Figure 49: *Particles found on stage 1 (left) and stage 2 (right) from the volatilisation of* As_2O_3 *at 315°C*

3.4.2.2 Discussion of results from As_2O_3 *volatilisation*

The particles observed on the impactor substrates from the two experiments do not necessarily provide a consistent story explaining particle formation and growth. There are three observations that suggest that there might be a different mechanism for particle growth of the larger particles (stage 1) than particle growth of the smaller particles (stage 5):

- Only larger particles were formed from the volatilisation of As_2O_3 at 315°C
- In the experiments conducted at 600°C, the particles on stage 5 are trapped in a pile but the particles on stage 1 are spread out in a single layer
- The shape of some of the particles present on stage 1 suggests surface growth.

The first two points are evident directly from the results but the third point requires more explanation. When crystals grow on a surface, there are three basic possibilities for how the surface will affect their shape depending on the adhesion energy of the crystals to the surface. The crystals can either grow on top of the surface with little interaction with the surface, they can grow as a thin layer over the entire surface, or they can have a level of interaction somewhere in between where the end product looks as if the crystal has actually sunk into the surface (Mutaftschiev, 2001). Pictures of the particles on stage 1 (see Figure 45 and Figure 48) show that many of the particles do exhibit what appears to be some form of truncation suggesting that they might be growing on a surface.

Particle growth on stage 1

The results from As_2O_3 volatilisation suggest that it is likely that the particles on stage 1 are being formed by a different mechanism from that giving rise to the smaller particles on the lower stages and that this mechanism might be surface growth directly on the impactor stage. In order to explore this hypothesis, a series of experiments were conducted whereby impactor substrates on stage 1 were left in place for between 1 and 6 volatilisations of As_2O_3 at 600°C and the particle number and sizes were compared. The theory behind this experiment was that if the particles had already grown in the combustion gas before the impactor, then the number of particles would increase on substrates subjected to an increasing number of runs and the particle size would remain similar. However, if the particles were in fact growing on the substrate, then the number of particles would stay the same with an increasing number of runs and the particle size would increase.

Figure 50 shows the particle size distribution for each of the cumulative run experiments from 1 to 6 runs. These results confirm that the particles present on stage 1 are actually growing on the impactor stage. The area distributions (Figure 50) show increased spread with increasing number of runs as well as a general trend of increasing particle size with increasing number of runs. This trend is shown more clearly in Figure 51 where it is plotted alongside the average number of particles found.

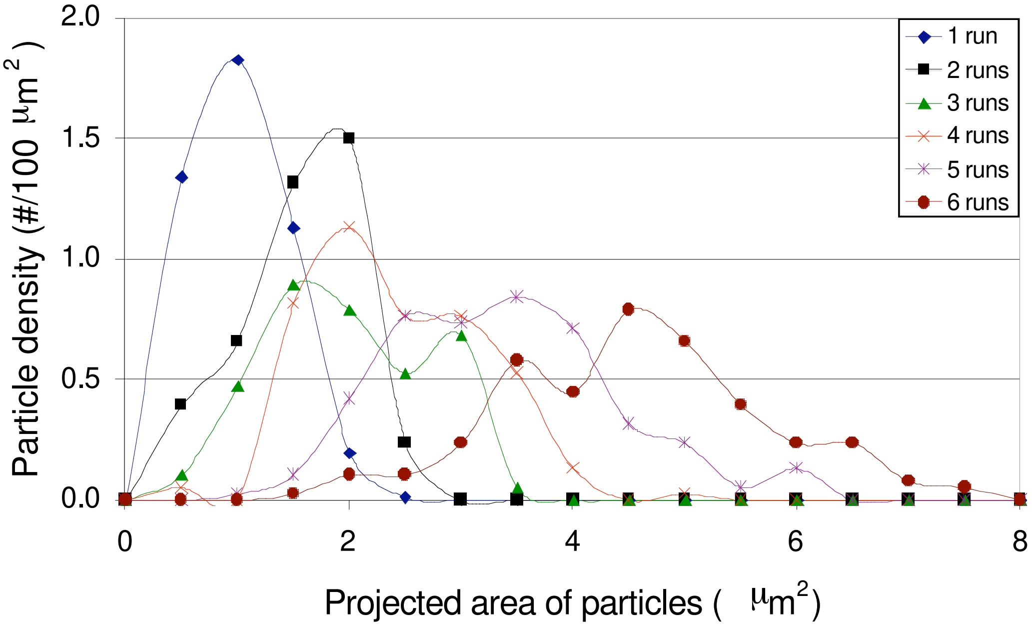

Figure 50: *Size distributions of cumulative run experiments*

The particle density in Figure 51 stays relatively constant between experiments and the average particle area on the SEM pictures of the substrates increased with an increasing number of runs. This confirms that new particles did not deposit onto the substrate, but instead that vapour condensed on previously existing particles.

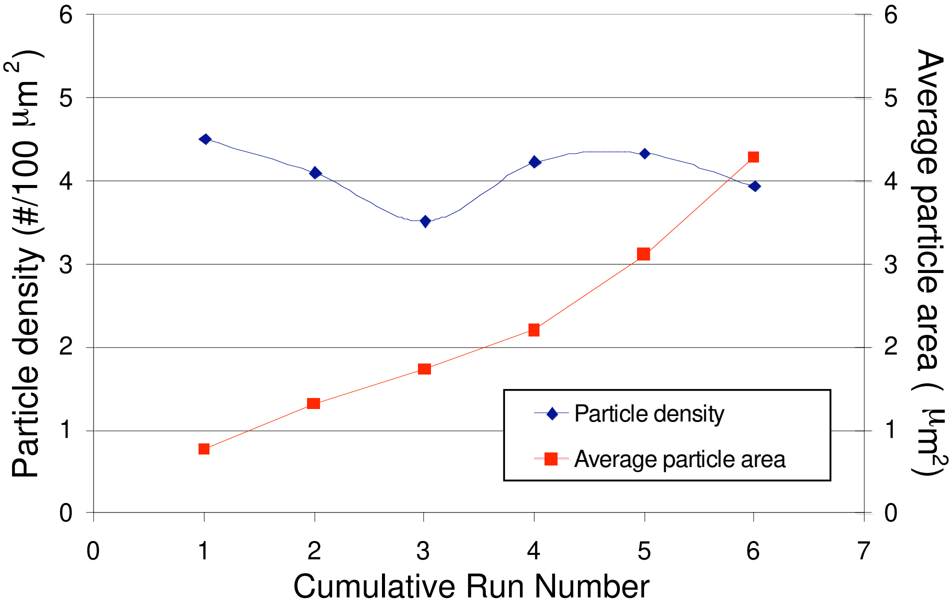

Figure 51: *Particle density and average size for 1 through 6 cumulative runs*

3.4.2.3 Volatilised arsenic from CCA-treated timber combustion

In order to see the arsenic more clearly, particulate samples were captured on aluminium substrates and placed in a plasma asher. The purpose of the plasma asher was to remove the top layer of soot in order to show what remained. Stage 1 had little to no soot and the remaining arsenic crystals are shown in Figure 52.

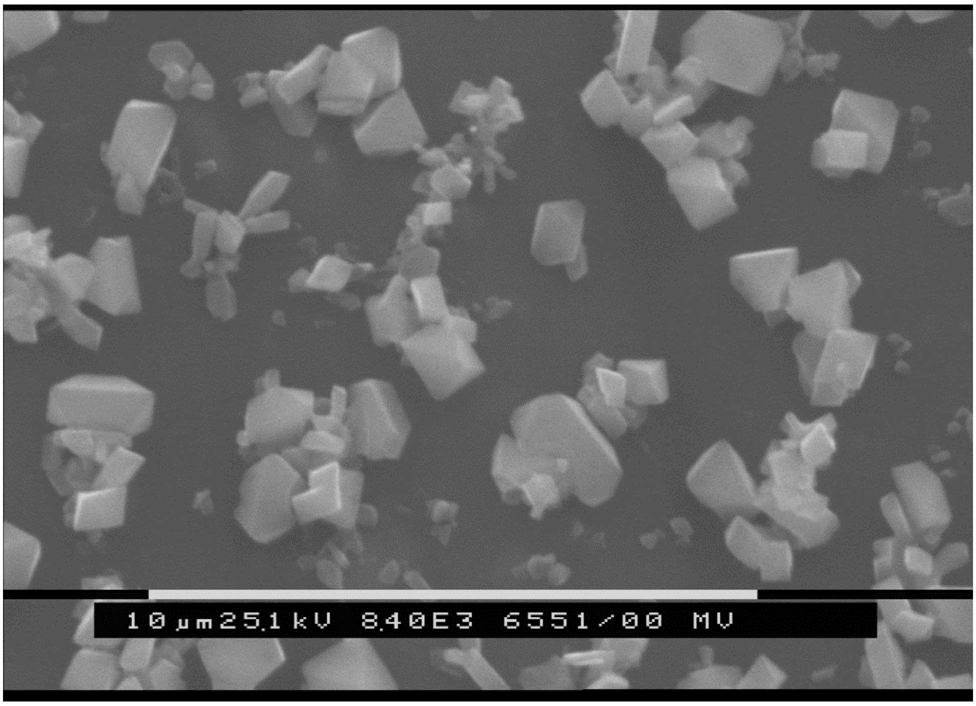

Figure 52: *Arsenic crystals present after plasma ashing of stage 1 from the combustion of CCA-treated timber at 600°C*

These crystals demonstrate the presence of gas phase arsenic that condenses onto the uppermost stage of the impactor. Figure 53 shows the particles present after plasma ashing of stage 6.

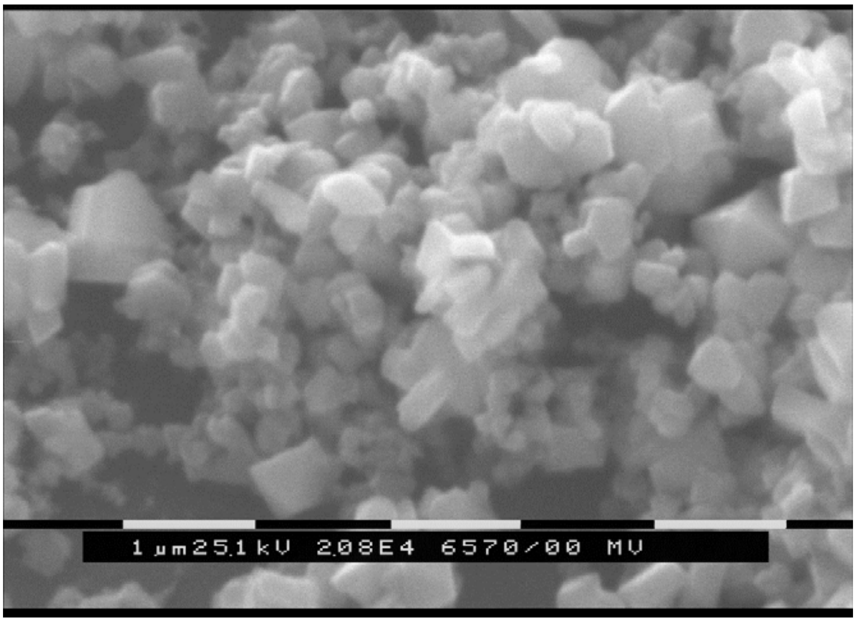

Figure 53: *As_2O_3 crystals after plasma ashing of the 6th impactor stage from CCA-treated timber combustion at 810ºC. Crystals are generally polyhedral with some octahedral forms present.*

Figure 52 indicates that at least some of the arsenic forms crystals separate to the soot particles. It can also be seen in this picture and a thorough search of the sample that only some arsenic crystals are octahedral in shape while the majority of arsenic crystals have some other shape. This does not mean that the arsenic has changed speciation as there are many factors that affect the shape of a crystal. Crystal growth takes places through the adsorption of molecules which either bond where they are adsorbed or travel to adjoining adsorption sites until they reach an active site where they can bond to the crystal. During crystal growth, impurities that might not be able to bond at an active site can compete for adsorption sites which in turn can change the final shape of the crystal (Faktor and Garrett, 1974). Hence, in this case it is possible that carbon molecules or compounds are competing to some extent for adsorption sites but cannot be incorporated into the growing crystals thereby altering the shape of the crystals from that which was observed in the As_2O_3 volatilisation experiments.

3.4.3 Mass distributions of arsenic particles

Qualitative observations from the previous section suggest that quantitative mass distributions will show a smaller and a larger mode. It was confirmed in Section 3.4.2.2 that the larger mode (particles present on stage 1 of the cascade impactor) is a result of gas-phase arsenic oxide condensing directly on the impactor stage. This means that the particles present in the gas phase are actually characterized by the smaller mode. However, it is important to note that the mass found on stage 1 represented on the order of one half of the total mass of arsenic recovered which indicates the presence of a significant amount of arsenic still in the gas phase at the impactor.

3.4.3.1 Mass distribution of arsenic from As_2O_3 volatilisation

No particulate arsenic was found from the volatilisation of As_2O_3 at 315°C. The mass distribution of arsenic from the volatilisation of As_2O_3 at 600°C is shown in Figure 54.

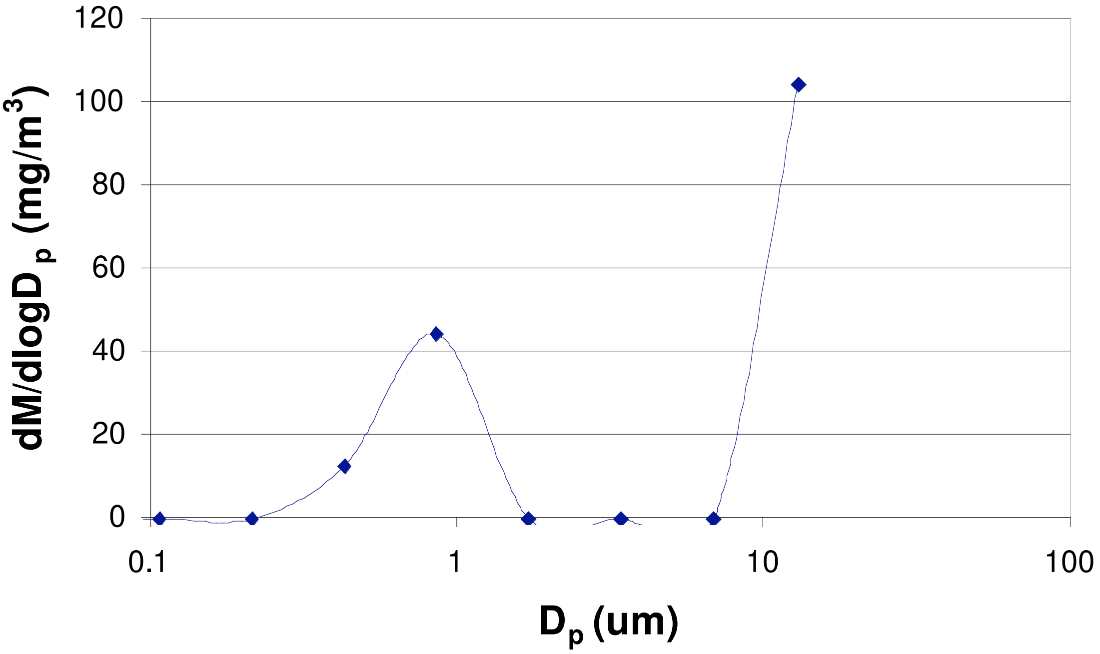

Figure 54: *Arsenic particle size distribution from the volatilisation of 5 mg of As_2O_3 at 600°C.*

3.4.3.2 Mass distribution of arsenic from CCA-treated timber combustion

Figure 55 shows the mass distribution of arsenic in the particles sampled from the combustion of CCA-treated timber at 600°C and 810°C. The combustion temperature appears to have no effect on the mass distribution. These mass distributions show that arsenic is found in smaller particles when volatilised during CCA-treated timber combustion than when it is volatilised as As_2O_3.

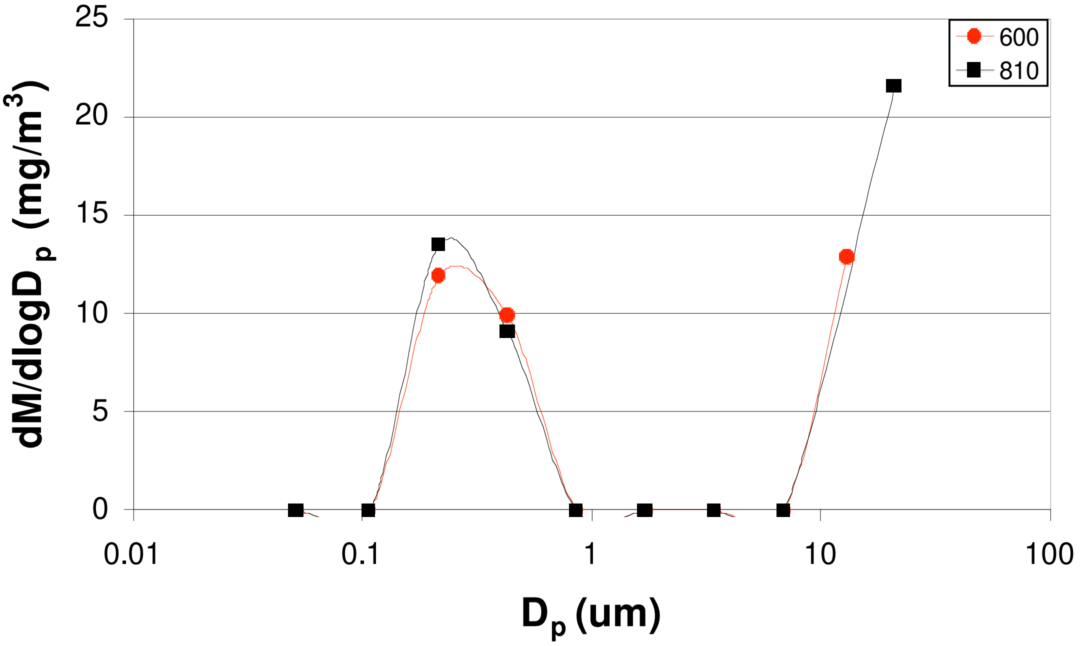

Figure 55: *Arsenic mass distribution from the combustion of CCA-treated timber at 600°C and 810°C.*

3.4.4 Discussion of results

The presence of gas phase arsenic at the 1st stage of the impactor is significant. In the experiments, there are two different pathways for arsenic oxide to make the transition from the vapour to the solid phase. It can either nucleate homogeneously or condense onto a surface. The presence of piles of particles found on the 5th stage of the cascade impactor (see Figure 48) is evidence of homogeneous nucleation. Homogeneously nucleated particles are typically below 50 nm in diameter when first formed so these particles also show evidence of further growth through surface condensation. The presence of white powder on the tubing entering the impactor and condensed As_2O_3 on stage 1 of the impactor give evidence of surface condensation on the surfaces of the apparatus. During each experiment, homogeneous nucleation and surface condensation occur competitively within the hierarchy of which process occurs most easily.

Homogeneous nucleation requires a critical supersaturation ratio[4] in the gas phase to occur. The absence of homogeneously nucleated particles in the As_2O_3 experiments conducted at 315°C and the presence of surface condensation would suggest that homogeneous nucleation requires the higher driving force, or supersaturation ratio, of the two pathways.

The required supersaturation ratio for the homogeneous nucleation of As_2O_3 cannot be calculated with a great degree of accuracy from the experimental results but it can be estimated. According to FactSage, the saturated vapour pressure of As_2O_3 at 60°C (the gas temperature at stage 1 of the impactor) is of the order of 10^{-4} Pa. The total

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[4] The supersaturation ratio is the ratio between the vapour pressure of the substance and the saturated vapour pressure of the substance

mass of As_2O_3 present on the impactor from the volatilisation of As_2O_3 at 600°C was 160 μg with 100 μg present on stage 1 and 60 μg present on stages 5 and 6. This means that entering the impactor, at least 100 μg of arsenic was in the vapour phase and 60 μg was in the particulate phase. If it is assumed that the sampled arsenic was evenly distributed in the entire volume of sampled gas (3 L) then the vapour pressure of arsenic at the top of the cascade impactor was roughly 0.5 Pa. This is likely a significant underestimation of the actual vapour pressure of As_2O_3 as sample volatilisation occurred very quickly at 600°C meaning that all of the sampled arsenic was probably concentrated in a much smaller volume of gas than 3 L. Overall, the required supersaturation ratio for As_2O_3 homogeneous nucleation is estimated to be between 10000 and 20000. This is very high compared to the supersaturation ratio ~3 needed to cause condensation of water, for example, but it is not uncommon for such high values to be required for metals and their compounds. The conclusion that can be drawn from this exercise is that homogeneous nucleation will not likely be a major pathway for arsenic removal from the gas phase.

The effectiveness of surface condensation as a pathway for arsenic removal from the gas phase depends heavily on the surface involved. The experiment that proved that the particles present on stage 1 of the impactor are grown directly on the impactor substrate also proved that arsenic vapour will condense very quickly and preferentially onto a previously existing As_2O_3 crystal. The presence of crystals already on the impactor substrate inhibited the nucleation of new crystals as the arsenic bonded directly onto the previously existing crystals. Other surfaces such as soot showed little condensation of arsenic. The CCA combustion experiments show that there is still arsenic in the gas phase at the beginning of the cascade impactor despite the increase in available surface area in the form of soot and any other previously condensed volatiles. Arsenic crystals are also seen to form separately from the soot particles meaning that surface condensation of arsenic onto soot did not suppress homogeneous nucleation. Therefore, it appears that arsenic will condense easily onto previously condensed/nucleated As_2O_3 but with greater difficulty onto other surfaces.

The conclusions drawn above concerning homogeneous nucleation and surface condensation have implications with respect to the behaviour of volatilised arsenic in a thermal treatment facility for CCA-treated timber. The walls of the exhaust piping for combustion gas in a CCA combustion facility are likely to become coated with a layer of As_2O_3 crystals which in turn will become an efficient sink for gaseous arsenic. Whether or not homogeneous nucleation is suppressed is a more difficult prediction. It is likely that whatever gas handling technology is chosen, it will operate well above the temperature at which the combustion gas was sampled in the experiments. This means that the supersaturation ratio of the gas in a practical system will be less than the ratio of that pertaining to the inside of sampling probe in our experiments. In this case, homogeneous nucleation will be suppressed. On the other hand, the sampled combustion gas during the experiments passed to the impactor via a 6mm tube which was lined with condensed As_2O_3. This gaseous arsenic sink had a much larger surface to volume ratio than could be expected to be present in a practical exhaust system. Since the diffusivity of As_4O_6 in gas is significantly slower than the thermal diffusivity of the gas, the mean temperature of the gas as it passes along the pipe will drop somewhat faster than arsenic oxide can diffuse to the walls. This situation would lead to an increasing trend in the supersaturation ratio of the vapour and possibly to homogeneous nucleation and new particle formation in the gas phase.

4 TECHNOLOGY SELECTION AND DESIGN GUIDELINES

4.1 Background

This report set out to deal with combustion as a possible means of treating end-of-life CCA-treated timber. Since the time our work began in mid-2004, there has been significant convergence of thinking in the literature in support of combustion as the most appropriate thermal treatment technology.

Helsen and van den Bulck (2005) reviewed pyrolysis, gasification and combustion approaches and concluded that the best available thermochemical conversion technology is combustion. Their reasoning is essentially that which we provided in proposing to do this work – combustion allows the valuable product (energy) to be obtained in a centralised facility where the CCA components can be dealt with efficiently whereas pyrolysis and gasification will inevitably produce fuels that are contaminated, mostly with arsenic, and that are unsuitable for general distribution.

Jambeck *et al.* (2005, 2006) have made a life-cycle comparison of combustion versus disposal in a lined MSW landfill. While they found that, while the cost of combustion would be about double the cost of MSW disposal, the benefits of combustion were considerable. These benefits include possible green energy credits and major reductions in the volume of landfill required when the timber is reduced to ash. Significantly, they concluded that landfilled timber would actually release significantly more arsenic, albeit at lower concentrations. Furthermore, the management of a higher concentration leachate from ash deposits would be easier, because of the smaller collection area and smaller volume of leachate.

The UK WRAP report (WRAP, 2005) considered a wide variety of treatment options, excluding disposal to landfill, and concluded that combustion is the most highly developed of all the options currently available. It is concluded that there are no issues with an appropriately equipped incinerator except for the hazard posed by arsenic emissions.

A novel thermal technology known as Chartherm (Hery, 1997, 2005; Thermya SA, 2006) claims to provide a solution to the disposal of end-of-life thermal treatment technologies. The process appears to be one of partial oxidation at an unspecified temperature “substantially below that generally used for thermolysis”. Unfortunately, there are insufficient details of the process or of the verification of the company’s claims for us to be able to evaluate the process. The WRAP report (WRAP, 2005, p.47) actually contains more information than is available through the company’s publicity material. The authors of that report visited a pilot plant facility (10,000 tonnes pa) in February 2005 and expresses “some concern that the process is not as effective or technologically robust as the developer claims”, noting that the plant was not actually processing treated wood waste when visited, that there are no independently verified data accessible on the emissions from the plant and the quality of the carbon product, and that the plant “does not appear to be operating anywhere near its design capacity”. On the other hand, the company reports that a full-scale plant (of unspecified capacity) is successfully in operation (Hery, 2005). Processing costs via the Chartherm process have been estimated as between A$250 and A$750 per tonne. It seems prudent to monitor developments in this area, but, based on the evidence to hand, we believe that the Chartherm process cannot be described as commercial-ready nor even as proven.

In the remainder of this chapter, we consider combustion options for treatment of CCA-treated timber waste. The selection among options is determined in part by the emissions standards that have to be met, and by the size of the facility that can be sustained by a CCA waste stream.

4.2 Estimation of CCA-treated timber waste volumes in Australia

A recent publication of FWPRDC estimates that Australia produces 1,741,000 tonnes of wood waste annually (Taylor *et al.*, 2005). In NSW, approximately 10% of the total timber waste is treated timber waste, which we take here to be mostly CCA-treated timber. Applying this ratio to all states, then we estimate that 130,700 tonnes of CCA-treated wood waste are collected at Australian landfills every year, as summarized in Table 15.

Table 15: *Annual CCA-timber waste to landfill in Australia (Taylor et al., 2005).*

States	tonnes/year
NSW	33500
VIC	46700
QLD	20000
WA	11000
SA	13000
TAS	1500
ACT	2000
NT	3000
Total	130700

In addition to these quantities going to landfill, there are significant quantities of waste produced at vineyards in the form of broken CCA-treated in-line posts. These are generally left piled up at vineyards. It is estimated that some 627,000 tonnes of CCA-treated in-line posts are in use and that, on average, 1-2% (and up to 15% at some vineyards) may be broken and disposed of each year (McCarthy *et al.*, 2005). However, since the average life of plantings is around 25 years, an additional 4% should be included as being taken out of service.

Taking an overall rate of 6% of installed capacity requiring disposal each year leads to an estimate of ~37,000 tonnes of CCA-treated waste requiring disposal. Some of this goes to landfill and is presumably included already in Table 15 above. On the other hand, the wine industry has accumulated large stockpiles of end-of-life poles and these would feed into the waste stream if suitable disposal options were available.

From June 2006, the Australian Pesticides and Veterinary Medicines Authority (APVMA) banned the use of CCA-treated timber from some domestic applications that are touched frequently, such as handrails, playground equipment, garden furniture etc. It is expected that this ban will gradually decrease the Australian consumption of the CCA-treated timber, which is currently around 550,000 tonnes. However, considering the long service life of CCA-treated timber, and the amount of treated wood still in service, the flow of this material into the waste stream can be expected to remain steady for many years to come, possibly even increasing in the near term.

The specific focus on end-of-life CCA timber is occurring at the same time as a general tightening of waste management policies all around the world. For example, in 2003, the NSW government released *The NSW Waste Avoidance and Resource Recovery Strategy* in order to increase waste recovery. With this policy, industries producing wastes will require to take action to reduce its amount (Extended Producer Responsibility (EPR)). It is expected that this scheme will have an impact on the recycling turnovers and the new recycling technology developments.

We consider that a reasonable estimate of the total Australian CCA-treated timber flow that could be available to a suitable treatment technology is of the order of 180,000 tonnes per annum.

Taking the lower heating value of radiata pine as 18 $MJ.kg^{-1}$, the combustion energy content of this stream is approximately 110 MW thermal (based on an 8000 hour operating year). In small steam-raising plant, this could be converted to electricity at a rate of approximately 18% to generate a total of 20 MW electrical power.

4.3 Emissions and approaches to emissions control

Some arsenic is volatilised during thermal treatment and some of this material reports to the flue gas stream. Traditional approaches to combustion engineering have been to add pollution control devices downstream of the combustor, sufficient to satisfy air pollution standards.

4.3.1 Arsenic emissions standards

The standards for atmospheric emissions of arsenic depend very much on the jurisdiction, indicating some uncertainty yet in determining what an appropriate level should be. The standards for Australia are (Clean Air Society Of Australia & New Zealand, 1994)

- 10 $mg.Nm^{-3}$ for all states except Queensland;
- 20 $mg.Nm^{-3}$ in Queensland.

These concentrations are for a suite of metals (antimony, arsenic, cadmium, lead, mercury and vanadium) where the metal amount is determined as the element or in compounds.

From September 2005, new facilities in the state of NSW are required to meet a much lower standard of 1 $mg.Nm^{-3}$ regulated new facilities under the “Protection of the Environment Operations (Clean Air) Regulation 2002” of NSW. This brings NSW more into line with international standards including

- European Hazardous Waste Incineration directive, applicable to existing plant from 2005 limits emissions over a 30 minute average to 0.5 mg.Nm^{-3} for the combined metals antimony, arsenic, lead, chromium, cobalt, copper, manganese, nickel and vanadium.
- USEPA requirements are also 0.5 mg.Nm^{-3}

It is reasonable to expect that other states will move to the international standard.

4.3.2 Vapour pressure of arsenic oxide.

Arsenic (III) oxide is a relatively volatile compound. The ease of its volatilisation under combustion conditions translates at lower temperature to a significant vapour pressure that can easily exceed the emissions standards. This is shown in Figure 56 where the equilibrium arsenic content of vapour (which actually exists as As_4O_6) in contact with solid As_2O_3 is shown for four different data sources (Behrens and Rosenblatt (1972); Pupp *et al.* (1974); Dalewski (1999), and the Fact53 thermodynamic database described in Section 2.1. Of these sources, only Behrens and Rosenblatt (1972) and Pupp *et al.* (1974) are documented in the open literature. The two curves provided by Dalewski (1999) refer to different crystalline forms of As_2O_3 solid – monoclinic (M) which is claudetite and orthorhombic (O) which we take to be arsenolite and which was the form studied specifically by Behrens and Rosenblatt (1972) and Pupp *et al.* (1974). The crystal form observed in our studies of the condensation of volatilised arsenic is isometric in the shape of an octahedron (Section 3.4.2).

There is clearly some disparity in the values of vapour pressure presented in Figure 56. For the remainder of this discussion, we take the conservative approach and use the values provided by Dalewski (1999) for the monoclinic form of As_2O_3. Since this graph was found in other mineral industry documents also, this approach appears to align our discussion with the industry where there is much practical experience of arsenic condensation; it also gives a reasonable safety margin for temperature controls in practice.

Figure 56 reveals that achievement of the 10 mg.Nm^{-3} standard for arsenic emissions requires that gases containing As_4O_6 must be cooled to at least 90°C – any higher temperature will carry arsenic out of the system at concentrations higher than the standards. To achieve the new NSW standard of 1 mg.Nm^{-3} requires a final temperature of about 65°C which is exceptionally difficult for a flue gas which requires some temperature differential against ambient in order to rise through the stack and form a plume. Furthermore, even in a sulfur free system, a temperature of 65°C is very close to the dew point temperature of the flue gases – this condition must be strictly avoided if final particle collection devices such as bag filters are to operate properly.

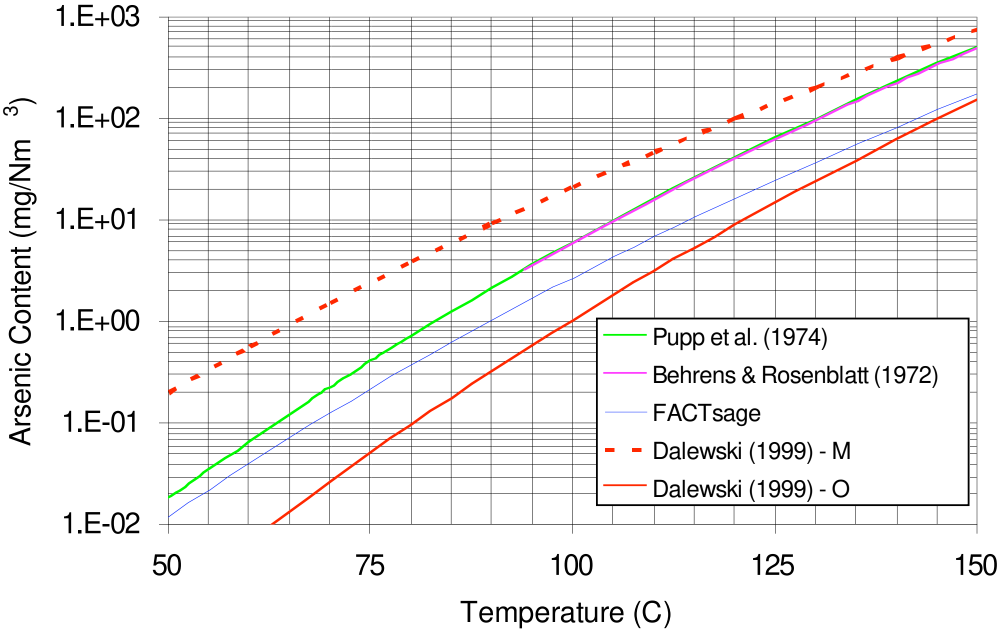

Figure 56: *Arsenic contents of* As_4O_6 *vapour over* As_2O_3*. Data for Dalewski marked M are for monoclinic* As_2O_3 *(claudetite).*

4.3.3 Controlling arsenic emissions in copper smelting

The copper production industry has dealt with arsenic emissions from its smelters for a long time and treatment strategies are well established. Although the arsenic loadings and temperatures in smelting are rather different from those likely to occur in flue gases from CCA-timber combustion, the approach and techniques that must be considered have similarities.

When copper concentrates are smelted most of the arsenic is vaporised as As_4O_6 (Piret, 1999). This gas must be removed before the SO_2 from the roasting operation can be used to produce sulfuric acid from the process gas, and cooling of the gas to cause condensation of the arsenic oxide is employed.

4.3.3.1 Process Gas Cooling

There are four types of process gas cooling methods; indirect cooling, direct cooling, evaporative cooling and two-step direct gas cooling, shown schematically in Figure 57.

Total gas volume and the moisture content of the process gas are important parameters for dry gas cleaning technology selection. High gas volume requires excessive investment in particle collection devices such as bag filters; a high moisture content may result in wet deposits and clogged filtration. While indirect cooling air has no effect on gas volume and the moisture content, it requires large cooling surfaces and large quantities of cooling air. Direct cooling with air, Figure 57(a), dilutes the moisture content of the process gas but increases the total gas volume to be treated. In contrast, evaporative cooling, Figure 57(b), increases the moisture content of the process gas with negligible effect on the total gas volume. A two-step cooling method, Figure 57(c), utilises the benefits of both evaporative and direct cooling.

These cooling methods are widely used in copper production, with particulars determined by specific process conditions. Cooling of the process gas will start the condensation of arsenic oxide but it is not usually possible to continue this cooling so far as to reach the regulated emission limits because of the problem of sulfuric acid formation and deposition. The acid dewpoint of roaster gases is typically in the temperature range 160ºC-270ºC (Dalewski, 1999). At these temperatures, the vapour concentration of arsenic exceeds the emissions limits even if all particulate arsenic oxide is removed via dry methods such as bag filters or electrostatic precipitators. Dry gas cleaning methods can therefore only be applied when there is a large excess of arsenic over sulfur in the gases (Dalewski, 1999).

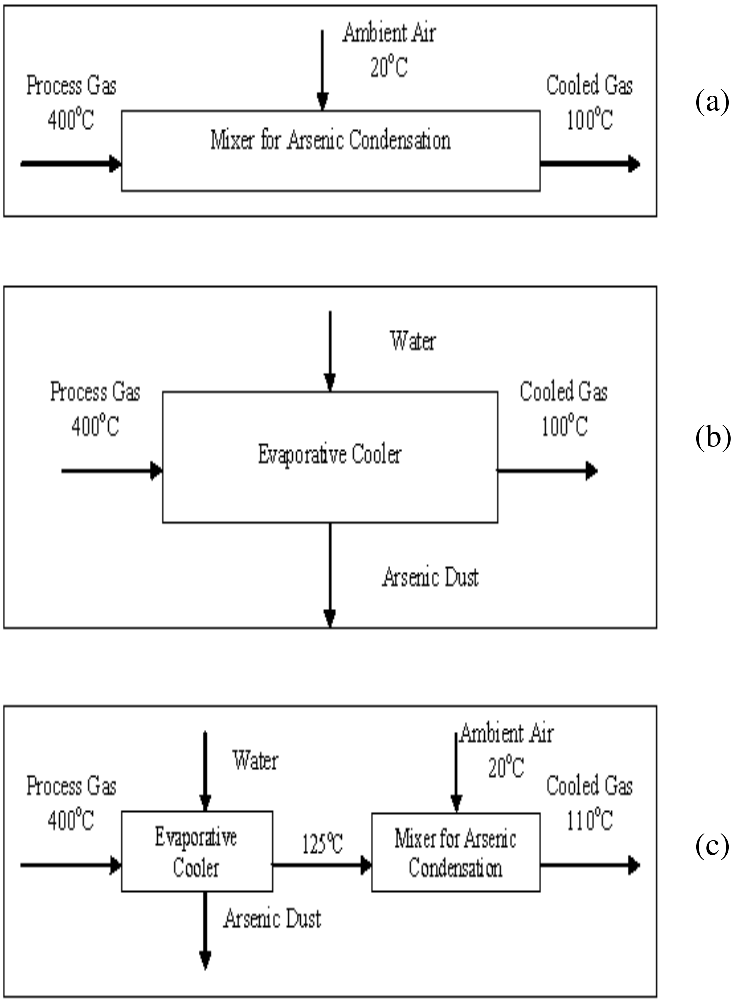

Figure 57: *Dry gas cooling methods: (a) Direct (b) Evaporative (c) Two step (Dalewski, 1999)*

4.3.4 Process Gas Cleaning

Common approaches to removing the arsenic are shown in Figure 58 (Dalewski, 1999). In Figure 58(a), the gases are cooled initially by evaporation of water spray. Mechanical collectors (e.g. cyclones) remove larger dust particles carried over from the smelter and return them to the smelter. A hot ESP stage for further dust removal operates at about 400ºC, after which the gases are cooled by mixing with air to bring the temperature down to the acid dew point (~170ºC for a low-sulfur ore) – the resultant condensed particles of arsenic oxide are collected with bag filters. As discussed in Section 4.3.2, a condensation temperature of ~60ºC would be needed to meet an emission limit of 1 $mg.Nm^{-3}$ (85-90ºC for 10 $mg.Nm^{-3}$) so some form of wet cleaning is required, most simply via wet ESP.

The alternative approach, now widely adopted in the industry (Grund *et al.*, 2005) involves the use of chemical reagents or sorbents to remove the arsenic from the vapour and stabilise it as a solid arsenate, as shown in Figure 58(b). The use of hematite is most common because it is cheap and readily available. Also the iron arsenate that is formed can be made as scorodite ($FeAsO_4.2H_2O$) which is one of the least soluble of the arsenates (Langmuir *et al.*, 2006). Another advantage of reaction with a sorbent is that larger particle sizes are created and these can be collected more effectively. However, similar to the previous method this method also requires a final wet cleaning section to achieve regulation limits levels.

Wet cleaning systems include wet scrubbers, ionizing washers, and wet electrostatic precipitators (Grund *et al.*, 2005). Typically the gases are washed with water or circulating sulfuric acid solutions in washing towers, Venturi scrubbers, or other apparatus before going to wet precipitators. Separation of the arsenic by the wash liquid is highly efficient, with the process water being circulated so as to operate with a high concentration of dissolved arsenic. The arsenic is generally precipitated with lime.

There has been limited work on the use of physical adsorbents as opposed to chemical sorbents for arsenic in the minerals industry. However, Wouterlood and Bowling (1979) carried out laboratory tests on the use of activated carbons and other potential adsorbents. They found that they could reduce the arsenic oxide vapour concentration at 200ºC by two orders of magnitude below its saturation value without cooling the gas. Active carbon, silica gel and alumino-silicate molecular sieve were effective adsorbents but $CaCO_3$, $Ca(OH)_2$, Na_2CO_3 and $KHSO_4$ were relatively ineffective as was a brown coal char.

Player and Wouterlood (1982) took the activated carbon process to an extended pilot trial at the Mt Isa smelter. They confirmed the results of Wouterlood and Bowling (1979) by achieving >99.9% reduction in the arsenic oxide concentration without cooling. The pilot plant suffered some problems - due to the combination of high temperature and high oxygen concentrations during process upsets, the activated carbon bed occasionally combusted, driving off its accumulated adsorbed arsenic oxide. Other problems that arose included heavy dust carryover from the smelter, which caused filter blockages, and some sulfuric acid formation in the system. This pilot study appears not to have been taken to full scale.

In summary, experience in the minerals industry has shown that dry cooling and condensation can meet the emissions standard of 10-20 mg.Nm-3. The use of high temperature reactive sorbents is common in modern plant but a wet final treatment stage is necessary to meet current international emission standards for arsenic < 1 mg.Nm^{-3}.

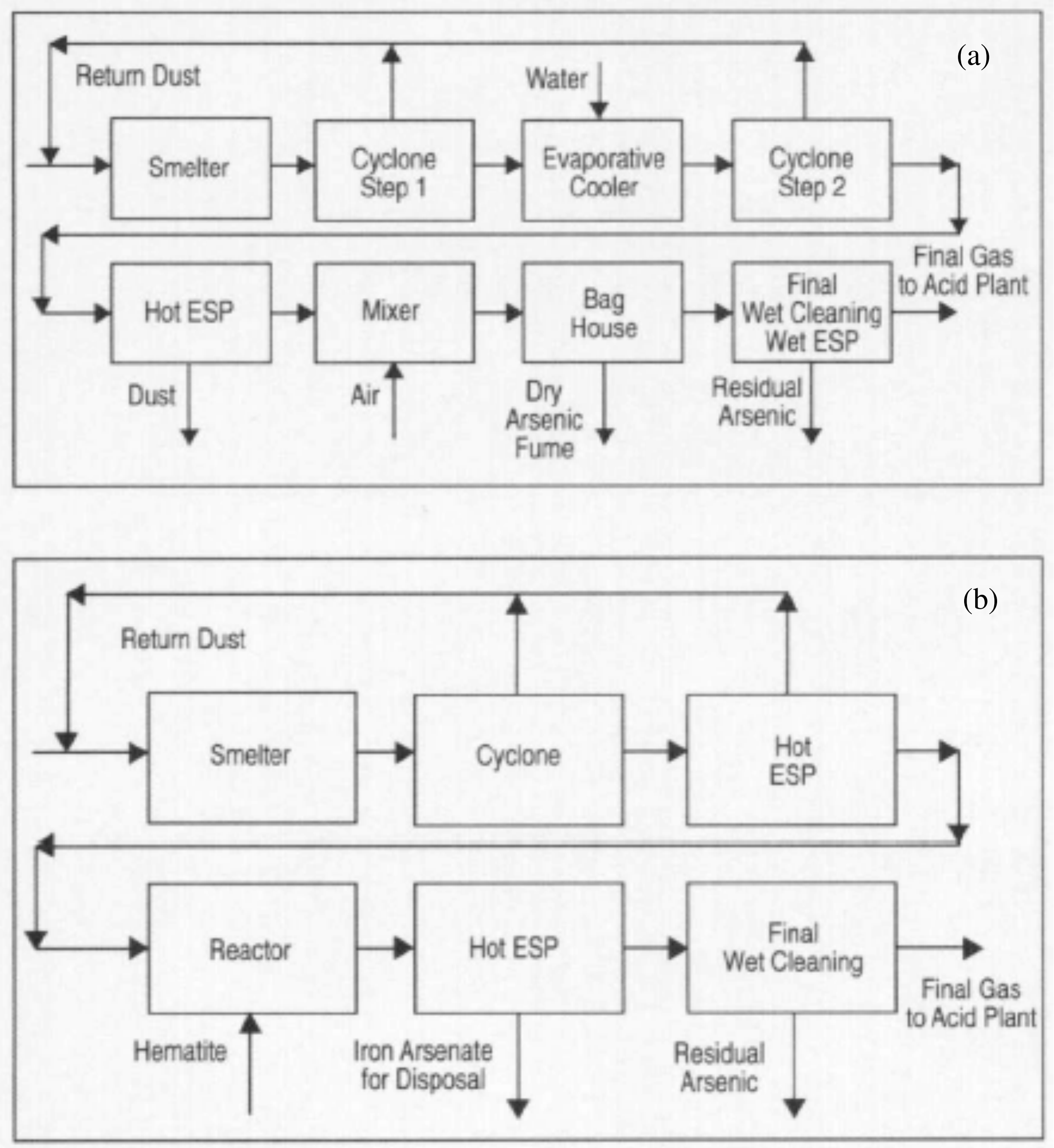

Figure 58: *Dry gas cleaning methods in copper production industry based on (a) arsenic condensation, (b) arsenic absorption. (Dalewski, 1999)*

4.4 Fuel Preparation

CCA-treated timber waste from various sources first needs to be chipped in order to burn efficiently. If the wood is transferred to the plant in logs a primary size reduction step and a metal removal step is necessary before the in-line secondary size reduction equipment. There are several types of size reduction techniques such as hammermills, knife mills, drum mills etc. The main difference between these techniques is the rotating parts. The operational efficiency and desired quality output should be considered when selecting size reduction methods. If the contamination is present to a great extent, hybrid type size reduction techniques could be employed. This type of equipment uses less sharp blades for durability with the intention of producing wood chips by a combination of impact force and cutting action. The primary and secondary reduction equipments are also accompanied with different types of screens to separate and re-feed the over-sized wood particles.

Due to high arsenic content of the CCA-treated timber, special care should be taken to provide a dust-free working environment during the timber size reduction stage. To achieve this, the mill may be ventilated with air at a velocity of 1 m/s in order to prevent any dust escaping from the openings. This ventilated air can also be utilised to cool down the flue gas to accelerate As_4O_6 condensation.

4.5 Combustion Technology

4.5.1 Cofiring

Cofiring is the practice of using biomass (or other) fuels as additives to fossil fuels such as coal. It is attractive because it makes use of existing capital infrastructure such as exists in large-scale power plants; it also means that the relatively high efficiency of conversion of thermal to electrical energy available in these plants is passed on to the biomass which, if burned alone in a small plant, can only achieve modest efficiencies. Most technical issues associated with cofiring have been shown to be addressable. Operating practice in Australia has been reported by Macquarie Generation in NSW, among others.

When it comes to cofiring of CCA-treated timber, there is less confidence about the suitability of this as a disposal technique. Dilution of the CCA components in cofiring is unlikely to be an acceptable means of meeting regulatory standards for emissions such as arsenic. On the other hand, a well operated waste incineration plant with appropriate emissions controls is acceptable for CCA-treated timber disposal in some European jurisdictions (Graf, 2002). Until 2004, the European Cooperation in the Field of Scientific and Technical Research ran project E22 – Environmental Optimisation of Wood Protection that included a working group WG 2: Impacts. This working group's reports (COST, 2004) provide some perspectives on developments and requirements for treated-timber disposal in Europe, but no clear picture emerges. Unfortunately, the subsequent Action E37 does not cover impacts. However, the general lack of hazardous waste incineration facilities in Australia means that developments in this country are unlikely to follow those in Europe (where landfilling of organic waste is now banned in an effort to promote waste-to-energy conversion).

Another form of cofiring that has been employed with CCA-treated timber and other wastes is fuel supplementation in cement kilns. In the case of CCA, the high concentrations of calcium as CaO in the furnace is believed to ensure that the As is taken up as refractory arsenates, as explored in our Sections 2.1.3 (equilibrium studies) and 2.2.4 (experimental). Combustion in a cement kiln is an acceptable disposal option for CCA-treated timber in Switzerland (Graf, 2002). In Australia, the Adelaide Brighton Cement company has examined the combustion of CCA-treated timber wastes for some years, in conjunction with the South Australian EPA. We have been unable to locate any public reports on the conduct of these trials or their outcomes, but some information is obtainable from evidence given at a Productivity Commission enquiry (Productivity Commission, 2006). Apparently, tests with up to 10% fuel as CCA-treated timber have not caused stack emissions limits to be exceeded (presumably referring to a 10 $mg.Nm^{-3}$ limit).

The UK WRAP report (WRAP, 2005) documents a number of uses of CCA-treated timber waste in cement kilns. In France, CCA-treated wood waste is not currently burned in cement kilns but tests are underway (Cornillier, 2005). A looming issue here is that the EC Chromium (VI) directive restricts the level of chromium in cement to 2ppm, which would restrict the fuel load to be carried by CCA-treated timber in a cement kiln to about 0.2%. If this level comes to be applied in Australia, with its local annual production of cement of 9.2 million tonnes, the maximum amount of CCA-treated wood (containing an assumed average of 4 g $Cr.kg^{-1}$) that could be taken up by the cement industry would be only ~ 5000 tonnes of timber annually.

4.5.2 Dedicated combustion facilities for CCA-treated timber

This section has been prepared with the assistance of Mr. Ian Pennington from Austrian Energy and Environment (Australia) (AE&EA) Pty. Ltd. and of Mr. Gerard Reyerink from Alstom Power Pty. Ltd. - Environmental Control Systems. While data and examples are taken from their respective companies, no endorsement of particular manufacturers is intended in the following discussion.

It was estimated in Section 4.2 that the total volume of CCA-treated timber that might be available across the whole of Australia is 180,000 tonnes per annum, corresponding to a thermal firing rate of 110 MW. Figure 59 is an indicative technology selection chart supplied by AE&EA - even the entire CCA-timber waste stream amounts to a relatively small unit on this chart. If combustion were chosen as a solution for disposal of end-of-life CCA-treated timber, there would presumably be a number of plants spread across the country. These would be significantly smaller than the 110 MW – for the purposes of the ensuing discussion, we consider plants sized at 10,000 tpa (nominally 6 MW), 30,000 tpa (20 MW), and 100,000 tpa (60 MW).

A power plant that is burning CCA-treated timber waste with 100,000 tpa throughput produces approximately 70 tonnes per hour of steam at a 40 bar pressure and 400ºC temperature. Such a plant can generate up to $13MW_e$ electricity depending on the turbine selection.

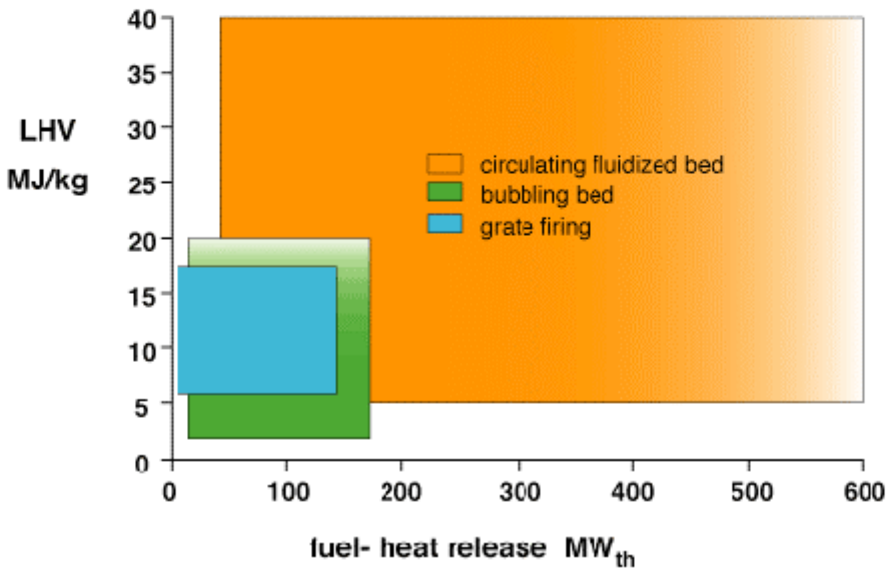

Figure 59: *Combustion technology selection chart used by Austrian Energy and Environment (Australia) Pty. Ltd.*

The intersection of the expected calorific value (lower heating value, LHV in Figure 59) and the range of thermal sizes to be considered suggests that grate firing or a bubbling fluidised bed will be the most suitable combustion technology for these applications. A circulating fluidised bed at these scales is likely to be excessively costly to build.

In general, AE&EA would recommend grate-fired combustion technology for throughputs less then 100,000 tpa because grate-fired boilers require lower capital and operating costs. Grate-fired combustors have the added advantage that they are used in many parts of the world for (hazardous) waste incineration. While the bubbling fluidised bed technology is a relatively new technology, it offers some advantages for the degree of automation that can be achieved and the ability to use in-bed sorbents such as limestone for capture of volatilised species such as As_2O_3.

4.5.2.1 Bubbling Fluidised Bed Combustion (BFBC) Technology

Fluidised bed technology in boilers (Figure 60) is particularly advantageous for fuels with variable characteristics such as may be expected with a waste timber resource. The chemical composition of CCA-treated timber waste varies widely depending on the application environment of the timber; the timber will come mixed with other materials, including paint coating, dirt, and other wood. The ability to adjust the operation temperature of these units also offers better opportunities for fine tuning the combustion conditions. For example, by changing the operation temperature the ratio of arsenic in flue gas to bottom ash could be adjusted.

The combustion temperature range of bubbling fluidised beds is usually lower in comparison to grate-firing, of the order of 800-900ºC. While these temperatures are high enough to cause significant arsenic volatilisation, they appear not to cause any copper or chromium volatilisation, which cannot be guaranteed at higher temperatures. The low combustion temperature also offers low NO_x emission.

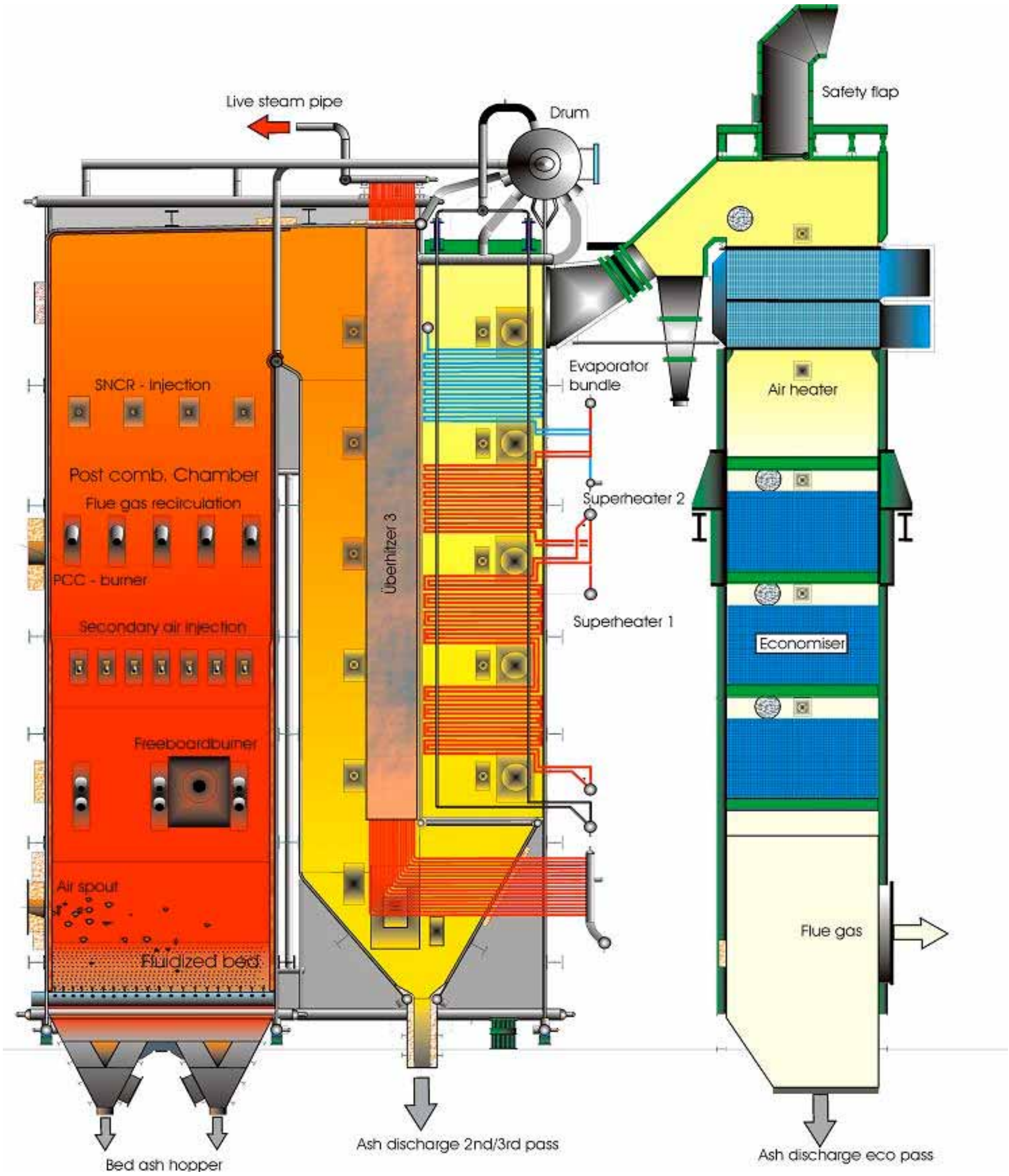

Figure 60: *Bubbling Fluidised Bed Boiler.*

The ability of the BFBC to accept reasonably large fuel particle sizes (approx. 3 mm) is also a benefit for wood combustion as wood pulverisation is an expensive process. Sand is often used as a bed material. Limestone addition to the bed to capture sulfur is a proven technology in coal combustion and could be applied without difficulty to CCA-treated timber waste combustion to recover arsenic in the bottom ash. Elutriated char particles can be collected with a mechanical collector and fed back into the bed for complete combustion.

Steam is produced in the in-bed tubes and then super heated with the particle-free flue gas. Subsequently, the flue gas is treated at the gas cleaning section before being released to the atmosphere. The bottom ash will consist mainly of the timber preservation chemicals (i.e. chromium, copper and arsenic) and some mineral matter content of the virgin wood.

A disadvantage of the BFBC is its use of in-bed tubes for steam-raising. The relatively high heating value of dry wood (18-20 $MJ.kg^{-1}$) means that in-bed tubes are subjected to significant stresses and need to be replaced more frequently, probably every two to three years. This results in some plant down time, and incurs maintenance costs.

4.5.2.2 Grate-Firing Combustion Technology

Grate firing is depicted in Figure 61. With this technology, combustion is carried out on a moving or vibrating grate while air is fed evenly from below the grate. The fuel can be presented with relatively large particle size, thereby saving in grinding and pulverisation. Secondary and tertiary overfire air may be used also to ensure complete burnout of hydrocarbons, and to control NO_x emissions. However, in comparison with fluidised-bed combustion, the combustion stability is relatively poorer in grate firing. This technology offers a lower capital cost and reduced electrical consumption compared with fluidised beds.

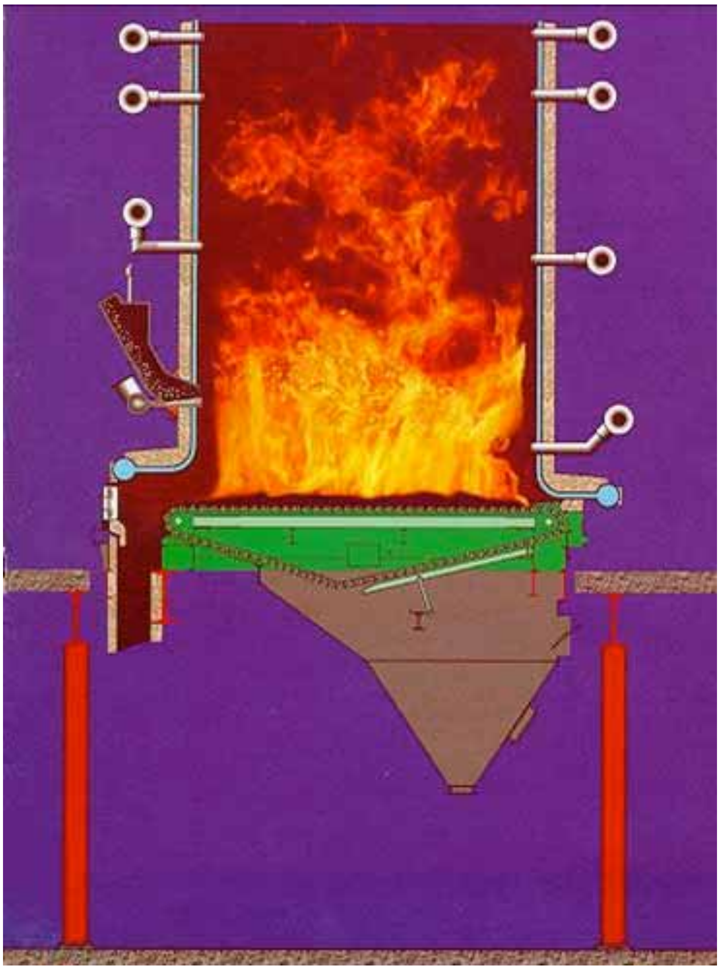

Figure 61: *Grate-firing Spreader Stoker Boiler.*

Ash that is formed in the combustion and falls through the grate (bottoms ash) is collected easily. Fly ash, which is entrained in the flue gases, collected first by mechanical collectors before going to final collection devices. A disadvantage of grate firing is that its fly ash may contain 50% or more of unburnt carbon, making the ash harder to dispose of while also increasing its volume.

Injection of sorbents (e.g. limestone for sulfur capture) above the bed is practiced with grate firing although it is clearly not as easily and effectively implemented as in a fluidised bed. It is expected that this method would be effective also for capture of volatile arsenic emissions in the case of CCA-timber combustion.

4.5.2.3 Preferred combustion technology

Based on the great amount of experience in their installation and operation, and on their lower costs of capital and of operation, it is expected that grate firing would be the more likely choice of technology for a dedicated CCA-timber combustion facility. Depending on valuation of the energy produced and on whether in-bed sorption of arsenic is seen as desirable, the bubbling fluidised bed could also be employed.

Our results indicate that complete capture of the arsenic oxide vapour is very difficult to ensure. Therefore, whether or not some sorbent is added, there will need to be significant emphasis on flue gas treatment in order to eliminate arsenic emissions.

4.6 Flue gas treatment

4.6.1 Chemical sorbents

The requirements of a sorbent technology, such as the injection of limestone, if it alone is to limit emissions to a satisfactory level are very demanding. The flue gas volume generated in the combustion of a typical radiate pine timber is ~8 Nm^3kg^{-1}. The arsenic in the timber feed considered in the experimental work conducted as part of this project was 3500 $mg.kg^{-1}$ (Table 5), giving rise to a hypothetical maximum arsenic loading of 440 mg $As.Nm^{-3}$. An emission limit of 10 $mg.Nm^{-3}$ would therefore require that about 98% of the total arsenic loading be retained in the solid ash and sorbent. None of the tests reported in Section 2.2.4 satisfied this requirement even when calcium hydroxide was impregnated into the wood prior to combustion and in great excess. We also note that sulfur capture using limestone injection is typically no better than 90% efficient even in fluidised bed environments, and rarely that good in furnace injection – it is extremely unlikely that arsenic oxide would be captured with any greater efficiency.

If the emission limit is reduced to 1 $mg.Nm^{-3}$, the situation becomes even more difficult, with more that 99.7% retention of arsenic needed to reduce emissions to the necessary level.

Therefore, while chemical sorbents can clearly retain significant fractions of the fuel arsenic in the solid phase with the wood ash, this technology is unlikely to be adequate alone to meet emissions standards. This is in accord with practice in copper processing.

4.6.2 Meeting the 10 mg.Nm^{-3} limit

As discussed in Section 4.3.1, the existing standard for atmospheric emissions of arsenic in most Australian jurisdictions is 10 mg.Nm^{-3}. The major emitters are the smelters which are generally located far from major population centres. The emissions standard is usually met by cooling the roaster off-gases – as can be seen from Figure 56, a temperature of 85-90ºC will have a vapour pressure of As_4O_6 low enough to meet this standard. The final control device encountered by the flue gases as they go to the stack is generally a bag filter which collects the particulate As_2O_3.

Bag house filters operate efficiently in the size range typically encountered. However, as the particulate load build up, the pressure drop across the bags becomes excessive and the bags must be cleaned. This is usually accomplished by shaking of the bags to cause the accumulated dust to drop into hoppers below the bags. This shaking also causes some fine dust to penetrate the bag and be emitted. The significance of the puff of dust associated with bag cleaning depends on how frequently it is carried out, and how that cycle compares with the averaging time for the emissions monitoring. A short averaging time will accentuate the effect of the bag cleaning because the emissions during that operation are higher than the average steady-state emissions.

It is noteworthy that much As_2O_3 actually condenses on the cooling surfaces, rather than homogeneously in the gas phase to form new suspended particles. The explanation for this is provided by the experiments discussed in Section 3.4.4 of this report: As_4O_6 requires a very large supersaturation ratio for it to be able to form new particles and in the presence of an existing As_2O_3 surface is far more likely to condense on that surface than to create new particles. This existing surface may be in the form of suspended particles or as particles that have grown on or transported to the surface. From a practical standpoint, this propensity does require direct cooling surfaces to be cleaned from time to time.

4.6.3 Getting to a 1 mg.Nm^{-3} limit

In principle, reducing the emissions from 10 to 1 mg.Nm^{-3} appears to be a simple matter of reducing the flue gas temperature from ~85ºC to perhaps 60ºC (Figure 56). However, this is not so easily accomplished because the lower temperature requires a much larger heat transfer area and therefore a larger capital investment; and the heat transfer surface is very likely below the dewpoint of the combustion gases and so would be covered with condensate, leading to wet dust and solidified deposits.

Rather than using additional primary heat transfer surface, a large volume of ambient dilution air could be used to cool the gases. However, this also causes difficulties because the much greater volume of flue gas now requires a correspondingly greater number of bag filters. Furthermore, the actual emission rate of arsenic is not decreased proportionately by this method because there is a greater volume of flue gas, albeit with a lower concentration of arsenic.

However the gases might be cooled, there remains the problem of dust emissions associated with intermittent cleaning of the filter bags. It is in fact likely that the average emissions associated with this operation already exceed 1 mg.Nm^{-3}.

Here the practice at smelters meeting the lower limit is instructive – these plants invariably employ wet gas cleaning as the final stage. However, this is likely to be an expensive approach for small scale plant. An experimental alternative might be the use of active carbon filters, as demonstrated for smelter gases previously (Wouterlood and Bowling, 1981; Player and Wouterlood, 1982).

Wouterlood and Bowling (1979) found very high capture efficiences and breakthrough loadings of arsenic oxide in excess of 30% by weight for a variety of different activated carbons and it seems very likely that use of a final filter in this way could be used to bring the arsenic emission from around the thermally achievable limit (~10 mg Nm^{-3}) to very much lower values. Since reaching 10 mg Nm^{-3} entails capturing the nominally 98% of the arsenic in the treated timber, the arsenic fraction that would need to be captured by the carbon filter would be <2%. The spent carbon could then most easily be disposed of by simply injecting it along with fresh CCA into the same combustor, or it could be combined with the combustion ash for alternative disposal.

4.7 Ash Disposal

Ash from the combustion of CCA-treated timber is comprised mostly of oxides of the CCA metals and has some intrinsic value. Arsenic that is volatilised in the combustion zone is collected in relatively pure form as As_2O_3 downstream. However, the world market for arsenic is shrinking rapidly, and the value of this material is questionable. Arsenic that remains behind in the residual ash serves essentially as a contaminant of the copper and chromium components - it is unlikely that any arsenic-contaminated ash would be marketable in its own right, particularly as the quantities involved are small (~ 1000 tonnes per annum) and the economic options for recovery of these metals are limited.

The mineral industry uses sorbents, principally Fe_2O_3, to capture much of the arsenic from its smelter offgases. The arsenic loads in CCA-treated wood combustion are much lower (by orders of magnitude) than in smelting and it is not clear whether the same relief of load on the downstream collectors is so necessary or even advantageous. Our work has shown that the arsenic and chromium components are much more leachable if combustion is carried out in the presence of significant quantities of calcium sorbent, $Ca(OH)_2$ – the increase in ash volume due to the sorbent, and the increased availability to leaching of these metals suggests that the landfilling of this ash+sorbent product is not desirable.

Direct land filling of the ash from CCA-treated timber combustion has the advantage of requiring a much lower weight and volume of material than if the timber itself were landfilled. Jambeck *et al.* (2005, 2006) have suggested that, on a life-cycle basis also, landfill disposal of the ash is preferred.

Given that copper smelters operate in Australia to recover copper from arsenic-containing ores, it might be feasible to send CCA-treated wood ash to such smelters for disposal. The ash material flow is miniscule relative to that of the ores being processed so the ash could presumably be accommodated without too much difficulty. Not only would the copper in the ash be recovered, but this approach would also take advantage of the installed capacity for arsenic capture and stabilisation. For the arsenic and copper components at least, this would truly be a closing of the life cycle as smelting operations have been the source of much of the arsenic and of the copper that have gone into making the CCA chemicals.

4.8 Preliminary designs

In considering conceptual designs for a dedicated combustion facility for disposal of CCA-treated timber, we have selected a grate-fired unit and emphasised

- energy recovery
- safety and emissions standards
- cost

No features have been included that are not reasonable from the point of view of standard practice in biomass combustion facilities, except for those that are deemed essential for the safe handling of the CCA-treated wood (dust control) and for meeting the emissions standards, for which the limit of 10 mg.Nm^{-3} is taken as the base case. Treatment or disposal of the ash is not considered.

4.8.1 A 100,000 tpa facility

Error! Reference source not found. presents a schematic of a grate-fired combustion facility for an annual throughput of 100,000 tonnes, which is believed to be the largest that could be considered, given the material flows estimated previously (Section 4.2). For the most part, this is a standard design for which there is abundant operating experience with a variety of fuels, including biomass. Annual availability of a plant of this kind is expected to be 8000 hours.

The temperature of the gases leaving the boiler/economiser is nominally 175ºC and this would generally be cooled further just enough to be safe for the downstream bag filters. During the wood burning process, incandescent particles may be produced and carried over to the gas cleaning section where they can cause "pinholing" of the bags. Therefore particles >60 μm must be removed ahead to the bag filter, usually in simple cyclonic collectors or proprietary spark arrestors.

For this larger plant, a combination of evaporative cooling and dilution air is recommended for cooling to ~85ºC necessary to meet the 10 mg.Nm^{-3} arsenic emissions limit. The dilution air has an additional important function in that it is introduced via the timber mill in order to prevent CCA-contaminated dust outflow from openings and to provide safer working levels around this equipment.

It is believed that wet-gas cleaning or possibly activated carbon beds should be employed beyond the bag filter if the arsenic emission standard to be met is to be 1mg.Nm^{-3}. In principal, the bag filter could be dispensed with if wet gas cleaning were to be employed (as in the minerals industry), but careful assessment of the ability of the cleaning system to remove any minor chromium volatilisation that might occur would be necessary in this case. If a carbon filter is installed, the bag filter should be retained in order to reduce the load on the carbon and avoid excessive costs of replacement – the carbon would probably be able to be regenerated (Player and Wouterlood, 1982).

4.8.1.1 Filter bags

Filter bags that are made of felted acrylic material are recommended for the capture of arsenic and possibly little amount of chromium oxides in the flue gas stream. Using a combination of evaporative cooling and diluted air-cooling allows a smaller number of bags relative to cooling by air dilution only. A maximum filtration velocity of 0.016 $m.s^{-1}$ is imposed to ensure capture of sub-micron arsenic particles. The maximum velocity with one cell off line during maintenance periods should not exceed 0.02 $m.s^{-1}$. Alstom Power Environmental Control Systems recommend pulse-cleaned bag filters for this application, using compressed air with pressures of 450-600 kPa and "on line" cleaning.

4.8.1.2 Safety and operational issues

Arsenic trioxide is classified as "Dangerous Goods". Special care must be taken during maintenance of the filter bags and associated equipment. Appropriate and approved safety gear such as respirator, gloves and safety glasses should always be worn when maintenance is carried out. When working near open doors or hatches or inside the bag house, pressurized air breathing masks should be worn.

The gas after the filter will continue to cool down. Therefore, As_2O_3 will further condense and cause build up in the outlet duct exhaust fan and stack. Periodic cleaning of this equipment should also be carried out.

4.8.2 30,000 tpa and 10,000 tpa facilities

These units are relatively small combustion facilities. Table 16 compares the process conditions for each of these plants with those for the 100,000 tpa plant. The smaller plants run with a higher air/fuel ratio than the larger and have a gas temperature at the economiser outlet of around 250ºC, both of these changes reducing the thermal efficiency of the plant.

Cooling to 85°C by air dilution only is recommended for these smaller plants for which the cost of installing quench cooling is disproportionate.

Table 16: *Process data for 85°C flue gas temperature.*

Case 1 Evaporative Cooling and Dilution Air from wood mill				
Boiler Feed	TPA	100,000	30,000	10,000
Availability	Hr/Annum	8000	8000	8000
Volume after Air Heater	Am^3/s	**37**	**16.5**	**5.5**
	Nm^3/s	22.5	8.6	2.9
Temperature after air heater	°C	**175**	**250**	**250**
Temperature after Evap Cooler	°C	**120**	**120**	**120**
Volume after Evap Cooler	Am3/s	33.68	13.53	4.51
Temperature at Bag Filter	°C	85	85	85
Volume to bag filter	Am3/s	48.88	19.66	6.55
Filtration Velocity	m/s	**0.016**	**0.016**	**0.016**
Bag filter collection area	m^2	3055	1229	410
6m bags*127 Dia	No Off	1273	513	171
3.6 m bags*100 Dia	No Off	2680	1079	360
Case 2 Dilution Air from wood mill only				
Boiler Feed	TPA	100,000	30,000	10,000
Availability	Hr/Annum	8000	8000	8000
Volume after Air Heater	Am^3/s	**37**	**16.5**	**5.5**
	Nm^3/s	22.5	8.6	2.9
Temperature after air heater	°C	**175**	**250**	**250**
Temperature at Bag Filter	°C	85	85	85
Volume to bag filter	Am^3/s	77.05	44.24	14.75
Filtration Velocity	m/s	**0.016**	**0.016**	**0.016**
Bag filter collection area	m^2	4816	2765	922
6m bags*127 Dia	No Off	2007	1153	385
3.6 m bags*100 Dia	No Off	4225	2426	809

Notes:

1) Numbers in bold are the given values by AE&EA and Alstom Power Pty. Ltd.
2) The outlet temperatures given for boilers in Table 2 are "practical" levels for this application, but could be lowered. However this may not be economical.
3) Because of the fineness of the dust, a relatively low filtration velocity of 0.016m/s is recommended. The maximum velocity with one filter cell off line during maintenance periods should not exceed 0.02 m/s.

5 SUMMARY AND CONCLUSIONS

In this section the results presented in Chapters 2, 3 and 4 are discussed in the context of the project objectives presented in Section 1.2

Chapter 2 presents a study of arsenic volatilisation, using both thermodynamic equilibrium analysis and experimental investigation. The thermodynamic analysis proved to be somewhat dependent on the choice of database, with the two pure substance databases, Fact53 and SGTE, each having deficiencies – for example, SGTE does not include As_4O_6 which is known to be the vapour form of As_2O_3 and as a result seriously underpredicted the extent of arsenic volatilisation that might be expected at temperatures up to at least 1100°C. Even when the two databases had the same species, the relative abundance of these species under specific conditions was found to be significantly different with the two databases. It is concluded that the databases for the system studied here are not sufficiently well developed for thermodynamic equilibrium modelling to provide a reliable insight into the likely behaviour of CCA combustion ash.

The experimental work concentrated on characterising the ash formed from the combustion, with and without the presence of sorbents intended to promote the capture and retention of arsenic in the residual ash. In the absence of any added sorbent, our results parallel those obtained in our earlier work (Stewart *et al.*, 2004) and others. There is some ash volatilisation even at a combustion temperature of 600°C and it now seems clear that all thermal processes to treat CCA-impregnated timber will suffer some level of arsenic volatilisation. Higher temperatures promote arsenic volatilisation, as expected, and by 900°C more than 30% of the arsenic is lost from the wood during its combustion. In this work we found no evidence of loss of chromium from the ash during combustion up to 900°C, even in the absence of sorbent additions.

There have been many reports of the use of sorbents capable of reacting with arsenic in particular and preventing its volatilisation, coming from the coal combustion literature as well as from work on the roasting of arsenic-containing ores. We have investigated this promising approach to arsenic capture, employing a number of potential sorbents, including $Ca(OH)_2$, MgO, Fe_2O_3, K_2SO_4, and Al_2O_3. Of these, the calcium material is the most effective, followed by magnesium. The iron has no influence on arsenic volatilisation, even up to molar ratios of Fe:As > 5. Additions of potassium actually promote arsenic volatilisation, presumably by interacting with sorbents (notably calcium) that are inherently contained in the wood ash. Alumina may also promote arsenic loss, but the effect is weak. Retention of chromium (and copper) remained complete up to 900°C.

More detailed investigation of the use of calcium-based sorbents was undertaken in order to understand the potential of this promising technique. Scanning electron microscopy showed that the added calcium powder actually interacted more intimately with chromium than with arsenic. Wet impregnation of the wood with a soluble calcium salt prior to combustion, which would have produced a much more highly dispersed calcium addition, gave no significant improvement in arsenic retention over dry powder addition.

An interesting effect of calcium sorbent addition is that it rendered the arsenic and the chromium in the ash much more leachable (in dilute acetic acid conditions) than it would otherwise be. This would generally be seen as a disadvantage if the material were intended for disposal in a landfill, but it may open the route to wet processing of the ash followed by controlled precipitation as insoluble arsenates, as practised in the minerals industry.

The use of sorbents appears to have a serious shortcoming in that complete retention of the arsenic in the ash could not be effected, even with wet impregnation in large excess. This is significant because just 2% of arsenic volatilisation is sufficient for the combustion flue gases to exceed the current emission standards for arsenic (10 mg.Nm^{-3}) – it is instructive to compare with capture of SO_2 by limestone injection, a process which is typically only 70 to 90% effective in practice. Therefore, post-combustion treatment of the flue gases would remain indispensable even if sorbents were to be applied. We conclude that the use of sorbents to inhibit arsenic volatilisation is unlikely to offer much practical benefit in a dedicated facility for CCA-treated timber combustion.

Chapter 3 presents a detailed study of the solids that are formed when volatilised arsenic condenses from the gas-phase on cooling. To our knowledge this is the first study of this kind, and it has produced some surprising and important results. In general, there is a significant barrier to the formation of new particles from As_4O_6 as the gas is cooled. We estimate that a supersaturation ratio of the order of 20,000 is required to achieve new particle nucleation – this corresponds to requiring a temperature approximately 100°C below the local saturation temperature before new particles will actually form. In practice, the arsenic is much more likely to deposit on surfaces, especially on pre-existing particles of As_2O_3 – this process occurs readily even when concentrations are very close to the saturation condition. Observations of the formation of an arsenic oxide fume from combustion of CCA-treated timber have come from open burning studies where there are no surfaces present to compete with nucleation, and, as specifically demonstrated in this work, when a relatively high concentration vapour is cooled very rapidly. This result has significant impact on the design of cooling and particle collection systems downstream of a combustor burning CCA-treated timber.

Chapter 4 synthesises the work from the first two Chapters, plus other related research work reported in the literature, with experience from the smelting industries and design principles for wood-fired boilers. It discusses a number of issues arising, options, and tradeoffs that need to be considered in designing a dedicated facility for disposal of CCA-treated timber waste.

The annual flow of end-of-life CCA-treated timber to landfill and stockpile is estimated to be of the order of 180,000 tonnes per annum. Combustion of this biomass would release 110 MW thermal energy which, in small plant, could be used to raise steam and generate approximately 20 MW of electrical power. While this would be a small contribution to the overall energy economy, it would be greenhouse neutral, or better, relative to landfill disposal. At the same time it would lead to a huge reduction in landfill volume and, according to recent life cycle studies, would present a better outcome for ash management, even if the ash were sent to hazardous waste landfill.

The main technical issue associated with combustion of CCA-treated timber is the control of emissions of arsenic (as oxide) to the atmosphere. The vapour pressure of As_2O_3 is such that the flue gases need to be cooled to about 85°C in order for an emission standard of 10 mg.Nm^{-3} (current in most States of Australia, with Queensland requiring <20 mg.Nm^{-3}). This is technically achievable using dilution or evaporative cooling, as is practised currently in the smelting industry around the country. Conventional bag filters are used to capture the arsenic particulate that is formed when the gases are cooled.

Essentially no volatilisation of copper occurs in CCA-treated wood combustion. Chromium volatilisation, if it occurs at all, is restricted to temperatures > 900°C. These volatiles can be expected to condense outside the high temperature zone of the combustor, with the resulting particles being captured in flue-gas treatment devices such as bag filters.

Cofiring of CCA-treated timber in existing large scale combustion systems such as coal-fired boilers is unlikely to be acceptable because of the general increase in total emissions that would be likely to occur. Some promising results have been obtained with co-firing of CCA-treated wood in cement kilns, where the high temperatures and high loadings of calcium oxide promote the scavenging and retention of the CCA metals in the clinker. A possible limitation on this approach is the downward trend in tolerance of metals in cement – recent European standards limit chromium to just 2 ppm, at which level the Australian cement industry would have the capacity to absorb no more than 5000 tonnes of typical CCA-treated timber per annum.

In general combustion environments, the use of chemical sorbents, such as calcium oxide, to trap arsenic in particular appears to have limited utility. Unrealistically high capture efficiencies (>98%) are required for this to be a complete solution even for an arsenic emission standard of 10 mg.Nm^{-3}. The use of sorbents also increases the volume of ash that has to be dealt with.

The construction of dedicated combustion facilities for disposal of CCA-treated timber is believed to be the most secure thermal processing route to meeting with increasingly stringent environmental regulations. The size of individual dedicated facilities for Australia would probably be in the range of 10,000 to 30,000 tonnes per annum. These are relatively small combustion facilities for which bubbling fluidised bed technology or grate firing would be appropriate. On balance, a grate-fired system is recommended because of its simplicity, reliability and proven operating performance in biomass combustion.

Process conditions are provided for a range of plant sizes from 10,000 to 100,000 tonnes per annum. Air dilution is used to cool the gases after the usual heat recovery economiser in order to cause arsenic oxide vapour to condense and bring the arsenic content of the flue gases to less than 10 mg.Nm^{-3}. Bag filters are employed to capture particulate ash consisting of fly ash and condensed arsenic oxide.

It should be noted that international standards for arsenic emissions are typically 1 mg.Nm^{-3}, or less in some jurisdictions. The State of NSW has announced that new plant from the end of 2005 must meet a standard of 1mg.Nm^{-3}, and it would be prudent to expect other States to move to this standard also. This standard cannot readily be met by cooling of the gases – in roasting of arsenic-containing ores, a final wet cleaning system, including wet electrostatic precipitators is employed to ensure the more stringent standards are met. The extra capital and operating expenses of installing wet gas cleaning on small plant is likely to be significant. An alternative approach might be to employ active carbon filter beds for which some promising test data are available.

There are a number of options for disposal of the ash from the combustion of CCA-treated timber. The world market for arsenic is shrinking rapidly, in part because of restrictions on its use in timber preservation. While the other metals are potentially more valuable, the quantities involved are small (~ 1000 tonnes per annum) so the economic options for recovery of these metals are limited. One option might be to send the material to copper smelters where the copper could be recovered and where facilities for stabilisation of arsenic are in place. Even if the ash goes to a hazardous waste landfill, this appears to be a better outcome than sending the end-of-life timber directly to landfill.

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APPENDIX 1: SPECIES IN THERMODYNAMIC EQUILIBRIUM CALCULATIONS

A1.1 Arsenic compounds in FACT53 Thermodynamic Database

Ag3AsO4	S		AsF3	l,g		FeAsS	S
AlAs	S		AsF5	G		GaAs	S,l
As	S,l,g		AsH3	G		H2AsO3[-]	aq
As2	G		AsI3	S,l,g		H2AsO4[-]	aq
As2O3	S1,s2,l		AsN	G		H3AsO4	aq
As2O5	S		AsO[+]	aq		HAsO2	aq
As2S2	S,l		AsO2[-]	aq		HAsO3F[-]	aq
As2S3	S,l		AsO3F[2-]	aq		HAsO4[2-]	aq
As2Sb2	G		AsO4[3-]	aq		InAs	S,l
As2Sb2O6	G		AsS	G		MnAs	S
As2Se2	G		AsSb	G		Na3As	S
As2Se3	S,l		AsSb3	G		NH4H2AsO4	S
As2Te3	S,l		AsSb3O6	G		Ni3(AsO4)2	S
As3	G		AsSe	S,g		NiAs	S
As3Sb	G		AsTe	G		Re3As7	S
As3SbO6	G		BiAsO4	S		Sr3(AsO4)2	S
As4	G		Ca3(AsO4)2	S		Zn3(AsO4)2	S
As4O6	G		Cd3(AsO4)2	S		Zn3As2	S1,s2
As4Se3	S,g		Cd3As2	S		ZnAs2	S
As4Se4	G		Co3(AsO4)2	S			
AsBr3	G		Cu3(AsO4)2	S			
AsCl3	l,g		Cu3As	S			

A1.2 Arsenic compounds in SGTE Pure Substances Thermodynamic Database

AlAs	S,G		As2Te3	S,L		AsI	G
AlAsO4	S		As2Zn	S		AsI2	G
As	S,L,G		As3P	G		AsI3	S,L,G
As[+]	G		As3Sb	G		AsIn	S,L,G
As2	G		As4	G		AsInO4	S
As2Ba3O8	S		As4O10	G		AsK3O4	S
As2Be3O8	S		As4O6	G		AsLaO4	S
As2Ca3O8	S		As4O7	G		AsLi3O4	S
As2Cd3	S,L		As4O8	G		AsMn	S
As2Cd3O8	S		As4O9	G		AsMoO4	S
As2Co3O8	S		As4S4	S1,S2,L1,L2,G		AsN	G
As2Cr3O8	S		As7Re3	S		AsNa3	S
As2Cu3O8	S		As8Ni11	S		AsNa3O4	S
As2Fe3O8	S		AsAu3O4	S		AsNi	S
As2Hg3O8	S		AsB	S		AsO	G
As2I4	G		AsBiO4	S		AsO2	G
As2I6	G		AsBr3	S,G		AsO4Rb3	S
As2Mg3O8	S		AsCl3	L,G		AsO4Re	S
As2Mn3O8	S		AsCrO4	S		AsO4Sc	S
As2Ni3O8	S		AsCs3O4	S		AsO4Tl	S
As2Ni5	S		AsCu3	S		AsO4Y	S
As2O3	S1,S2,L		AsCu3O4	S		AsP	G
As2O5	S,L		AsF	G		AsP3	G
As2O8Pb3	S		AsF3	L,G		AsS	G
As2O8Sn3	S		AsF5	G		AsSb	G
As2O8Sr3	S		AsFeO4	S1-S3		AsSb3	G
As2O8Zn3	S		AsGa	S,L,G		AsSe	G
As2P2	G		AsGaO4	S		AsTe	G
As2S3	S,L		AsGe	S		Ti3As2O8	S
As2Sb2	G		AsH	G			
As2Se3	S,L		AsH2	G			
As2SiZn	S		AsH3	G			

APPENDIX 2: PAPERS, POSTERS AND PRESENTATIONS

Papers

Joseph M. Rogers, Mary Stewart, James G. Petrie and Brian S. Haynes; *Deportment and management of metals produced during combustion of CCA-treated timbers*. Journal of Hazardous Materials, In Press, Available online 5 April 2006.

Rogers, J.M., M. Stewart, J.G. Petrie, and B.S. Haynes. Deportment of Metals from the Combustion of CCA (Chromated Copper Arsenate) Treated Timber. Proceedings of Chemeca 2004. Sydney, Australia.

Presentations

Rogers, J.M., M. Stewart, J.G. Petrie, and B.S. Haynes. Deportment of Metals from the Combustion of CCA (Chromated Copper Arsenate) Treated Timber, presented at Chemeca. 2004 Sydney, Australia.

Deportment of Metals from the Combustion of CCA-treated Timbers; presented to Timber Preservation, Brisbane, 2-3 December 2004.

Rogers, J.M., M. Stewart, J.G. Petrie, and B.S. Haynes. Deportment and Management of Metals Produced During Combustion of CCA-Treated Timbers, presented at 1st International Conference on “Engineering for Waste Treatment: Beneficial Use of Waste and By-Products" (WasteEng 2005), Albi, France; 16 – 18 May, 2005.

The Combustion of CCA-treated Timber: Metals Behaviour and Resulting Implications, presented to Residues to Revenues, Rotorua and Melbourne, October 2005.

Posters

The Combustion of CCA-treated Timbers; presented at University of Sydney Chemical Engineering Foundation Research Day; October, 2005.