DEPORTMENT AND MANAGEMENT OF METALS PRODUCED DURING COMBUSTION OF CCA-TREATED TIMBERS

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Abstract

Experiments were conducted to study CCA-treated wood combustion over a range of temperature and oxygen concentrations with a view to understanding the factors affecting energy and metals recovery from waste treated timber. CCA-treated wood was burned in a furnace at temperatures from 400-940ºC and oxygen concentrations between 5-21%. The ash and condensed volatiles were digested for total concentrations of metals and subjected to leaching tests to determine the stabilized concentrations of metals. Arsenic volatilization increased with increasing furnace temperature whereas the copper and chromium reported mainly to the ash product. The effect of oxygen concentration was weak although it appeared that more arsenic volatilizes at higher oxygen concentrations. However, a larger proportion of the arsenic in the ash generated at lower oxygen concentrations is solubilized during leaching tests, hence the concentration of stabilized arsenic in the ash is relatively unaffected by oxygen concentration.

Keywords: CCA, Combustion, Arsenic volatilization, Ash stability

1. Introduction

Recent changes in government policy globally (USA: US EPA, 2001; Europe: CEC, 2003; Australia: APMVA, 2003; New Zealand: ERMA, 2002) have focused on the environmental effects of the use of CCA (chromated copper arsenate)-treated timbers. Increasingly these policy positions are expanding to include full consideration of the management of these timbers at the end of their useful life. At the same time, interest in renewable fuels is increasing along with interest in energy from waste technologies (WMAA, 2003). End-of-life CCA-treated timber represents a source of energy and metals while at the same time posing a disposal problem due to the toxicity of arsenic and chromium, which must be managed regardless of the chosen method of disposal. Thermal treatment of CCA-treated timbers represents an opportunity to recover the energy content of the wood; and, potentially, the impregnated metals either for reuse or subsequent benign disposal.

A first order technology assessment of the thermal treatment of CCA timber wastes has been conducted (Stewart et al., 2000). This process reviewed technology efficiency with respect to energy recovery and environmental stability of wastes incorporating consideration of pyrolysis, gasification and combustion. This initial study highlighted the fact that metals are likely to report to the desired product stream in gasification (metals in the fuel gas product) and pyrolysis (metals in the char and/or liquid products). For this reason, and given the potential for treated timbers to present in feedstocks to other thermal processes, the decision was made to investigate combustion of CCA treated timbers further.

Previous work on the combustion of CCA treated timber focused mainly on the quantity of metals volatilized, either over a range of temperatures (McMahon et al., 1986; Cornfield et al., 1993) or a range of oxygen concentrations (Dobbs and Grant, 1978). The leaching characteristics of the ash have mostly been tested separately and in general for ash burned under a given combustion condition (Solo-Gabriele et al., 2002). To date, there have been no studies that attempt to measure the extent of volatilization of metals over a range of temperatures and oxygen concentrations while at the same time determining the effect of these combustion conditions on the stability of the resulting ash. In this paper we present results that illustrate the effect of these

different combustion conditions on the deportment of the metals (copper, chromium and arsenic) to the flue gas and the ash residues of combustion as well as the stability of these ash residues.

2. Experimental Method

2.1 Sample Preparation
Wooden spheres were cut from six 1m x approx 125mm diameter freshly impregnated Radiata pine poles supplied by Auspine Ltd. The spheres ranged between 25-30mm in diameter, with mass between 3 and 5g.

2.2 Experimental Rig
Figure 1 shows a schematic of the experimental rig. The combustion of the CCA-treated wood samples was carried out in a non-porous ceramic furnace tube with an Al_2O_3 content of 60%. The inside diameter of the tube is 40 mm. The temperature of the gas and sample was maintained at the required combustion temperature by supporting the furnace tube in a vertically aligned Lindberg/Blue model HTF55347C 5.1 kW 3-zone tube furnace.
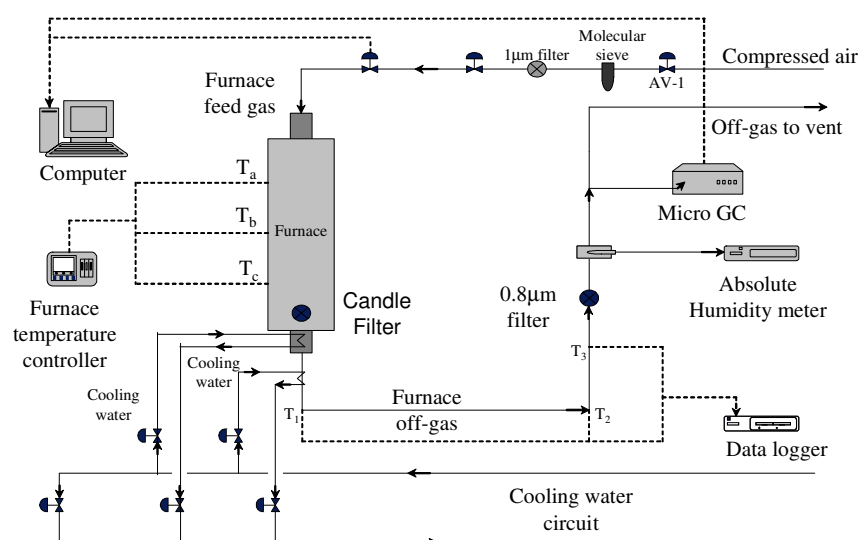
Figure 1: Schematic of Experimental Rig

The process air enters the top of the furnace and passes downwards through the furnace and past the sample. The sample itself is located at the base of the lowest heating element, thus allowing the air stream to approach the tube wall temperature.

The wood sample is held in an Inconel mesh basket attached to the front face of a hot gas filter. The filter is constructed from a chequerboard-pattern diesel soot filter capable of trapping particles down to at least 0.1µm. The filter element has a standard cell density of 15.5 cells.cm^{-1} (Corning International, 1998), with individual channels open and plugged at opposite ends. The gas thus enters the open end (axial flow), flows through the walls (radial flow) into the adjacent channel and exits via the adjacent channel (axial flow). The overall diameter of the cylindrical filter candle is 25mm; its length is 127 mm. The ceramic filter element separates the solids (ash) from the volatile materials such as arsenic which reported to the vapour phase.

At the start of a run, the filter candle plus sample holder and sample are inserted into the base of the tube furnace. All gas flow from that point passes around the sample and through the candle filter. Since the candle rapidly assumes a high temperature, species volatilised during the combustion of the sample pass through the filter, while fly ash is collected on it.

2.3 Off-gas Analysis
The gas was cooled and passed through a 0.8 µm filter for condensed volatiles followed by an absolute humidity meter and a micro GC for the measurement of water vapour, carbon dioxide and carbon monoxide.

2.4 Wood and Ash Analysis

The ash and volatile matter content of the wood have been determined by thermogravimetric analysis (TGA) and a TC/TOC/TIC analyzer was used to determine the total carbon, total organic carbon and total inorganic carbon content. Solubilising the ash for analysis of total metals has presented a significant number of complications. Literature indicated that prior workers used nitric acid (HNO_3) and peroxide (H_2O_2) to dissolve ash samples (Solo-Gabriele et al 1999a; Felton and de Groot, 1996). However, this method resulted in incomplete dissolution of the combustion ash samples. Considerable time has been spent developing/selecting a suitable method for digesting the ash. The wood, ash and the arsenic containing particulates were digested in a 2:1 volumetric ratio of perchloric ($HClO_4$, 4.8N) and nitric acids (16N) in sealed Teflon-lined stainless-steel vessels heated to approximately 180°C for 2-4 hours. This ensures no loss of volatiles and has been found to digest the majority of the ash samples produced at furnace temperatures below 1027°C. However, we have yet to achieve complete solubilisation of ash produced during combustion experiments carried out at a furnace wall temperature of 1072°C. Work in this area is ongoing.

The arsenic, chromium and copper concentrations in the resulting solutions have been determined by Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP AES). Two leaching tests were performed on the ash and volatile matter. An ash sample (0.025 g) was combined with 25 mL of either de-ionized water (DWL) or dilute acetic acid (DAAL) and swirled for 18 hours and the concentrations of the leachate were measured by ICP AES

2.5 Experimental Regime

The experimental regime explored both temperature and oxygen concentration ranges. The three sets of gas compositions explored were 5, 10 and 21% O_2. For each of these gas compositions seven furnace temperatures in the range 510 to 1070°C have been examined. These furnace temperatures relate to calculated gas temperatures at the surface of the wood sample ranging from 400-960°C. At least six repeat runs have been performed at each temperature and oxygen concentration.

3. Results

3.1 Sample Variability

There was considerable variation in As, Cr and Cu content of the feed. The average and standard deviation of the analysed metals content (by mass of element) of the feed was found to be:

- $[As]_{av}$ = 0.266% (standard deviation = 0.07%)
- $[Cr]_{av}$ = 0.350% (s = 0.09%)
- $[Cu]_{av}$ = 0.221% (s = 0.05%)

The mass ratios of the metals with respect to each other were much more constant thereby allowing for normalization of analyses results.

- $[As]/[Cu]$ = 1.21 (s=0.06)
- $[Cr]/[Cu]$ = 1.58 (s=0.05)

3.2 Deportment of Metals

Figure 2 shows the recovery of metals to the ash. However, as discussed above, the original concentration of metals in the specific samples is a relatively uncertain value. For this reason Figure 3 has been developed. Copper was not present either in the filters or deposited on the pipes and was considered non-volatile (see Stewart et al., 2004 for a full discussion). In Figure 3 we use a double normalisation with respect to copper to reduce the effect of sample variability. We term this value "Retention" and calculate it according to these equations:

$$\text{Arsenic Retention} = \frac{\left(\dfrac{[As]}{[Cu]}\right)_{ash}}{\left(\dfrac{[As]}{[Cu]}\right)_{feed}} \qquad \text{Chromium Retention} = \frac{\left(\dfrac{[Cr]}{[Cu]}\right)_{ash}}{\left(\dfrac{[Cr]}{[Cu]}\right)_{feed}}$$

This retention term is an indication of how much of the metal contained in the feed reports to the ash. Figure 3 indicates that the majority of the Cr from the feed reports to the ash product of combustion, while As is depleted from the solid during combustion. This is in line with expectations that volatilisation of arsenic is a likely result of combustion and other thermal treatment strategies. The depletion of arsenic suggests that there may be a trend of decreasing arsenic volatilization with decreasing comburant oxygen concentration, specifically at 5% oxygen.
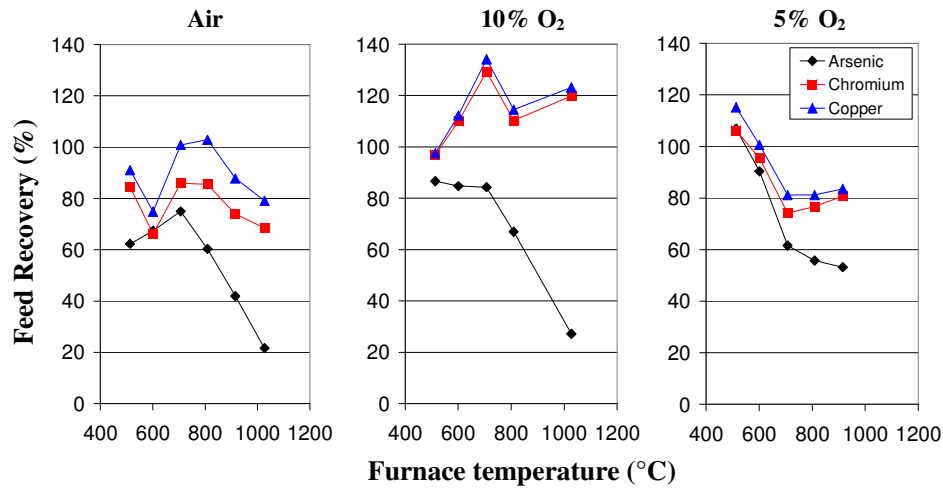
Figure 2: Recovery of Metals to Ash at Different Combustion Temperatures in Air
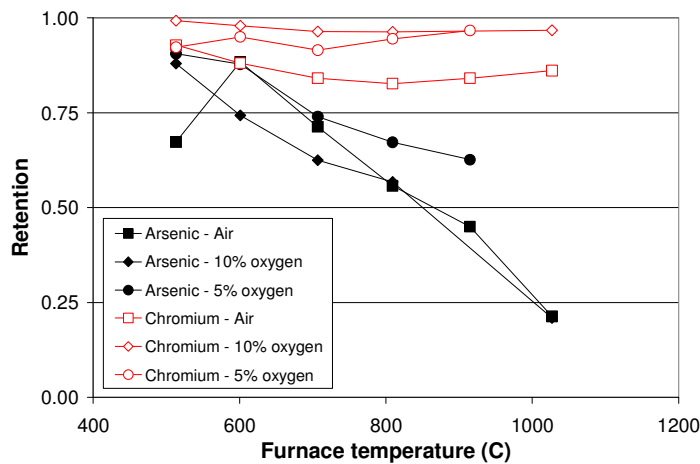

Figure 3: Retention of Metals from the Solid Products of Combustion in Air

3.3 Stability of Metals

The stability of the metals in the ash was measured using two leaching tests: the de-ionized water leaching test (DWL) and the dilute acetic acid leaching test (DAAL). If the arsenic did not leach during these two tests, then it is said to have been stabilized in the ash. Figure 4 shows the proportion of each metal in the ash solubilized during each of these tests for ash generated in 10% oxygen. The results were similar for the other two oxygen concentrations.

Both copper and chromium were generally stable in the ash, becoming very stable in ash produced at high temperatures. Arsenic exhibited a more complex behaviour becoming most stable at mid temperatures and least stable at high temperatures.

Figure 5 shows the percentage of the arsenic present in the feed wood recovered during the DAAL. The percentage of arsenic recovered to the dilute acetic acid increased with decreasing oxygen concentration. This seems to be the reverse of the trend in the retention graph (Fig.3) which showed that arsenic volatilization likely decreased with decreasing comburant oxygen concentration. Therefore, when the percentage of feed arsenic that is considered stabilized is plotted versus furnace temperature (figure 6) all three lines lie on top of each other. Thus the concentration of oxygen does not of itself affect the concentration of arsenic stabilized in the ash.
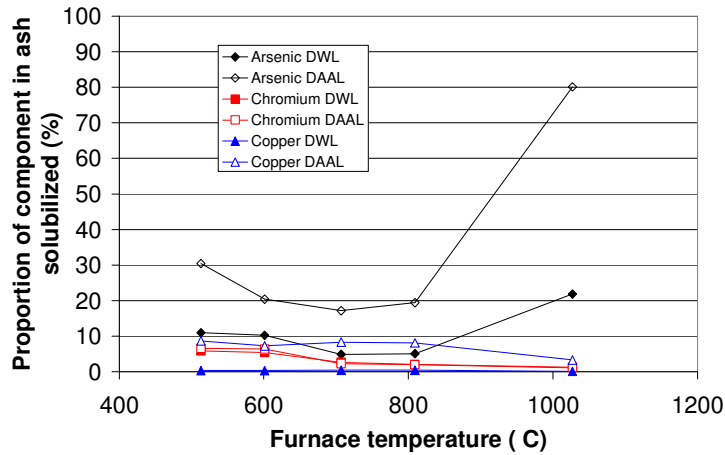

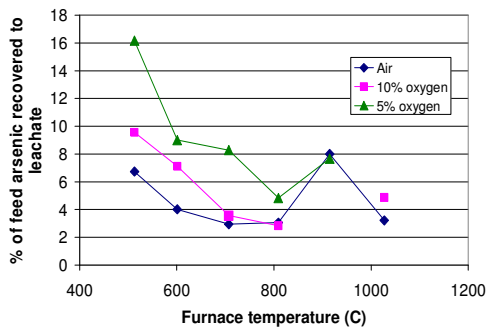**Figure 4:** *Proportion of Metals in Ash Solubilized During Leaching Tests*

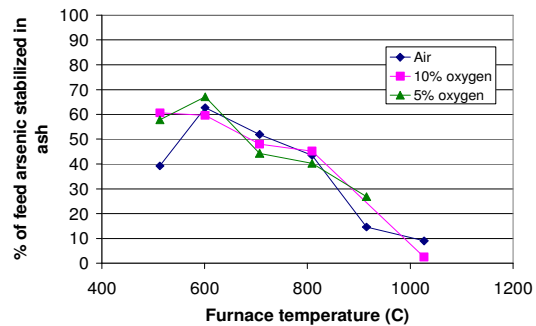*Figure 5: The Percentage of Feed Arsenic Recovered to DAAL Leachate*

Figure 6: The Percentage of Feed Arsenic Stabilized in Ash

4. Discussion

Figures 7, 8, and 9 summarize the results. Copper did not volatilize and was most stable in ashes generated at medium to high temperatures. Chromium showed low levels of volatilization and similar increased stability in medium to high temperatures as copper. Increasing amounts of arsenic volatilized with increasing temperature and arsenic was least stable in the ash generated at high temperatures.
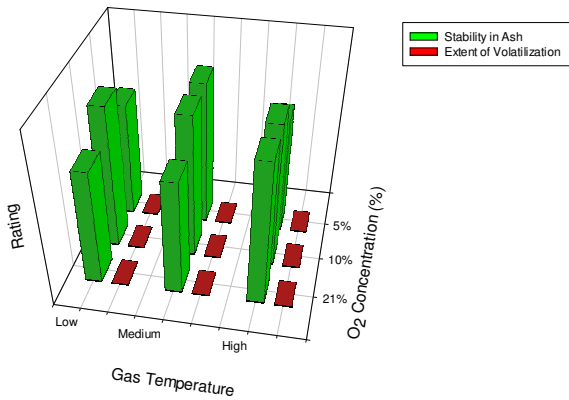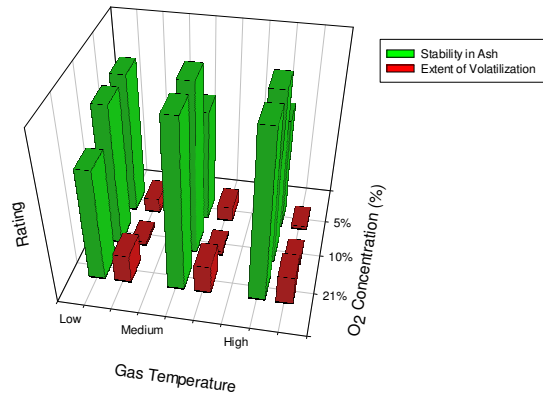
Figure 7: Summary of Results for Copper

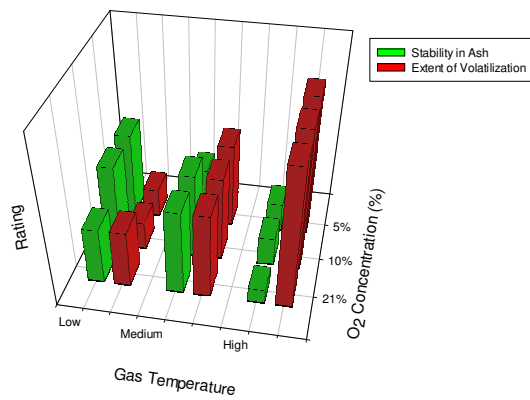*Figure 8: Summary of Results for Chromium*

Figure 9: Summary of Results for Arsenic

The ideal for controlled CCA-treated timber combustion is to recover the energy and recycle the metals while producing solid and gaseous wastes that are environmentally safe. The results above however argue that these ideals cannot all be met simultaneously and that some trade-offs are probably necessary.

Previous work in both combustion (Dobbs and Grant, 1978) and pyrolysis (Helsen and van den Bulck, 2003) has found that some arsenic volatilizes. Recently, researchers studying pyrolysis have concluded that it would be impossible to pyrolyse CCA-treated timber without the volatilization of some arsenic (Helsen et al., 2004). Very low temperature arsenic volatilization starting at 250°C has been observed by Kakitani et al. (2004) in some samples, which they propose is a result of the presence of unfixed arsenic in the treated timber. We also find some arsenic volatilization at our lowest combustion temperatures, under which conditions there is substantial tar formation in our experiments. The implication appears to be that all thermal treatments give rise to some level of arsenic volatilization.

Increasing temperature did not lead to an increase in the volatilization of chromium in the range of temperatures investigated in this study. Cornfield et al. (1993) and Dobbs and Grant (1978) found negligible amounts of chromium volatilization in the temperature range of 400-800°C. Thermodynamic modelling of CCA-treated timber combustion conducted by Sandelin et al (2001) does not predict any chromium volatilization until approximately 1300°C. The mechanism behind the low-temperature volatilization of chromium observed in this study has not been investigated but, similarly to arsenic, it may be linked to the presence of unfixed chromium in the wood.

The environmental consequences of arsenic volatilization are linked to the mechanism by which the arsenic condenses to form particles in the waste gas. The size of particles in which arsenic is found is important from a human health perspective as particles below 1 μm in diameter are considered especially dangerous due to their ability to penetrate deeply into the lungs. While no studies have as yet been conducted on treated timber

combustion to determine the mechanism of arsenic condensation, research in coal combustion has shown that arsenic tends to be concentrated in the submicron range of entrained particles found in the waste gas (Linak and Wendt, 1994). Combustion technologies for CCA-treated timber will hence have to incorporate a method for removing entrained particles from the waste gas.

Low temperature combustion does not volatilize as much arsenic, which could be important depending on the efficiency of the particle removal technology. However, the resulting ash must be considered in terms of the three available management options: the metals can be separated and recycled, the ash can be used as a source of metals for CCA-treated timber manufacturing, or the ash can be disposed of. Ash generated at low temperatures would contain a mixture of all three metals, thereby increasing the difficulty of metals separation and recycling. The ash produced at low temperatures is also the least stable with increased leaching of both chromium and copper meaning that safe disposal would be more difficult.

Arsenic volatilization and entrained particle removal are inevitable, but can actually be turned into a benefit for high temperature combustion conditions. At these conditions, most, if not all, of the arsenic volatilizes, thus allowing for the separation of arsenic from the chromium and copper. Trapping volatilized arsenic in flue dust with the intention of recycling is already being used in the mining industry in copper, gold and lead smelting. The ash waste from high temperature combustion contains approximately 19% chromium as metal and 14% copper as metal thereby having a higher intrinsic value in terms of metals recycling. Alternatively, the ash could also be disposed of more safely than if it contained a significant concentration of arsenic since it is resistant to leaching and highly refractive.

Speciation of the arsenic and chromium in the ash can likely be inferred from the leaching characteristics of the ash. The ash generated at low temperatures is less stable and exhibits leaching of chromium, which is likely indicative of the presence of Cr(VI) as it is the more water soluble form. Cr(VI) is a known carcinogen and hence the ash would be classified as a toxic waste and would require special disposal. A higher percentage of the arsenic present in the ash leached from high temperature ashes than low temperature ashes. The more soluble form of arsenic, As(III), is likely present in the ash generated at high temperatures whereas the less soluble As(V) is likely present in low and medium temperature ashes. As(III) is also toxic and hence ash containing As(III) would also require special disposal. Further research is required in this area.

5. Conclusion

The following conclusions can be drawn from these results:

Increasing the furnace temperature results in:

- An increase in the stability of the ash; i.e. a more aggressive medium is required to solubilise the material,
- A decrease in the arsenic concentration of the ash fraction
- An increase in the amount of arsenic reporting to the volatile fraction.

However, increasing the temperature of the furnace across the range from 601-1027°C has no significant effect on:

- The concentration of copper and chromium in the ash
- The recovery of copper and chromium to the ash fraction

Oxygen concentration appears to have no effect on the concentration of stabilized arsenic in the ash.

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