

Department 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 to 940 °C and oxygen concentrations between 5 and 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 volatilisation 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 volatilises at higher oxygen concentrations. However, a larger proportion of the arsenic in the ash generated at lower oxygen concentrations is solubilised during leaching tests, with the result that the concentration of stabilized arsenic in the ash is relatively unaffected by oxygen concentration.

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1. Introduction

Recent changes in government policy globally [1–4] 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 [5]. 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 by Stewart et al. [6]. 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 be 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 volatilised, either over a range of temperatures [7,8] or a range of oxygen concentrations [9]. The leaching characteristics of the ash have mostly been tested separately and in general for ash burned under a given combustion condition [10]. To date, there have been no studies that attempt to measure the extent of volatilisation 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 department 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.

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2. Experimental method

2.1. Sample preparation

Wooden spheres were cut from six 1 m poles (diameter approximately 125 mm) of freshly impregnated Radiata pine supplied by Auspine Ltd. The spheres were cut and turned from the region midway between the heartwood and the outer surface. They ranged in diameter from 25 to 30 mm, with mass between 3 and 5 g.

2.2. Experimental rig

Fig. 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 was 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.

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 before contacting the sample.

The wood sample is held in an Inconel mesh basket attached to the front face of a hot gas filter. At the start of a run, the hot gas filter plus sample holder and sample are inserted into the base of the pre-heated tube furnace. All gas flow from that point passes around the sample and through the candle filter.

The candle filter consists of a Corning International DuraTrap CO 100/17 filter measuring 25.4 mm diameter \times 127 mm long. The filter is constructed from a chequerboard-pattern diesel soot filter capable of trapping particles down to at least $0.1 \mu\text{m}$. The filter element has a standard cell density of $15.5 \text{ cells cm}^{-2}$ 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 candle is heated by the gas and species volatilised during the combustion of the sample pass through the filter, while fly ash is collected on it. In fact, collection of the material from the filter after a run showed negligible fly ash, indicating that the ash not volatilised during the combustion was not being entrained into the gas stream during the experiments.

The gas leaving the filter was cooled and passed through a $0.8 \mu\text{m}$ filter for condensed volatiles. Analyses of the cooled gas were conducted by an absolute humidity meter and a micro GC for the measurement of water vapour, carbon dioxide and carbon monoxide.

After a number of runs, the piping connecting the filter exhaust to the analysers was washed with dilute acetic acid and ethanol and the washings were analysed for dissolved metals by ICP-AES.

2.3. 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 [11,12]. However, this method resulted in incomplete dissolution of the combustion ash samples. Considerable effort has been devoted to 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 , 70%) and nitric acids (HNO_3 , 63%) in sealed Teflon-lined stainless-steel vessels heated to approximately 180°C for 2–4 h. This ensures no loss of volatiles and has been found to digest the majority of the ash samples produced

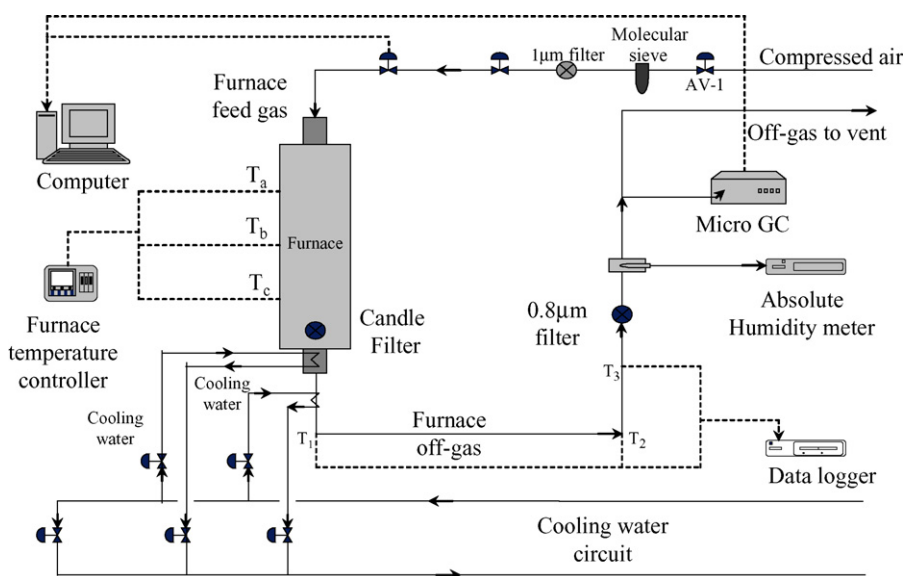


Fig. 1. Schematic of experimental rig.

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 developed based on standard leaching protocols (TCLP) but modified to use the small amount of ash produced in the experiments. 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 h and the concentrations of the leachate were measured by ICP-AES.

2.4. Experimental regime

The experimental regime explored both temperature and oxygen concentration ranges. The three sets of gas compositions explored were 5, 10 and 21% O₂. For each of these gas compositions seven furnace temperatures in the range 510–1070 °C have been examined. These furnace temperatures relate to calculated gas temperatures at the surface of the wood sample ranging from 400 to 960 °C. At least six repeat runs have been performed at each temperature and oxygen concentration [13].

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.d. = 0.09%).
- [Cu]_{av} = 0.221% (s.d. = 0.05%).

The mass ratios of the metals with respect to each other were much more constant thereby allowing for normalization of anal-

yses results.

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

3.2. Department of metals

It is desired to know the how much of the CCA metals reports to the residual ash, and how much is volatilised. Fig. 2 shows the apparent department of the metals to the ash under different combustion conditions, but this information is difficult to interpret because, as discussed above, the original concentrations of metals in the individual samples show significant variability; furthermore, there was a significant loss of volatiles in the sampling train ahead of the final filter.

Analysis, by EDS, of the material captured on a final filter showed that it is mostly arsenic with only small amounts of chromium, while copper was not detected. The walls of the sampling train, when rinsed first with dilute acetic acid and then with ethanol after a series of experiments yielded only arsenic. These results suggest that copper is not volatilised in the experiments, while there may be a small extent of chromium volatilisation. Arsenic is clearly the dominant volatile element but we are unable to close the material balance because only 30% of the apparent loss of arsenic from the ash could be accounted for, 5% on the filter papers and 25% in the sample train deposits. It is likely that the remaining arsenic passed through the sampling system as oxide vapour or very fine particulate.

Turning to a more detailed analysis of the loss of metals from the ash, we note that because copper appears not have been volatilised, we can use its concentration in the ash in a given experiment to normalise the concentrations of the other species, arsenic and chromium. We can now define the “Retention” of arsenic and chromium in the ash as:

$$\text{Arsenic retention} = \frac{([\text{As}]/[\text{Cu}]_{\text{ash}})}{([\text{As}]/[\text{Cu}]_{\text{feed}})},$$

$$\text{Chromium retention} = \frac{([\text{Cr}]/[\text{Cu}]_{\text{ash}})}{([\text{Cr}]/[\text{Cu}]_{\text{feed}})}$$

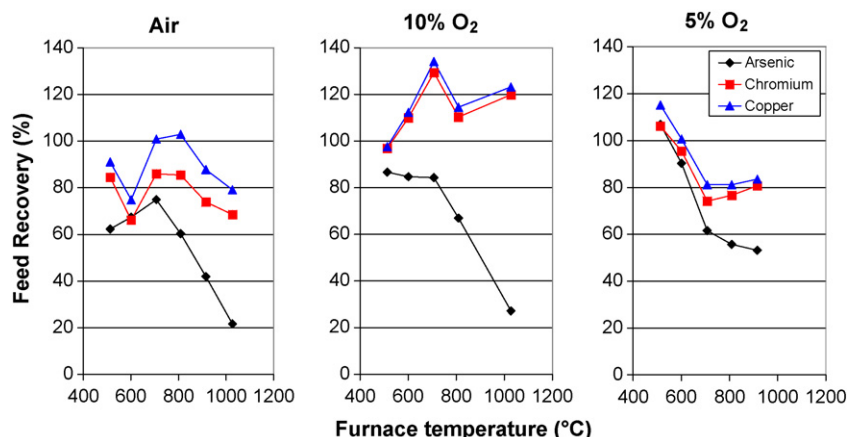


Fig. 2. Apparent recovery of metals to ash at different combustion temperatures in air.

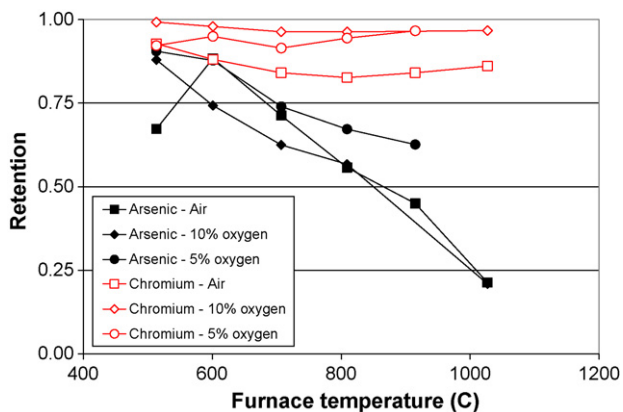


Fig. 3. Retention of metals from the solid products of combustion in air.

The retention of copper is unity, by definition. Fig. 3 shows the results from Fig. 2 presented in this way and the trends are now much clearer. The majority of the Cr from the feed reports to the ash product, which is consistent with the fact that only small amounts of this element were found downstream of the hot candle filter. On the other hand, As is significantly depleted from the solid during combustion, the lost material reporting to the volatile fraction. This is in line with expectations that volatilisation of arsenic is a likely result of combustion and other thermal treatment strategies. The effect of oxygen concentration on the loss of As from the ash is relatively weak, although the results at 5% O₂ do suggest that there is less volatilisation at lower oxygen concentrations.

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. Fig. 4 shows the proportion of each metal in the ash solubilised 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.

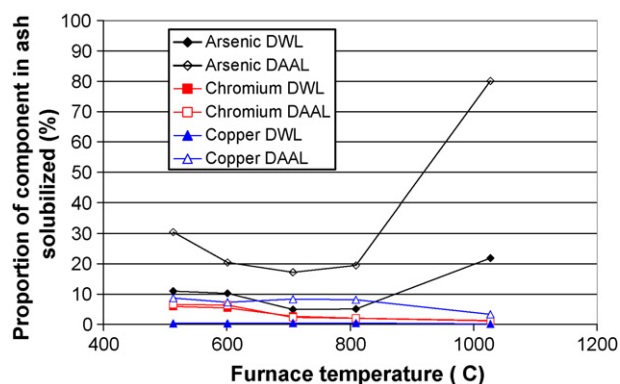


Fig. 4. Proportion of metals in ash solubilised during leaching tests.

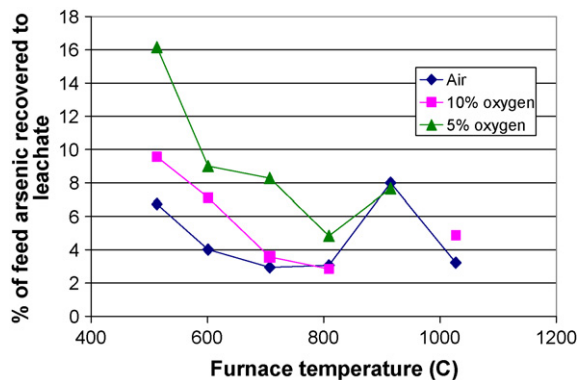


Fig. 5. The percentage of feed arsenic recovered to DAAL leachate.

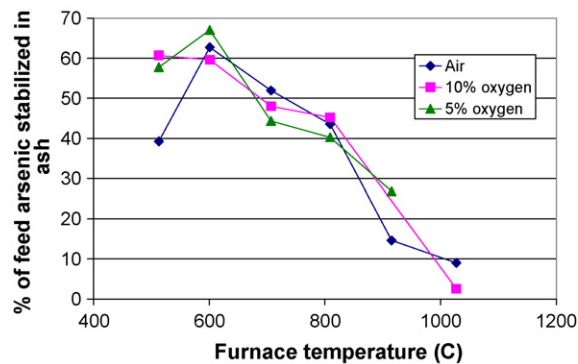


Fig. 6. The percentage of feed arsenic stabilized in ash.

Arsenic exhibited a more complex behaviour becoming most stable at mid temperatures and least stable at high temperatures.

Fig. 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 is the reverse of the trend in the retention graph (Fig. 3) which showed that arsenic volatilisation likely decreased with decreasing oxygen concentration. Therefore, when the percentage of feed arsenic that is considered stabilized is plotted versus furnace temperature (Fig. 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.

4. Discussion

Figs. 7–9 summarize the results by showing the stability and extent of volatilisation of the metals over the range of experimental conditions. Low, medium and high gas temperatures correspond to furnace temperatures of 400, 700–800 and over 1000 °C, respectively. Copper did not volatilise and was most stable in ashes generated at medium to high temperatures. Chromium showed low levels of volatilisation; like copper, its stability in the residual ash was greater after medium to high temperature combustion. Increasing amounts of arsenic volatilised with increasing temperature and arsenic was least stable in the ash generated at high temperatures.

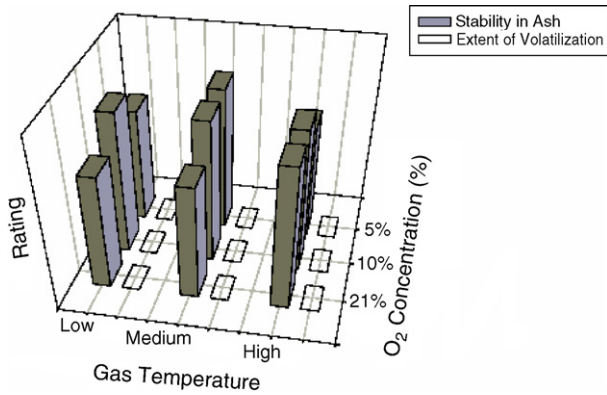


Fig. 7. Summary of results for copper.

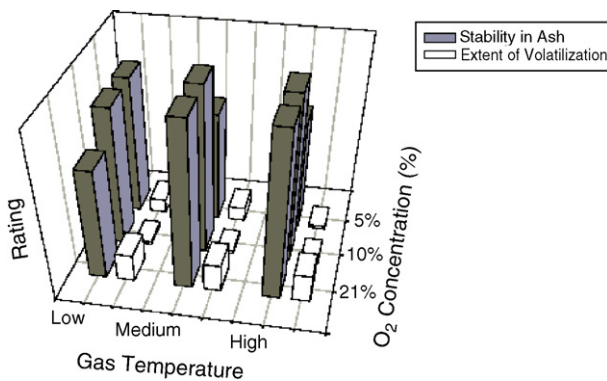


Fig. 8. Summary of results for chromium.

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 [9] and pyrolysis [14] has found that some arsenic volatilises. Recently, researchers studying pyrolysis have concluded that it would be impossible to pyrolyse CCA-treated timber without the volatilisation of some arsenic [15]. Very low temperature arsenic volatili-

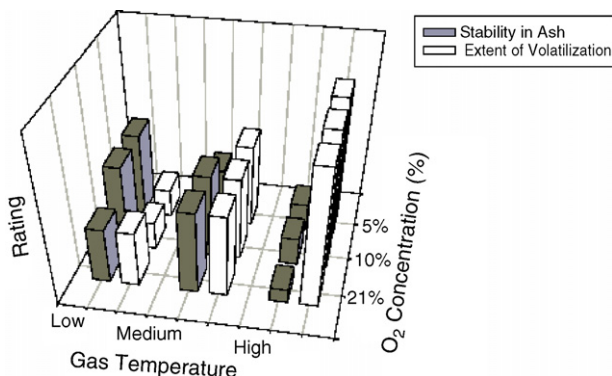


Fig. 9. Summary of results for arsenic.

sation starting at 250 °C has been observed by Kakitani et al. [16] in some samples, which they propose is a result of the presence of unfixed arsenic in the treated timber. We also find some arsenic volatilisation 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 volatilisation.

Increasing temperature did not lead to an increase in the volatilisation of chromium in the range of temperatures investigated in this study. Cornfield et al. [8] and Dobbs and Grant [9] found negligible amounts of chromium volatilisation in the temperature range of 400–800 °C. Thermodynamic modelling of CCA-treated timber combustion conducted by Sandelin et al. [17] does not predict any chromium volatilisation until approximately 1300 °C. The mechanism behind the low-temperature volatilisation 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 volatilisation 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 [18]. 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 volatilise 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 volatilisation 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 volatilises, thus allowing for the separation of arsenic from the chromium and copper. Trapping volatilised 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 low arsenic content of this ash means that it could also be disposed of more safely, especially as the copper and chromium in the ash are resistant to leaching. However, it should be noted that

any arsenic that is collected with the residual ash after high-temperature combustion is relatively easily solubilised, so it would be important to ensure that the highest possible deportment of the arsenic to the volatiles is achieved for this disposal option.

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 to be present in the ash generated at high temperatures whereas the less soluble As(V) is more likely present in low and medium temperature ashes. As(III) is also toxic and requires special disposal. Further research is required in this area.

5. Conclusion

In the combustion of CCA-treated timber, the arsenic in the wood is increasingly volatilised as the temperature is raised above 500 °C, with the result that the ash residue is depleted in arsenic, relative to the CCA proportions in the treated timber. An increase in combustion temperature also enhances the leachability of the arsenic that does report to the residual ash, leaving that material more difficult to dispose of safely. However, at sufficiently high combustion temperatures, essentially all the arsenic is lost from the residual ash. The oxygen concentration in the comburant appears not to affect significantly either the extent of volatilisation or the leachability of the residual ash.

There is no evidence of copper volatilisation in this work but some fraction (<20%) of the chromium may report to the volatiles, although there is no clear trend with temperature. However, the increasing the combustion temperature does reduce the leachability of chromium and copper in the residual ash. The ash formed at the highest temperatures in this work (>1000 °C) is actually not completely dissolved in concentrated nitric/perchloric acid mixtures.

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