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Development of design criteria for integrated treatment technologies for thermal processing of end-of-life CCA-treated timber products – Volume 1

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

Prepared for the

Forest and Wood Products
Research and Development Corporation

by

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EXECUTIVE SUMMARY

The principal objective of the present project has been to provide process design guidelines for integrated treatment facilities for the thermal processing of end-of-life CCA-treated timbers, paying due consideration to technology specification, off-gas management/reuse and ash management/reuse. The flow of end-of-life CCA-treated timber to landfill and stockpile in Australia is estimated to be of the order of 180,000 tonnes per annum. This biomass 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.

A detailed study of arsenic volatilisation, using both thermodynamic equilibrium analysis and experimental investigation, has been undertaken. The thermodynamic analysis proved to be somewhat dependent on the choice of database. 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 combustion ash from CCA-treated timber.

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.

We have investigated the ability of a number of potential sorbents to capture arsenic, 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, and possibly of alumina also, actually promote arsenic volatilisation, presumably by interacting with sorbents (notably calcium) that are inherently contained in the wood ash. Retention of chromium (and copper) remained complete up to 900°C.

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 a only slight improvement in arsenic retention over dry powder addition.

It was notable that additions of calcium to the wood 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.

Overall, 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. In a practical installation, limestone injection can effect the capture of SO_2 only with an efficiency of 70-90% efficiency and one could not expect better results for arsenic capture. This means that post-combustion treatment of the flue gases would remain indispensable even if sorbents were to be applied. We therefore conclude that the use of chemical sorbents to inhibit arsenic volatilisation is unlikely to offer much practical benefit in a dedicated facility for CCA-treated timber combustion.

Once volatilised, arsenic oxide leaves the hot zone in which it was generated and it begins to condense as a solid as the gases cool. For typical As_2O_3 loadings from the combustion of CCA-treated timber, this process will begin below about 150°C. We have shown that there is a significant barrier to the formation of new particles from arsenic oxide vapour as the gas is cooled – the first particles form only after the gas has cooled nearly 100°C below its saturation temperature. Therefore arsenic oxide is more likely to condense on surfaces, with extensive fine particle formation only expected where there are no such surfaces, such as in open burning of CCA-treated timber.

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 but more stringent limits on the chromium content of cement would mean that the capacity of the Australian cement industry to take waste CCA-treated timber would be very small.

The size of individual dedicated combustion facilities for disposal of CCA-treated waste timber in Australia would be in the range of 10,000 to 30,000 tonnes per annum, for which grate firing is the most appropriate technology, given its simplicity, reliability and proven operating performance in biomass combustion. Air dilution or evaporative cooling after water injection can be used to cool the gases to about 85°C in order to meet an arsenic emission standard of 10 $mg.Nm^{-3}$ (current in most States of Australia; 20 $mg.Nm^{-3}$ in Queensland). This mirrors current practice 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.

It should be noted that international standards for arsenic emissions are typically 1 $mg.Nm^{-3}$, or less in some jurisdictions and the state of NSW has announced that new plant from the end of 2005 must meet a standard of $1mg.Nm^{-3}$. This standard cannot readily be met by cooling of the gases and a final wet cleaning system, including wet electrostatic precipitators is required. 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.

Options for disposal of the ash from the combustion of CCA-treated timber are limited. The quantities are small (perhaps 1000 to 2000 tonnes per annum in Australia) and the world market for arsenic is shrinking rapidly. 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.

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1 INTRODUCTION

The management of CCA[1]-treated timber wastes is a significant issue for the treated timber industry, as has been highlighted by a recent APVMA[2] review of arsenic treated timbers (APVMA, 2005). While the annual amount of new CCA timber that is produced is likely to decrease in the future, the rate at which end-of-life material enters the waste stream is still rising and will do so for some years yet. These problems are being faced by related industries throughout the world and the past few years have seen an upsurge in research and publications on the whole question of treated wood waste.

1.1 Background

Generally, end-of-life CCA-treated timber is currently not classified as a hazardous waste in various jurisdictions around the world, including in Australia. In Australia, the APVMA (2005) report concluded that the material is generally not hazardous and has chosen only to restrict its use in timber products where there may be exposure to children - from 8th June 2006, it is an offence to sell CCA preservative chemical for treating timber products intended for use as garden furniture, picnic tables, exterior seating, children's play equipment, patio and domestic decking, and handrails. However, the classification of this material remains a topic of debate between the industry, government and community groups and the situation may change. It has been suggested in the UK (WRAP[3], 2005) that most end-of-life CCA-treated timber actually falls under the definition of hazardous waste material contained in the EC Hazardous Waste Directive but the point is moot since no organic wastes are accepted at landfills in the EU since 2005. By contrast, the US Code of Federal Regulations specifically excludes CCA-treated timber waste from being considered a hazardous waste (US CFR, 2006).

Methods for handling end-of-life CCA-treated timber include re-use, recycling, landfill disposal, and thermal treatment. The approaches to disposal are diverse – ranging from a ban on landfill and compulsory use of combustion in Switzerland to a wide use of landfill in unlined sites and an avoidance of combustion in the USA (WRAP, 2005). In Australia, disposal appears generally to be to landfill but there are concerns with leaching from such sites (APVMA, 2005).

A previous desktop study providing input to the Treated Timber Advisory Group of the (then) NSW Western Sydney Waste Board highlighted the thermal processing of CCA-treated timber, with energy recovery, as a viable option for improving the resource-use efficiency of this material (Stewart *et al.*, 2001).

The disposal of treated timbers to landfill equates to loss of a valuable resource. There are existing drives to divert material from landfill. This, coupled with the understanding that:

- The metals with which the wood is treated are potentially mobile under landfill conditions
- Decomposition of wood renders significantly more global warming potential gases than does combustion

led to the proposal that the combustion of treated timber in a controlled manner recovers both its energy content and the CCA metals would provide significant benefit to the wood

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[1] Chromated Copper Arsenate

[2] Australian Pesticides and Veterinary Medicines Authority

[3] Waste and Resources Action Program

products industry, and contribute to the closure of the value chain around CCA, whilst producing environmentally stable residues.

This desktop study explored, on a theoretical basis, the merits and issues associated with three potential options for end-of-life CCA-treated timber management:

- Pyrothermal processing
    - Pyrolysis
    - Gasification
    - Combustion
- Bio-processing
    - Production of Methane
    - Production of Alcohols
- Co-utilisation as part-substitute fuels or raw materials for product manufacture
    - Production of building composites
    - Co-firing through thermal processes (Cement Kilns, Smelters, Power Plants)

Analysis of these technologies was limited to a first order assessment guided by an understanding of the operating conditions of the different technologies, and the potential performance of the CCA metals (Cr, Cu and As) under these operating conditions. Environmental and (to a limited extent) economic issues and considerations associated with these options were discussed. These options included:

- Determining and managing the fate of metals
- Management of all emissions (solid, liquid and gaseous)
- Potential for product and energy recovery from these systems

The conclusion of this work was that combustion of CCA-treated timbers was preferred because it actively separates the metals from the desired product (energy) and has the potential to deliver residues which are environmentally stable.

Subsequent work by our group (Stewart *et al.*, 2004) investigated the combustion of CCA-treated timbers in a laboratory furnace under well-defined combustion conditions with specified gas composition (5% < mole fraction of O_2 < 21%) and temperature ($400 < T < 960$ °C). There are two possible destinations for the metals present in CCA-treated timbers – incorporation into the ash residue, or volatilisation into the flue gas (followed by subsequent deposition as the flue gases are cooled). Of the metals entering the system:

- All the copper reports to the ash
- More than 90% of chromium reports to the ash
- Arsenic reporting to the ash ranges from 20% to 80%

A complicated pattern of behaviour emerges for the environmental stability of the solid residues. Of particular significance is the fact that some of the residues from high-temperature combustion (>1000 °C) are extremely refractory and difficult to leach. While this means that it is not possible to recover the metals for reuse easily, it also means that these materials are extremely stable and unlikely to have adverse environmental effects in the short term.

The results from the experimental work are summarized in the figures below which present the volatility and stability of the metals (Cr, Cu and As) across the temperature ranges investigated for the different oxygen concentrations in the combustion gas. Volatility is an indication of the potential for the metal to report to the off-gas from the process. Stability is an indication of the environmental stability of the solids recovered from the system. In the figures Rating refers to the qualitative performance of the system in these indicators. Rating ranges from Low to High.

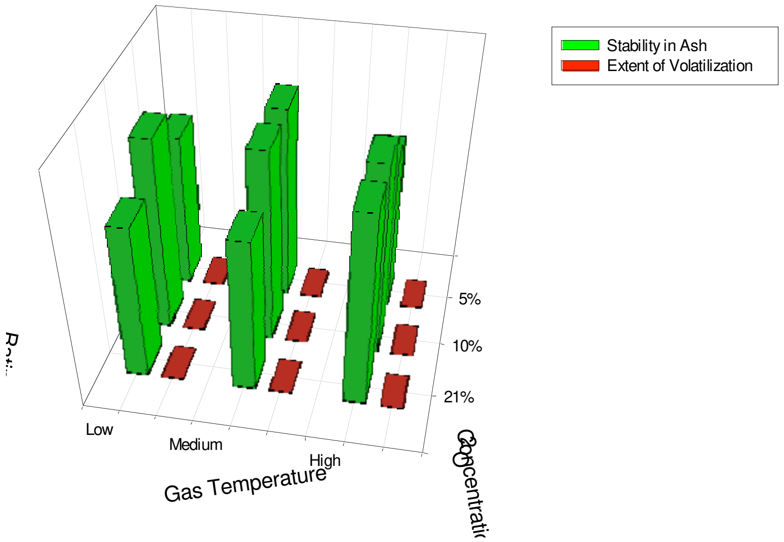


Figure 1: *Volatility and stability of copper (Stewart et al., 2004).*

This result demonstrates that copper is essentially not volatile in the system. Further, copper present in the solid products of combustion is relatively stable.

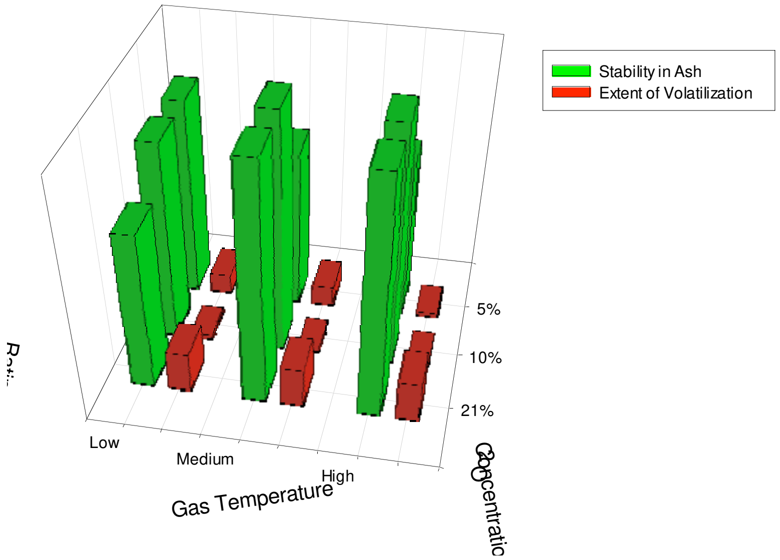


Figure 2: *Volatility and stability of chromium (Stewart et al., 2004).*

Chromium is more volatile in the system than copper; however, this volatility is relatively limited. Chromium in the residue is most stable for the 10% oxygen and ("standard") air cases. This result demonstrates that the region between air and 10% oxygen is the preferred operating region for cases where chromium stability is the over-riding consideration.

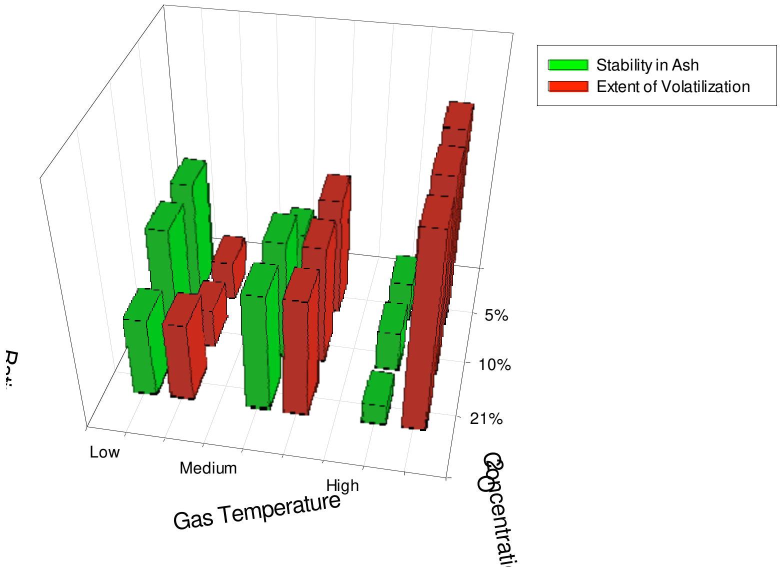


Figure 3: *Volatility and stability of arsenic (Stewart et al., 2004).*

The volatility of arsenic is higher than either copper or chromium. While oxygen concentration has a small effect on arsenic volatility, the volatility of arsenic increases markedly with increasing temperature. The stability of arsenic in the aggregated solid residues exhibits a more complicated behaviour. In air, the stability of arsenic is highest at medium temperatures but lower at low temperatures and lowest at high temperatures. This trend is somewhat repeated to a lesser degree for 10% O_2 but the stability of the arsenic in the ash generated from combustion in 5% O_2 decreases with increasing temperature. Arsenic in residues from low oxygen concentration regimes is, in general, less stable than that from higher oxygen concentration regimes.

1.2 Project Objectives

The principal objective of the present project has been to provide process design guidelines for integrated treatment facilities for the thermal processing of end-of-life CCA-treated timbers, paying due consideration to technology specification, off-gas management/reuse and ash management/reuse.

Other outputs of the project to inform the process design guidelines are:

- More detailed understanding of the speciation and deportment of arsenic and chromium in the system.
- Detailed physical and chemical characterisation of the residual ash and of the ash fume formed from condensation of volatile components, principally arsenic.
- An investigation of combustion conditions to aid understanding of their effects on the recycleability/stability of metals in the products of combustion and their effects on technology selection.

1.3 Review of Recent Publications

Since commencement of this project, there have been a number of significant reports and scientific publications on the topic of treatment of end-of-life CCA-treated timber. These are reviewed here in order to place our work in the evolving context in which it was undertaken (July 2004 to June 2006).

The APVMA finalised its review (APVMA, 2005) of the registrations of timber treatment products containing arsenic. The review found that dislodgeable residues on CCA-treated timber structures may be higher than previously believed and that, while existing installations pose no significant threat, new installations where children in particular might be exposed, should be banned. However, CCA-treated timber may still be used for materials such as telegraph poles, fence posts, fence palings or other structural timbers, where frequent contact is unlikely. Therefore CCA-treated timber is likely to continue to be employed into the future and the issues associated with its disposal will remain important for many years to come.

An important analysis of the trade-offs between landfill disposal and combustion of CCA-treated wood waste has been undertaken by Jambeck *et al.* (2005, 2006) for conditions pertaining in Florida. They concluded that combustion would cost about twice as much as disposal in a lined MSW landfill, for the same mass of wood. However, there were significant benefits in combustion, ranging from possible green energy credits to major reductions in the volume of landfill required when the timber is reduced to ash. Furthermore, based on their earlier characterization of the leaching behaviour of ash from combustion of CCA-treated wood (Solo-Gabriele *et al.*, 2002) and from landfills (Townsend *et al.*, 2004; Khan *et al.*, 2006), they concluded that landfilled timber would actually release significantly more arsenic, albeit in a diluted form, than would landfilled ash. Chromium leaching from timber and from ash appear to be similar. While the leachate from ash deposits would be more concentrated, its management would be facilitated by the smaller collection area and smaller volume of leachate.

The UK WRAP report (WRAP, 2005) provided a comprehensive assessment of options for handling (excluding disposal to landfill) of treated wood waste, including CCA timber. They concluded that CCA-treated timber may be suitable for reuse but is a poor candidate for recycling (e.g. as chip in fibreboard or as mulch). While some exploratory techniques for chemical processing of the treated timber might prove suitable, the thermal treatment technologies, especially destruction by incineration, are the most highly developed of the all the options available. It is concluded that there are no issues with an appropriately equipped incinerator except for the hazard posed by arsenic emissions.

Hata *et al.* (2003) and Helsen and van den Bulck (2003) found significant volatilisation of arsenic even under mild pyrolysis conditions. Helsen and van den Bulck (2005) reviewed thermochemical disposal technologies for CCA-treated wood waste. They found that all thermal processes (pyrolysis, gasification, combustion, and co-combustion with another fuel) give rise to some volatilisation of arsenic. In particular, pyrolysis leads to a contamination of the tars and liquid products with volatilised arsenic, as previously concluded by Stewart *et al.* (2001). Gasification, for example in steam, would be attractive if all the arsenic were vaporised and could be recovered through intensive off-gas treatment. The authors conclude that the best available thermochemical conversion technology is therefore combustion with appropriate gas treatment technologies for the flue gases. The question as to whether the waste timber should be cofired is complex: if dilution is acceptable from an emissions and environmental impact standpoint, then the significant existing investment in large combustion facilities makes this attractive; on the other hand, mixing of CCA-treated timber with other fuels does require that any necessary treatment be applied to a larger volume of flue gas and/or ash. It should be noted that Helsen and van den Bulck (2005) report that, in some jurisdictions, such dilution of a hazardous waste is actually not allowed. One of the advantages of combustion is that steam and electricity may be produced - there may also be green credits for the use of the timber as a biofuel, but this is precluded in the EU which excludes any such credits for combustion of hazardous wastes.

Recently Helsen (2005) concluded that, since some arsenic will volatilise in any thermal treatment technology, it is likely that any such process will require flue gas treatment. In the presence of oxygen, this volatilised arsenic will exist in a number of states (AsO, AsO_2, etc at high) temperatures but as the gases are cooled, the dominant oxide becomes As_4O_6, which upon further cooling becomes supersaturated and forms fine particles of As_2O_3. However, this phase change is an equilibrium reaction and some arsenic remains in the vapour. Therefore, complete capture of the arsenic requires that both the gaseous and the particulate oxide in the flue gases must be treated. Helsen (2005) has reviewed some laboratory and pilot-plant data for arsenic capture and concluded that simple cooling cannot collect all the vapour phase arsenic oxides and that some physical or chemical sorbent is needed to effect complete capture. Possible sorbents include CaO or Na_2CO_3 as these react with the gaseous oxide to form stable low-volatility arsenates (Iida *et al.*, 2004).

Wasson *et al.* (2005) examined the ash characteristics and particulate emissions from open burning of CCA-treated timber. Approximately 12% of the arsenic in the timber reported to a fine, respirable aerosol phase with a mass-mean diameter below 1 μm; less than 1% of the copper or the chromium from the timber was found in the aerosol. While open burning is a very different combustion environment than would be expected in a controlled facility, this is the first characterisation of the aerosol that forms when volatilised arsenic recondenses via homogeneous nucleation in the gas-phase.

1.4 Report Structure

In Section 2, we describe and discuss experimental and thermodynamic modelling studies of the use of sorbents to minimise arsenic volatilisation during combustion of CCA-treated timber. Section 3 presents studies on the condensation of volatilised arsenic. In Section 4, we present a discussion of the issues involved in the design of equipment for the combustion of CCA-treated timber waste and provide guidelines and a conceptual design for a suitable facility. We present our conclusions and recommendations in Section 4.

2 ARSENIC VOLATILISATION

To be able to design a combustion control system for CCA-treated timber effectively, the behaviour of metals during combustion needs to be understood. Therefore, the aim of the work presented here was to:

- Use equilibrium modelling calculations to characterise ideal ash behaviour in CCA-treated wood combustion.
- Examine experimentally the effects of combustion conditions (e.g. temperature, wood particle size, residence time etc.) on the ash chemistry and structure, using the following instrumental techniques:
  - Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Atomic Absorption Spectrometry (AAS) analyses of digested samples.
  - Scanning Electron microscopy (SEM) for ash particle size and morphology.
  - X-Ray Diffraction analysis for identification of crystalline phases.
- Explore the use of possible sorbent materials to capture metal emissions from CCA-treated wood combustion.
- Identify process off-gases to be able to design an adequate environmental control system.

2.1 Equilibrium Modelling Of CCA-Treated Timber Ash

2.1.1 Approach

Although, in a real system, it is expected that the combustion process is affected by a number of aspects (e.g. mass transfer and kinetics), equilibrium calculations can provide a valuable fundamental understanding of the behaviour of metal species and potential sorbent materials to capture them (Sandelin and Backman, 1999). In this study, we use equilibrium calculations to determine the CCA-treated wood combustion products and the feasibility of using sorbents to capture toxic metals. The FactSage thermochemical software (www.factsage.com, Version 5.4.1) was used for the equilibrium calculations. Thermochemical data were obtained from the Fact53 database (Bale *et al.*, 2002; version from August 2005) or from the SGTE database also provided by FactSage. In each case, all the Cu-, Cr- and/or As-containing substances in the relevant database were included in the calculations. Appendix 1 lists the arsenic-containing substances.

The calculations have been carried out for the specific CCA-treated timber composition corresponding to the blended sample used in the experimental work carried out in this project. This composition, given in Table 1, was determined experimentally as described in Section 3.2.1. The equilibrium compositions of the ash were determined for the combustion of 1 kg wood with a stoichiometric air-to-fuel ratio (λ) of 1.2, for set temperatures up to 1200°C.

Table 1: *Wood matrix used in the thermodynamic equilibrium calculations.*

Component	mole/kg-wood
Carbon, C	39.80
Hydrogen, H	58.73
Sulphur, S	0.0374
Moisture, H_2O	2.28
Potassium, K	0.0138
Calcium, Ca	0.0225
Magnesium, Mg	0.0061
Sodium, Na	0.0100
Silicon, Si	0.0039
Arsenic, As	0.0430
Chromium, Cr	0.0923
Copper, Cu	0.0414

2.1.2 Equilibrium Modelling of CCA-Treated Timber Combustion

Figure 4 shows the equilibrium yields of CCA-treated wood combustion products containing arsenic, chromium and copper calculated using the Fact53 database. The main CCA-derived products in the temperature range 600-900ºC are As_4O_6(g), $Ca_3(AsO_4)_2$(s), Cr_2O_3(s) and CuO(s). At lower temperatures, As_2O_5(s) is the main arsenic-containing product but some volatilisation as As_4O_6 is predicted above about 550ºC and by 600ºC all solid As_2O_5 have been converted into gaseous As_4O_6. However, above this temperature, involatile $Ca_3(AsO_4)_2$ is formed, reducing the fraction of the arsenic reporting as As_4O_6 . Between 650ºC and 1000ºC, all the calcium that is present in the ash is locked up as the arsenate, with the remaining arsenic remaining as As_4O_6. Beyond 1000ºC, there is slight decomposition of $Ca_3(AsO_4)_2$ in favour of additional As_4O_6.

The dominant chromium species throughout the temperature range studied is Cr_2O_3(s) although there is a minor yield of $MgO(Cr_2O_3)$(s), limited by the amount of magnesium inherently present in the ash, which remains very stable up to 1200ºC. The only gaseous chromium species found is $CrO_2(OH)_2$(g) which is seen only at higher temperatures (> 800 ºC) and at low yield (less than 2% of total Cr at 1200 ºC).

There are no volatile copper species predicted and copper reports exclusively to the solid ash up to at least 1200ºC. The main copper-containing species are CuO, up to 1000ºC, and Cu_2O at higher temperatures.

The Fact53 database therefore predicts that, of the CCA metals, only arsenic should be expected to volatilise to a significant extent in combustion at temperatures up to 1200 ºC. The chromium (predominantly) and copper (entirely) constituents are expected to remain with the solid ash.

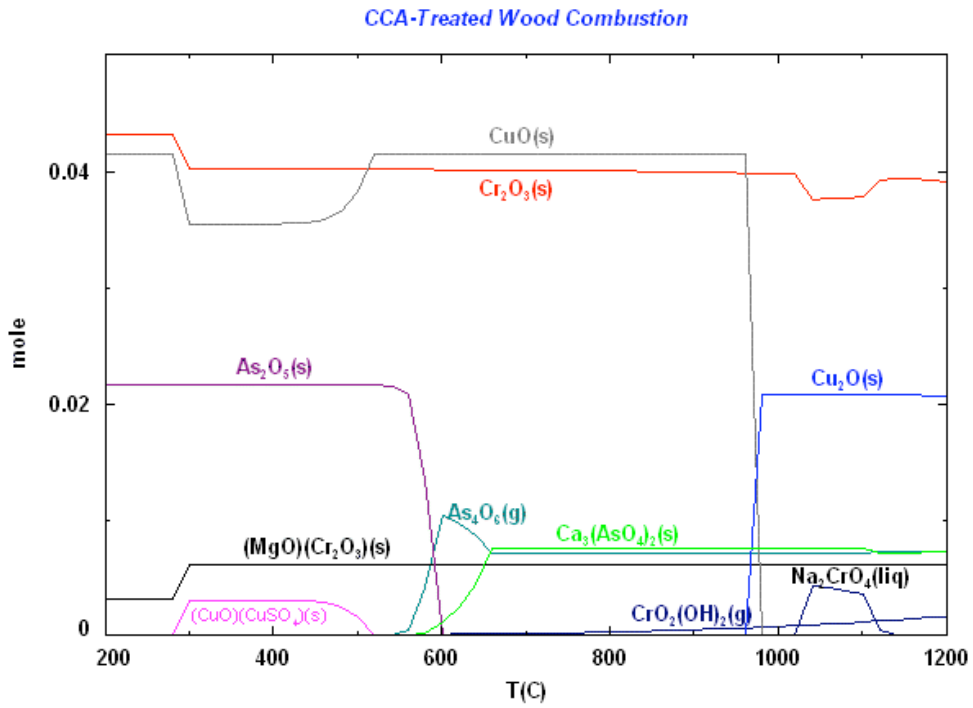


Figure 4: *Equilibrium amounts of main As-, Cr- and Cu-containing products of CCA-treated timber combustion, calculated using Fact53 thermodynamic database.*

Sandelin *et al.*and Backman (2001) employed the SGTE database in their equilibrium analysis of CCA-treated timber combustion products. Because of this, and because the SGTE database contains some different species from those in Fact53, we calculated SGTE equilibrium yields for the same conditions as employed in Figure 4. Results are shown for arsenic-containing species in Figure 5.

Comparison of Figure 4 and Figure 5 reveals extraordinary differences in the predictions of the two databases. With SGTE, the arsenic is essentially bound in the solid phase in a variety of arsenates at temperatures up to 1000 ºC, beyond which it begins to volatilise as simple oxides AsO(g) and AsO_2(g). Beyond 1200 ºC, essentially all the arsenic reports to the vapour phase.

It is beyond the scope of this work to explore in detail the differences between the predictions of the two databases. Some of the differences relate to the fact that SGTE includes some substances that are not present in Fact53 – e.g. chromium arsenate, CrAsO4, is dominant among the low-temperature SGTE products but is not included at all in the Fact53 database. Other differences clearly relate to differences in the thermodynamic data for specific substances in the two databases – Fact53 has As_2O_5 as the only As-containing product up to about 550ºC, but the formation of this species is entirely suppressed in the SGTE-based calculations.

While equilibrium calculations can only provide expectations for conditions of thermodynamic equilibrium, it is interesting to note that our earlier work showed significant volatilisation of arsenic at temperatures beyond about 600°C, which is more in keeping with the Fact53 results. Notwithstanding the differences between the results derived from the two databases, it is very clear that the formation of stable arsenates can inhibit the extent of arsenic vaporisation under combustion conditions.

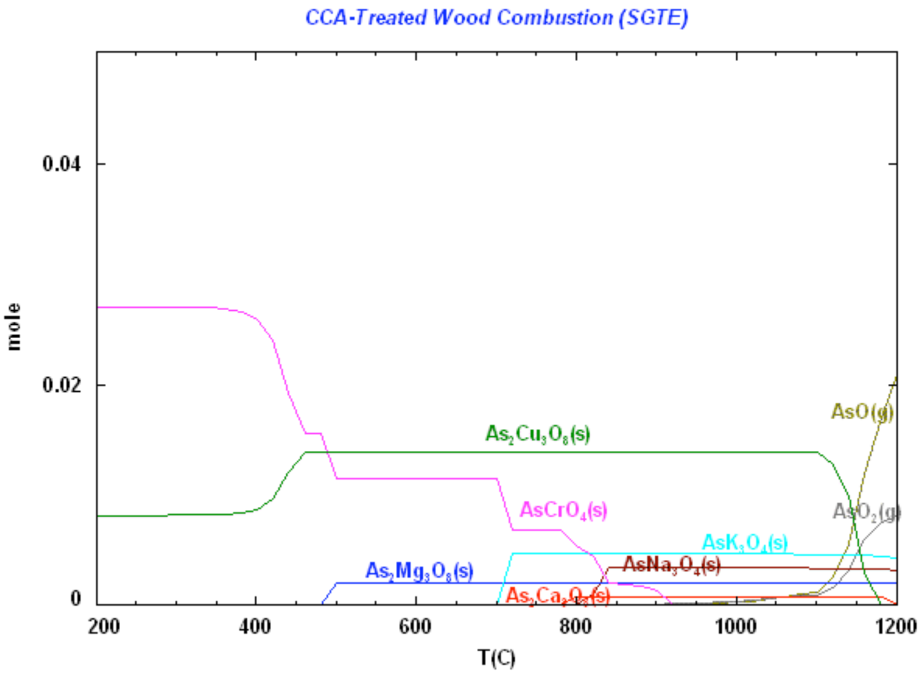
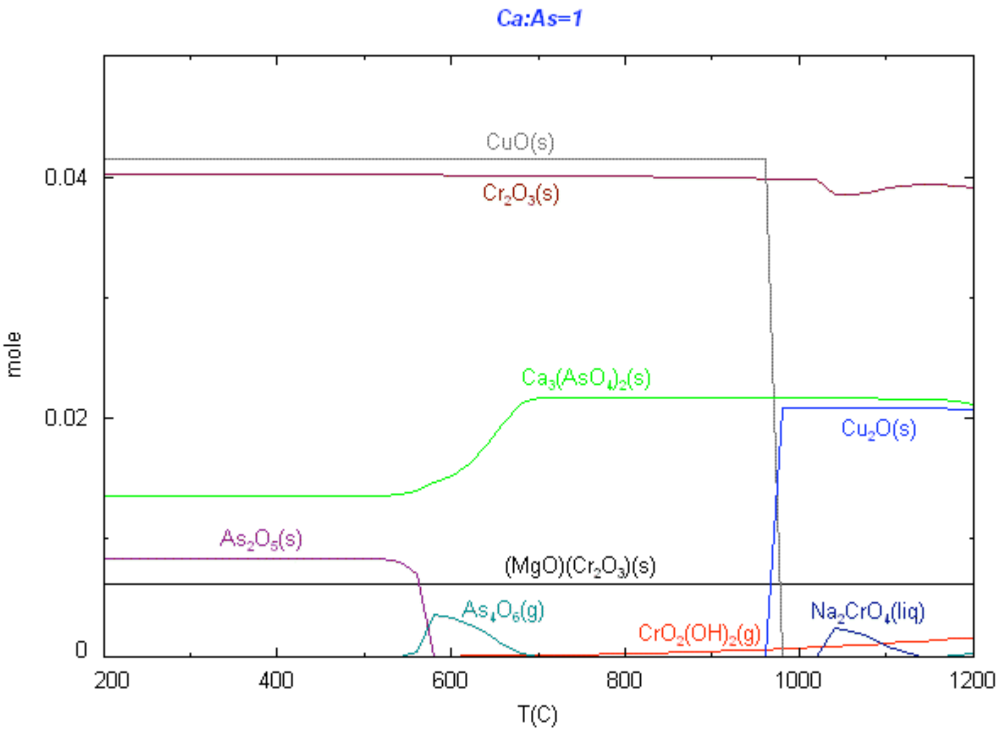


Figure 5: *Equilibrium amounts of main As-, Cr- and Cu-containing products of CCA-treated timber combustion, calculated using SGTE thermodynamic database.*

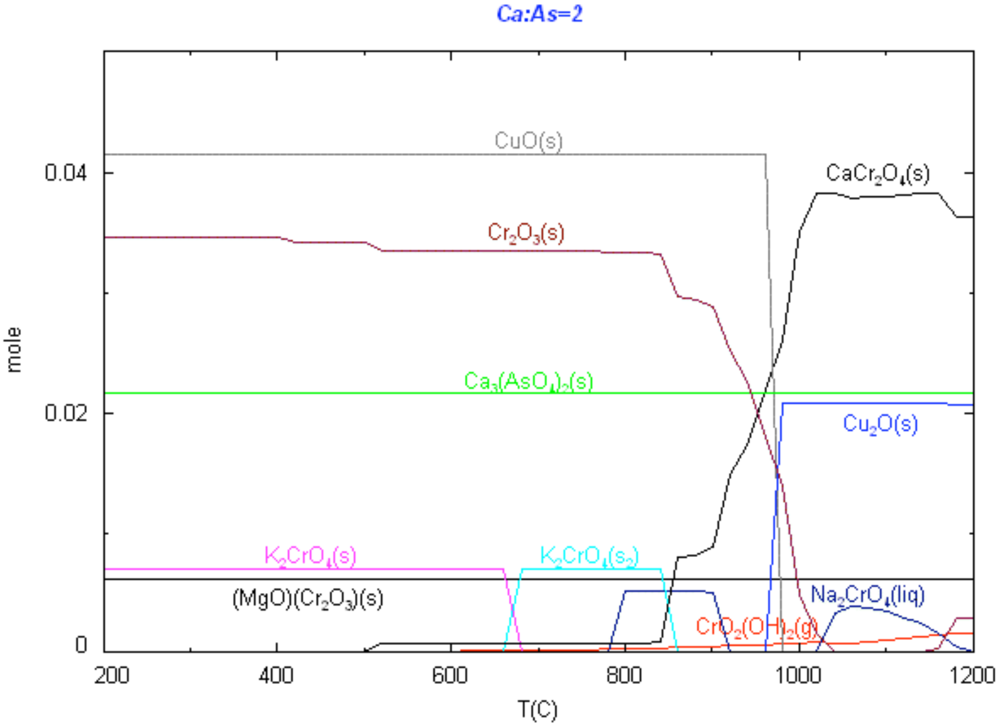
2.1.3 Effect of Calcium Addition on Equilibrium Ash Composition

There are numerous literature reports of the ability of calcium to form an arsenate that is thermally stable up to very high temperatures. Indeed, the vaporisation of arsenic in pulverised coal combustion at 1800 °C is suppressed by the formation of $Ca_3(AsO_4)_2$ (Linak and Wendt, 1994). The calculations employing both the Fact53 and the SGTE databases also predict that the calcium inherent in the wood ash (Table 1) can be responsible for stabilising arsenic in the solid phase.

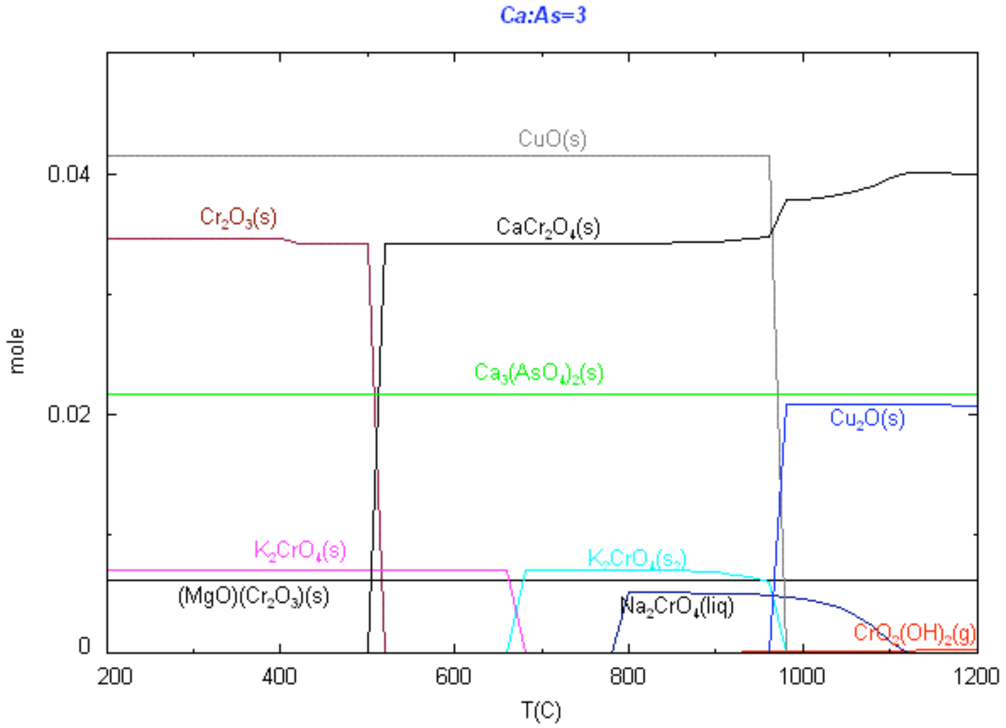
To investigate the variation in the equilibrium speciation of the metals upon addition of calcium, $Ca(OH)_2$ was included in the input mixture to the calculations in order to simulate the effects of different Ca:As molar ratios. As shown in Figure 6(a-d) for predictions based on the Fact53 database, increasing Ca additions suppress gaseous As_4O_6 formation in favour of solid $Ca_3(AsO_4)_2$. With sufficiently high Ca:As ratios (molar ratio > 2), the slight decomposition of $Ca_3(AsO_4)_2$ seen at higher temperatures in Figure 4 is also suppressed, suggesting that volatilisation of arsenic is completely suppressed throughout the temperature


Ca:As=1
mole
0.04
0.02
0
200
400
600
800
1000
1200
T(C)
CuO(s)
Cr_2O_3(s)
$Ca_3(AsO_4)_2$(s)
Cu_2O(s)
As_2O_5(s)
(MgO)(Cr_2O_3)(s)
As_4O_6(g)
$CrO_2(OH)_2$(g)
Na_2CrO_4(liq)

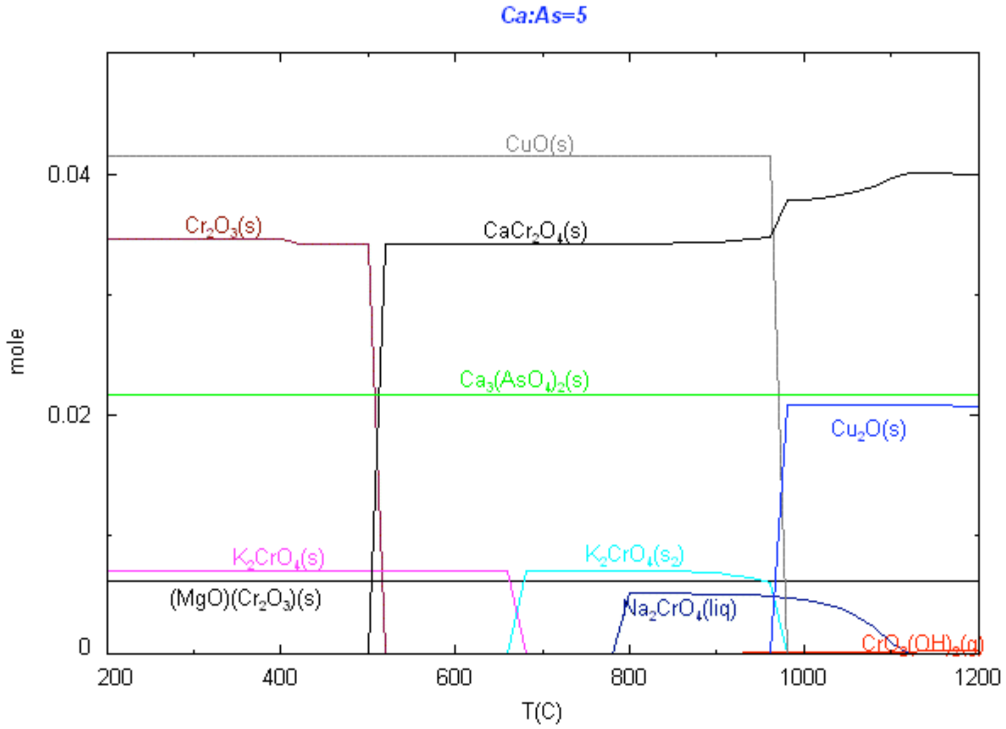
(a)


Ca:As=2
mole
0.04
0.02
0
200
400
600
800
1000
1200
T(C)
CuO(s)
$CaCr_2O_4$(s)
Cr_2O_3(s)
$Ca_3(AsO_4)_2$(s)
Cu_2O(s)
K_2CrO_4(s)
K_2CrO_4(s_2)
(MgO)(Cr_2O_3)(s)
Na_2CrO_4(liq)
$CrO_2(OH)_2$(g)

(b)



(c)



(d)

Figure 6: *Fact53 equilibrium predictions of effect of calcium sorbent additions.*
(a) $n_{Ca}:n_{As}=1$, *(b)* $n_{Ca}:n_{As}=2$, *(c)* $n_{Ca}:n_{As}=3$, *(d)* $n_{Ca}:n_{As}=5$

range considered. In addition, formation of the arsenic oxide As_2O_5, a known precursor for As_4O_6 vaporisation, is also suppressed.

The addition of calcium is predicted to produce some changes also in the speciation of the chromium components. Solid $CaCr_2O_4$, liquid Na_2CrO_4 and liquid K_2CrO_4 formation become favoured over solid Cr_2O_3 at higher temperatures. With high levels of calcium addition (Ca:As >2), the extensive formation of $CaCr_2O_4$ limits the extent of chromium vaporisation as $CrO_2(OH)_2$. Calcium additions have negligible impact on the speciation of copper which continues to report as CuO and Cu_2O. The addition of calcium is also predicted by the SGTE database to give rise to substantial formation of $Ca_3(AsO_4)_2$, as shown in Figure 7 for a molar ratio of Ca:As = 1, where the arsenate dominates the arsenic speciation above 900 ºC. The high-temperature volatilisation of arsenic is strongly suppressed. Greater additions of Ca reinforce the dominance of $Ca_3(AsO_4)_2$ and with Ca:As = 5, essentially all the arsenic reports in this form, as is also predicted by the Fact53 database in Figure 6(d).

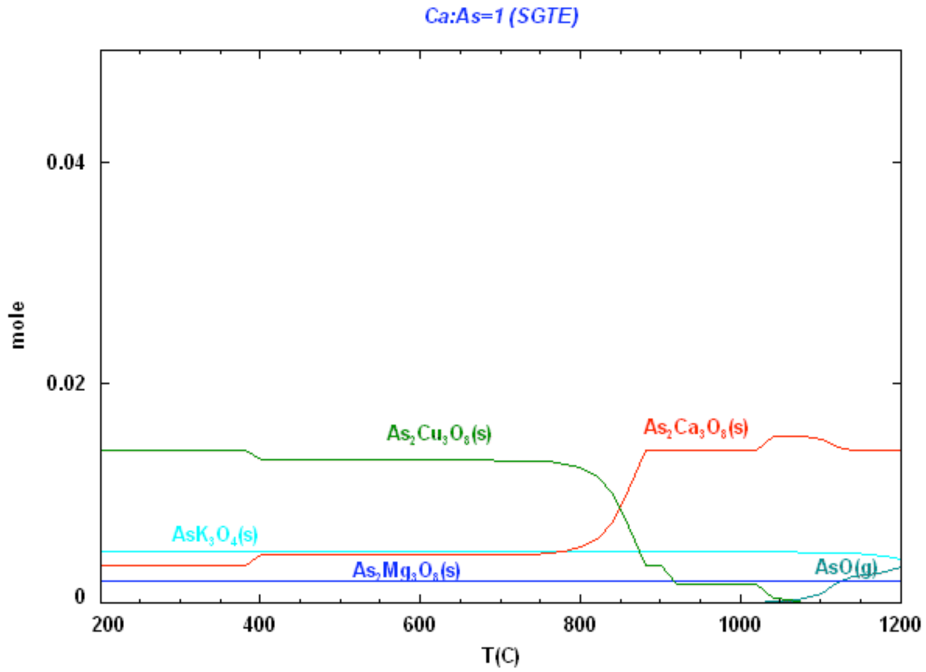


Figure 7: *SGTE equilibrium predictions for effect of calcium sorbent,* n_{Ca}:n_{As}=*1.*

2.1.4 *Effect of Other Potential Sorbents on Equilibrium Ash Composition*

The results obtained with the SGTE database in Figure 5 suggest the existence of a number of stable arsenates other than that with calcium. We have therefore examined this possibility in more detail for hypothetical additions of Al_2O_3, Fe_2O_3, K_2SO_4, and MgO. These calculations were carried out only with the SGTE database because of a lack of thermodynamic data on arsenic interactions with these metals in the FACT53 database. Results are presented graphically in Figure 8-Figure 11.

The addition of Al_2O_3 (Figure 8) leads to the formation of $AlAsO_4$ up to 1000ºC, but this decomposes to give various volatile arsenic oxides above this temperature. In the presence of iron (Figure 9), arsenic is bound predominantly as FeAsO4 between temperatures 900ºC and 1050ºC, but decomposition to volatile arsenic oxides is predicted to occur in this system also at higher temperatures. The arsenate is again formed (as K_3AsO_4) at temperatures above 700ºC when K_2SO_4 is added and in this case this remains stable to higher temperatures (Figure 10). Finally, in the presence of added magnesium, essentially all the arsenic is bound as a very stable arsenate, $Mg_3(AsO4)_2$, throughout the temperature range studied (Figure 11).

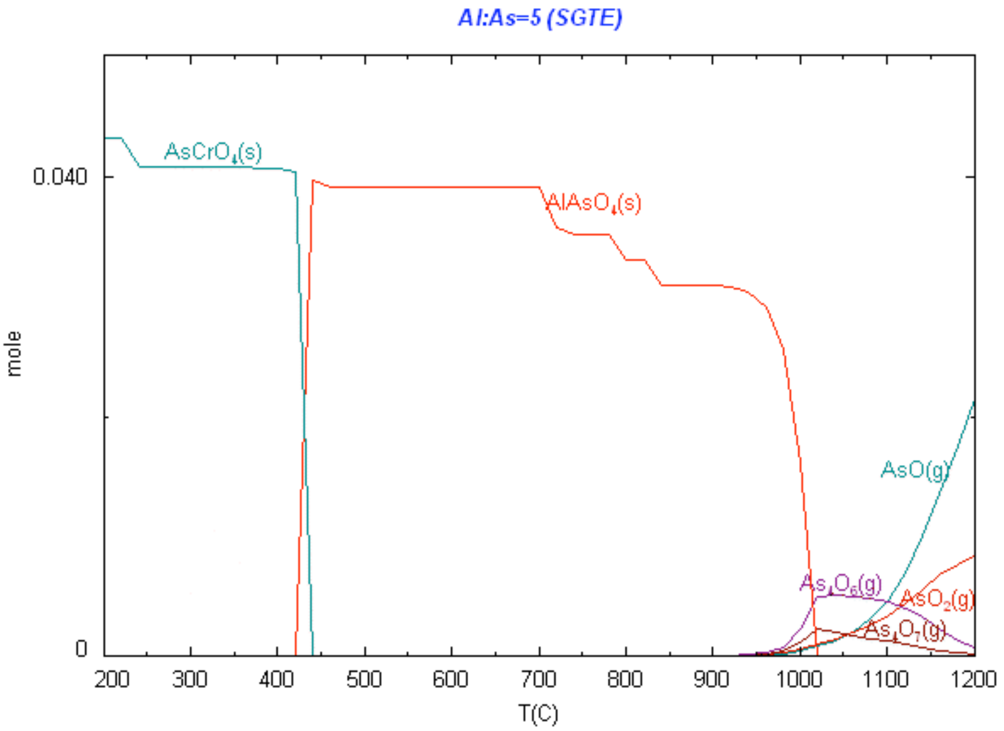


Figure 8: *SGTE equilibrium speciation of arsenic in the presence of aluminium additions.* n_{Al}:n_{As}=5.

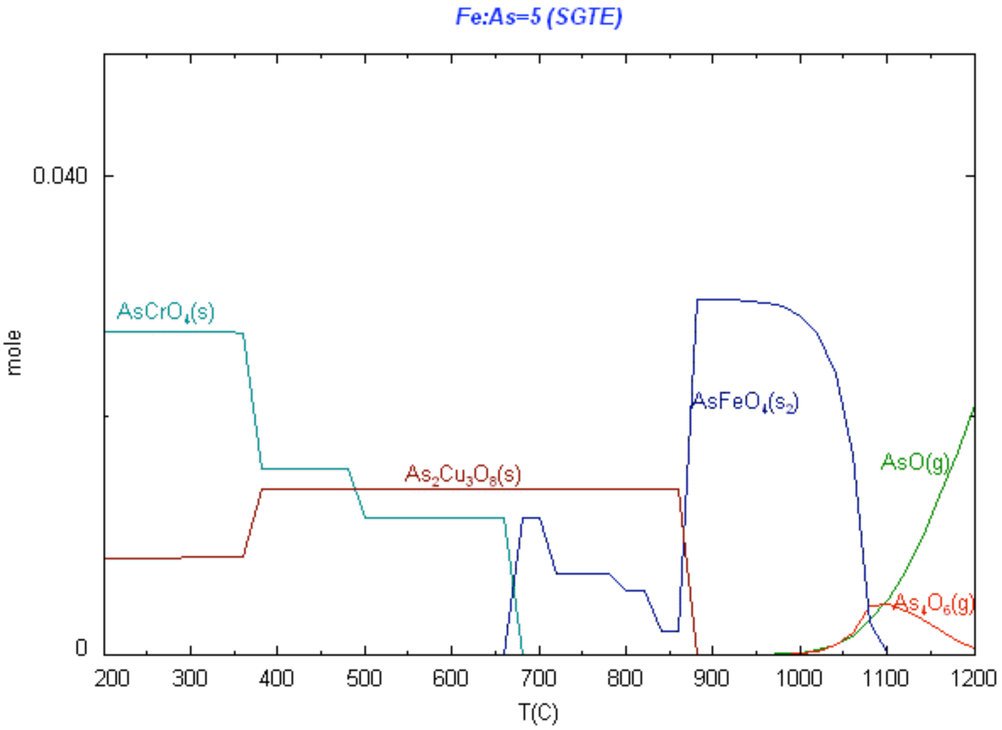
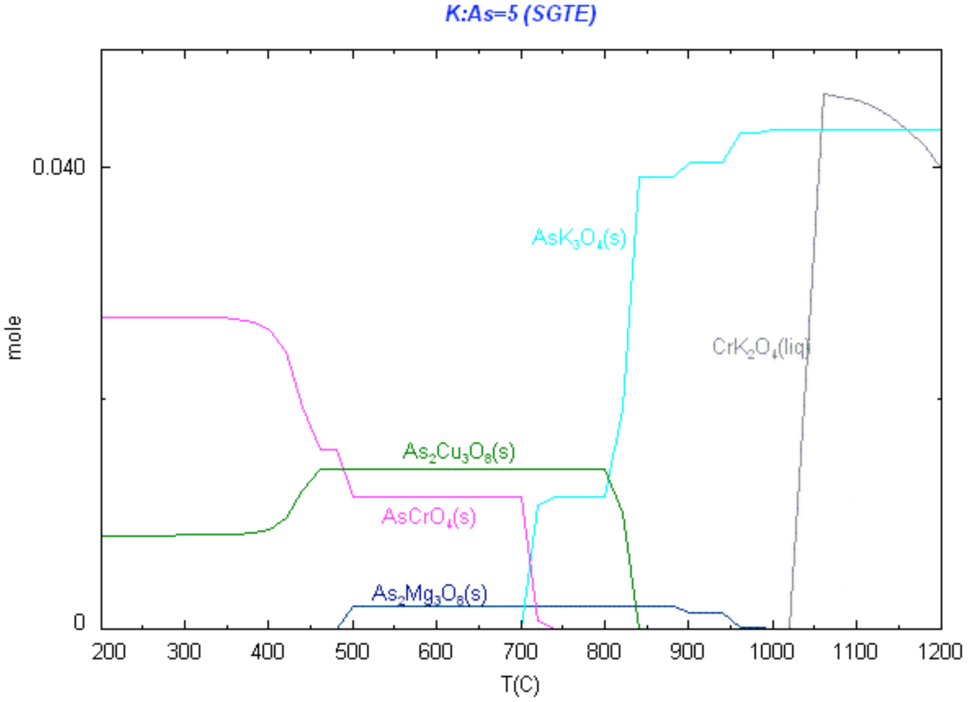
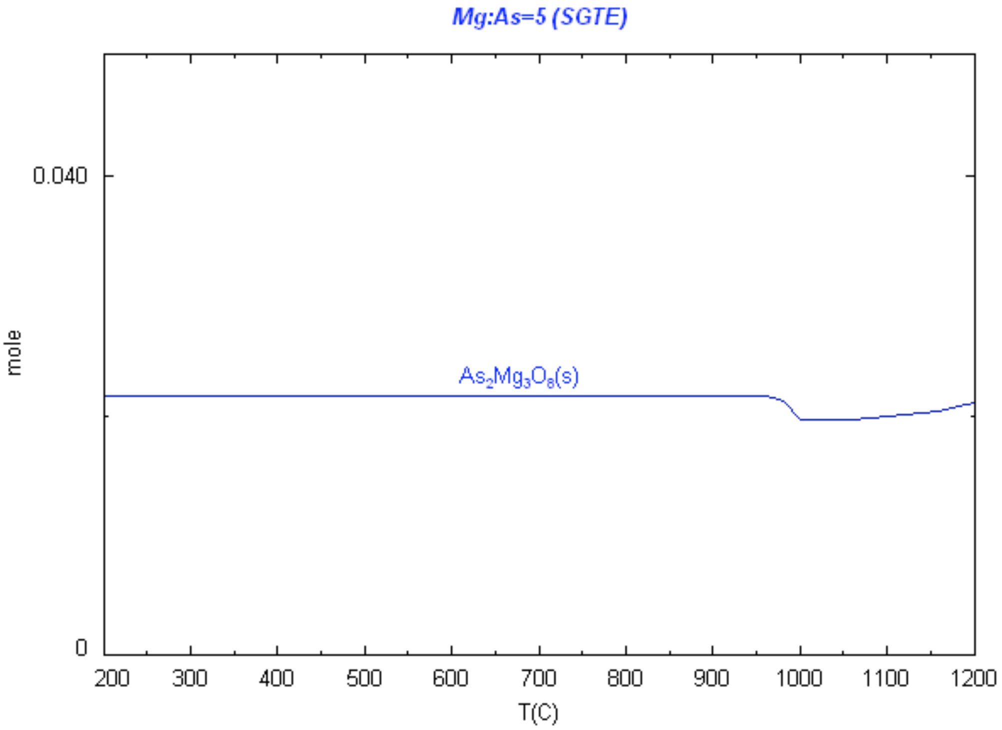


Figure 9: *SGTE equilibrium speciation of arsenic in the presence of iron additions.* $n_{Fe}:n_{As}=5$.



(f)

Figure 10: *SGTE equilibrium speciation of arsenic in the presence of potassium additions.* $n_K:n_{As}=5$.



(h)

Figure 11: *SGTE equilibrium speciation of arsenic in the presence of magnesium additions.* $n_{Mg}:n_{As}=5$.

2.2 Experimental Characterisation of Residual Ash after Combustion

2.2.1 Methods

In our earlier work (Stewart *et al.*, 2004), we combusted single lumps of wood that had been cut out of CCA-treated poles. While care was taken to cut the samples from approximately the same radial location of the poles (all of which came from a single batch of poles treated at level H4, there was significant intersample variability in the results. We used the copper in the ash as an inert tracer to compare the loss of arsenic under different combustion conditions. In this work, we have shredded a short length of CCA-treated pole and homogenised the sample in order to minimise intersample variability.

2.2.1.1 Wood Sample Preparation

The wood sample used in experiments was from the same batch of CCA-treated pine pole as used in our previous work - supplied by Auspine Ltd with a CCA treatment level H4.

The consolidated wood sample for the combustion studies was prepared by cutting long strips from the sample pole and milling these strips in a wood chipper. The whole cross-section of the pole was chipped and all the chipped material was blended to form a single sample. This sample was sieved into 3 size ranges, 0.30<d<0.80 mm, 0.80<d<1.40 mm, and 1.40<d<2.30 mm. Most combustion studies were carried out with the middle cut, 0.80<d<1.40 mm.

A cross-section of pole was cut and milled in a TEMA mill to create a fine powder. Samples of this powder were digested and analysed to provide a representative content of the CCA metals and other inherent mineral components in the wood prior to combustion.

2.2.1.2 Combustion Method

A sample of 1.00 g of sized wood chip was combusted in a CEM Phoenix microwave furnace to investigate the effects of combustion conditions on the metal content of the ash remaining after combustion. The sample was contained in an alumina dish which was placed in the pre-heated furnace for a defined period, typically 11 minutes, at fixed temperatures in the range 600-1000ºC. Following combustion, the resultant ash was brushed into a tared storage container for weighing and later analysis.

Combustion at 1000ºC led to some fusion of the ash to the alumina crucible. Furthermore, as found in our previous study, the ash recovered from combustion at this temperature could not be digested completely. Because these losses could not be quantified, we report here only those results obtained at furnace temperatures up to 900ºC.

2.2.1.3 Elemental Analysis of the Wood and Ash Samples

Wood samples were digested using 5 ml 70% reagent grade nitric acid (HNO_3) and ash samples were digested with 3.3 ml 70% reagent grade nitric acid with 6.7 ml 70% reagent grade perchloric acid ($HClO_4$) reagent solutions. A Milestone^{TM} Ethos SEL microwave solvent extraction lab station was employed to digest the samples. The procedure consisted of heating the sample to 200ºC in 30 minutes and retaining at 200ºC for 15 minutes while the digestion proceeded to completion. The system was allowed to cool and the digest was transferred into a volumetric flask and diluted to 200 ml for elemental analysis.

A Varian Vista AX CCD Simultaneous Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analyser was employed to perform elemental analysis on digests of wood and ash samples. The Varian SpectrAA 220 Atomic Absorption (AA) Spectrometer was also used with 10 mA lamp current and nitrous oxide-acetylene flame to analyse the Ca content of the ash produced.

AccuTrace^{TM} MISA #4 and MISA #6 ICP multi-element standards were used to calibrate the ICP-AES and AA analyses. The standards were diluted to between 1.56 ppm and 25 ppm for the analyses.

2.2.1.4 Other analyses

Samples of wood and ash were subject to other analyses to shed light on the ash behaviour and transformations occurring in combustion:

Image analysis

Scanning electron microscopy (SEM) analysis was used to investigate the wood and ash morphology, and for EDS microanalysis and X-ray mapping. The analysis was performed using the computer-controlled Philips XL30 CP scanning electron microscope at the Electron Microscope Unit of the University of Sydney. Samples for cross-sectional images were prepared by placing them into epoxy resins and polishing for high image quality.

X-Ray diffraction analysis

A Siemens XRD-5000 X-ray diffractometer (Electron Microscope Unit, University of Sydney) was used to record X-ray diffraction spectra. Ash samples were packed into glass sample holders. 30 kV and 30 mA Copper Kα radiation was used to scan over the angular 2θ range of 20–50º.

2.2.2 Characterisation of the Consolidated Wood Sample

2.2.2.1 Proximate and Ultimate Analyses

The proximate and ultimate analyses of the homogenised powdered wood sample (Section 2.2.1.1) were carried out by CCI Australia Pty Ltd in accordance with Australian and ASTM Standard Methods AS1038.3, AS1038.6.3.3, AS1038.6.4 (draft) and E872, E1755. The results of these analyses are shown in

Table 2.

Table 2: *Proximate and ultimate analysis of CCA-treated timber sample.*

Analysis Basis	**(ad)**	**(db)**	**(daf)**
Proximate Analysis			
Air Dried Moisture (%)	4.1		
Ash *at 575°C* (%)	1.6	1.7	
Volatile Matter (%)	81.7	85.2	86.6
Fixed Carbon (%)	12.6	13.1	13.4
Ultimate Analysis			
Carbon (%)	47.8	49.8	50.7
Hydrogen (%)	5.92	6.17	6.28
Nitrogen (%)	0.15	0.16	0.16
Total Sulphur (%)	0.12	0.13	
Oxygen (%) (by difference)	40.3	42.0	42.9

2.2.2.2 Distribution of CCA Metals in the Wood.

The penetration of CCA metals from the surface of the pole was studied. An 8 cm long radial strip was cut across the 1 cm long pole section, as shown in Figure 12. This strip was divided into 8x1cm pieces (W1, W2…W8), each of which was pulverised, digested, and analysed by ICP-AES. Analyses are reported on the basis of wood as received.

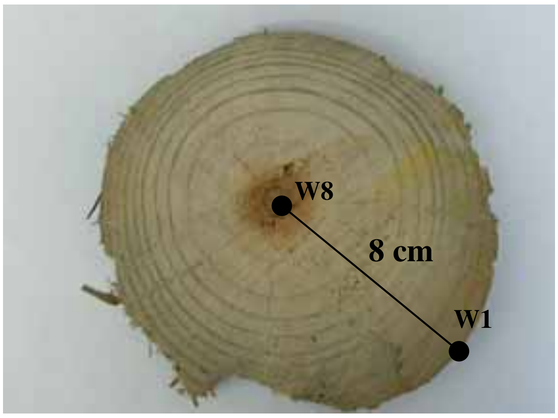


Figure 12: *CCA-treated timber sample.*

The analyses of the eight radial subdivisions are tabulated in Table 3 and the results for the CCA metals are plotted in Figure 13. While the results for the non-CCA elements (Ca, Mg, Na and K) show a more or less uniform distribution throughout, the CCA elements are present in high concentrations at the surface and are essentially absent from the central core of the section.

Table 3: *Elemental analysis of CCA-treated wood – from surface to the pith.*

	As mg/kg	Cr mg/kg	Cu mg/kg	Ca mg/kg	K mg/kg	Mg mg/kg	Na mg/kg
W 1	4400	9164	5583	1395	745	439	545
W 2	4928	7723	3698	-	657	-	434
W 3	2416	2902	1505	990	596	64	434
W 4	1108	1348	373	798	522	86	375
W 5	605	753	371	811	722	126	328
W 6	104	65	207	782	579	22	510
W 7	125	85	149	1253	586	132	406
W 8	236	226	174	2014	810	415	395

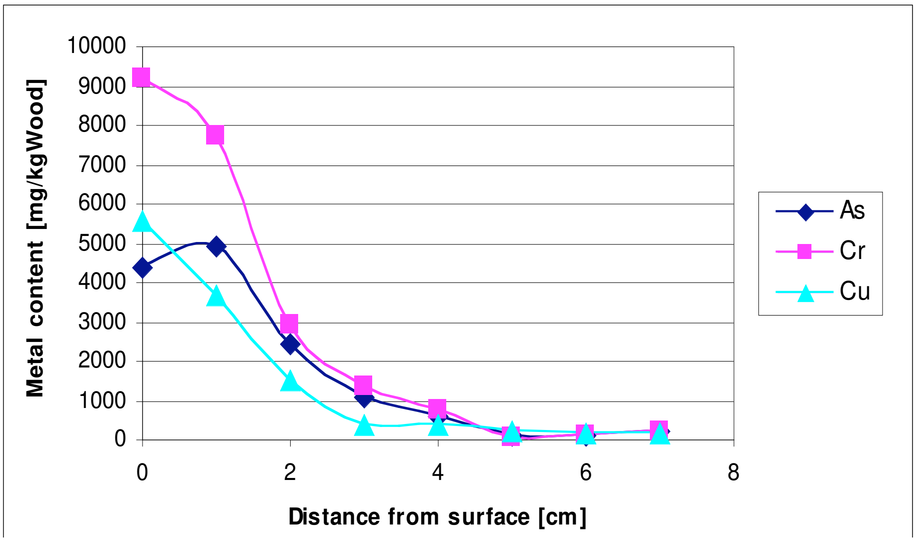


Figure 13: *Radial distribution of As, Cr and Cu in the pole sample.*

The radial variation of CCA species concentration is believed to be a major source of the intersample variability seen in our earlier work with lump samples. It is for this reason that we have elected to use homogenised whole-of-section samples in the present work.

2.2.2.3 Mineral constituent analysis

Five separate samples were taken from the pulverised wood sample (Section 2.2.1.1), digested, and analysed with ICP-AES. Results are shown in Table 4. The average of mineral matter content of these five samples was used in equilibrium calculations and also as the basis for tracking how much of the CCA components reports to the ash after combustion.

Table 4: *Elemental analysis of pulverised CCA-treated wood sample.*

	As mg/kg	**Cr mg/kg**	**Cu mg/kg**	**Ca mg/kg**	**K Mg/kg**	**Mg mg/kg**	**Na mg/kg**	**Si mg/kg**	**As/Cu**	**Cr/Cu**
Mix 1	3284	4861	2685	1024	550	130	234	133	1.223	1.810
Mix 2	3276	4849	2654	820	525	197	227	108	1.234	1.827
Mix 3	3285	4922	2686	805	539	202	232	120	1.223	1.832
Mix 4	3086	4585	2516	873	566	79	236	96	1.227	1.822
Mix 5	3211	4798	2624	978	528	129	225	93	1.224	1.829
Ave.	**3228**	**4803**	**2633**	**900**	**541**	**148**	**231**	**110**	**1.226**	**1.824**
Std Dev	**2.6%**	**2.7%**	**2.7%**	**10.8%**	**3.1%**	**35.2%**	**2.0%**	**15.2%**	**0.4%**	**0.5%**

Table 4 shows that the relative standard deviation in the analyses of the CCA components is very small, about 2.7%, confirming that the consolidated sample is well homogenised and that the reproducibility of the ICP-AES measurements is very good.

The observed treatment rate (As+Cr+Cu=10664 mg/kg) and the penetration zone (i.e. ≥20 mm) seen in Figure 13 indicate that the timber sample used in this study is type H4 as per AS 1604-2000 (Australian Standard, 2000), consistent with the given specification of the sample pole.

In our earlier study (Stewart *et al.*, 2004), we found that the ratios of concentrations of the CCA metals were remarkably constant, even in the presence of significant intersample variability in the lump samples employed in that work. The same observation may be made here, with the rightmost columns in Table 4 showing the mass concentration ratios As:Cu and Cr:Cu have a relative standard deviation of just 0.5%.

2.2.2.4 Effect of Particle Size

As described above (Section 2.2.1.1), three different size fractions of woodchip (+0.30 - 0.80, +0.80 -1.40, and +1.40 -2.30 mm) were prepared from the consolidated sample. Samples from each of these fractions were digested and analysed for their metal contents by ICP-AES. The results are shown in Table 5 where it is seen that there is no significant difference between the analyses of the different size fractions. We therefore conclude that there is no bias of the results introduced in the sizing of the consolidated wood chip sample. The middle size fraction (0.80 < d < 1.40 mm, nominal mean size 1.10 mm) has been used for detailed combustion studies.

Table 5: *Effect of wood chip size on CCA metal content.*

Av Particle Size (mm)	Sample No	mgAs/ kgwood	mgCr/ kgwood	mgCu/ kgwood	As/Cu	Cr/Cu
0.55	1	3640	4928	2797	1.301	1.762
	2	3350	4743	2674	1.253	1.774
	3	3288	4569	2574	1.278	1.775
Average		**3426**	**4747**	**2681**	**1.278**	**1.770**
1.1	1	3842	5697	3131	1.227	1.820
	2	3605	4888	2725	1.323	1.794
	3	3560	4829	2689	1.324	1.796
Average		**3669**	**5138**	**2848**	**1.288**	**1.804**
1.85	1	3636	5007	2764	1.315	1.812
	2	2989	4058	2350	1.272	1.727
	3	3596	5053	2832	1.269	1.784
Average		**3407**	**4706**	**2649**	**1.286**	**1.777**

The results in Table 5 show slightly higher levels of the CCA metals than seen for the pulverised wood sample in Table 4. In Table 6, the average results from all three size fractions in Table 5 are presented and compared with the averages obtained for the pulverised wood sample (Table 4) – the average As content is raised by 8.4%, the Cr by 1.3% and the Cu by 3.5%. We believe these small differences are due to the fact that the pulverised sample was taken from a whole section that was not included in the consolidated wood chip sample.

It is also apparent from Table 6 that the results for each of the metal concentrations show greater variability for the woodchip samples than for the pulverised sample, the overall standard deviation for the chipped samples being about 8% for each of the metals (c.f. 2.4% for the pulverised sample). Clearly there remains some intersample variations even when taking samples from the blended wood chip. However, the ratios of the metal contents continue to show relatively little variability, either among the wood chip samples (overall standard deviation < 2.6%) or between the woodchip and pulverised samples (average As:Cu increases by 4.8%, Cr:Cu decreases by 2.3%).

Table 6: *Comparison of analyses for chipped and pulverised samples.*

Global Average from Table 5	**mgAs/ kgwood**	**mgCr/ kgwood**	**mgCu/ kgwood**	**As/Cu**	**Cr/Cu**
Average for woodchip	3501	4864	2726	1.285	1.783
Rel.Std Deviation	7.2%	8.9%	7.7%	2.6%	1.6%
Relative to Table 4	**1.084**	**1.013**	**1.035**	**1.048**	**0.977**

2.2.3 Combustion Studies on the Consolidated Wood Sample

All combustion experiments were conducted with the median size fraction from the consolidated wood chip sample (0.80 < d < 1.40 mm, nominal mean size 1.10 mm). Table 7 shows results for the combustion of the sample at temperatures of 600, 700, 800, and 900°C. The duration of the combustion was not constant with temperature but it was important to ensure that combustion was complete in every case. At the same time, it was important to determine whether holding the ash sample in the furnace after completion of combustion of the wood would lead to composition changes unrelated to combustion, for example, by volatilisation. Therefore, for each temperature, experiments were performed for holding times in the furnace of 7, 11, 15, and 20 minutes – results for 7 minutes at 600°C are not shown because the sample was incompletely combusted under these conditions.

The ash generated at different residence times exhibited only minor variations in final CCA metals contents – the standard deviations at each temperature are at most 5.4% and are thus lower than obtained with the analyses of the unburned wood samples in Table 6. We conclude that there is negligible change in the concentrations of CCA components of the ash even when the ash is held for up to 15 minutes after completion of the combustion. In subsequent work, a fixed holding time of 11 minutes has been used.

Table 7: *The influence of furnace residence time on As, Cr and Cu content of the ash.*

Temp. (°C)	Time (mins)	mgAs/ kgwood	mgCr/ kgwood	mgCu/ kgwood	As/Cu	Cr/Cu	As/Cu vs Table 6	Cr/Cu Vs Table 6
600	11	2720	4156	2309	1.178	1.800		
	15	2828	4209	2351	1.203	1.790		
	20	2699	4013	2257	1.196	1.778		
	Ave	2749	4126	2306	1.192	1.789	0.928	1.004
	Std Dev	2.5%	2.5%	2.0%	1.1%	0.6%		
700	7	2487	4036	2257	1.102	1.788		
	11	2569	4050	2272	1.130	1.782		
	15	2523	3959	2208	1.143	1.793		
	20	2544	4033	2266	1.123	1.780		
	Ave	2531	4020	2251	1.125	1.786	0.875	1.002
	Std Dev	1.4%	1.0%	1.3%	1.5%	0.3%		
800	7	2456	4024	2258	1.088	1.783		
	11	2282	3841	2163	1.055	1.776		
	15	2373	3976	2239	1.060	1.776		
	20	2428	3952	2248	1.080	1.758		
	Ave	2385	3948	2227	1.071	1.773	0.833	0.995
	Std Dev	3.2%	2.0%	1.9%	1.5%	0.6%		
900	7	1897	3789	2187	0.867	1.733		
	11	1734	3501	1975	0.878	1.773		
	15	1684	3391	1935	0.870	1.752		
	20	1723	3376	1884	0.915	1.792		
	Ave	1760	3514	1995	0.883	1.763	0.687	0.989
	Std Dev	5.4%	5.4%	6.7%	2.5%	1.5%		

The yields of the CCA components reporting to the combustion ash, presented in Table 7, are all somewhat less (typically 20 to 50% lower) than the amounts in Table 6 for the wood sample itself. However, we do not believe that all this loss is due to volatilisation because of the behaviour of the element ratios. Table 7 shows that the ratio of Cr:Cu in the ash samples is essentially identical to (always within 1.1% of) that for the parent wood sample, which is at odds with a differential loss mechanism such as vaporisation, especially as it is known that copper does not vaporise at the relatively low temperatures of these experiments. Rather, we believe that there are systematic losses of ash from the experiments and subsequent analysis, for example in the transfer of the ash into the digester and in the digestion itself. At temperatures above 900°C, there were significant observable problems with fusion of ash to the furnace crucible in which the sample was held during combustion and some loss of ash from the analysis was therefore inevitable.

Because of these unquantifiable effects, and because of the remaining intersample variability among samples taken from the consolidated woodchip fraction, we will henceforth use the concept of retention defined in our earlier work (Stewart *et al.*, 2004). In this approach, we use copper as an internal standard, based on the observation that it does not volatilise and therefore reports exclusively to the ash fraction. The *retention* of arsenic and chromium in the ash after combustion can therefore be expressed via a double normalisation:

$$\text{Chromium Retention} = \frac{\left(\dfrac{Cr_{ash}}{Cu_{ash}}\right)}{\left(\dfrac{Cr_{feed}}{Cu_{feed}}\right)}$$

Equation 1

$$\text{Arsenic Retention} = \frac{\left(\dfrac{As_{ash}}{Cu_{ash}}\right)}{\left(\dfrac{As_{feed}}{Cu_{feed}}\right)}$$

In calculating these quantities, the ratios for the feed quantities are taken from Table 6.

Figure 14 shows the retention of arsenic and chromium in the combustion ash at different furnace temperatures, calculated using the above equations – i.e. that all the copper is retained in the ash. Clearly the chromium is also completely retained in the ash to a very great extent. However, significant loss of arsenic from the ash is apparent even at 600°C and this loss increases steadily as the temperature increases. Figure 14 also shows data for arsenic retention from our earlier report (Stewart *et al.*, 2004) which indicate significantly greater losses of arsenic at any given furnace temperature. The earlier experiments were conducted with single suspended blocks of wood, for which the intersample variability was quite large. Moreover, as will be discussed in more detail in Section 4 of this report, such suspended samples burn 200°C or more hotter than the nominal furnace temperature due to the combustion heat release – such a large temperature overshoot is not believed to occur in the present experiments which have the wood chip spread out in a thin layer over the floor of the alumina container.

The confirmation of significant arsenic loss at relatively low combustion temperatures emphasises an issue facing all thermal treatment technologies, including combustion and pyrolysis, namely that arsenic volatilisation occurs at low temperatures and is essentially unavoidable in the absence of external reagents such as lime addition.

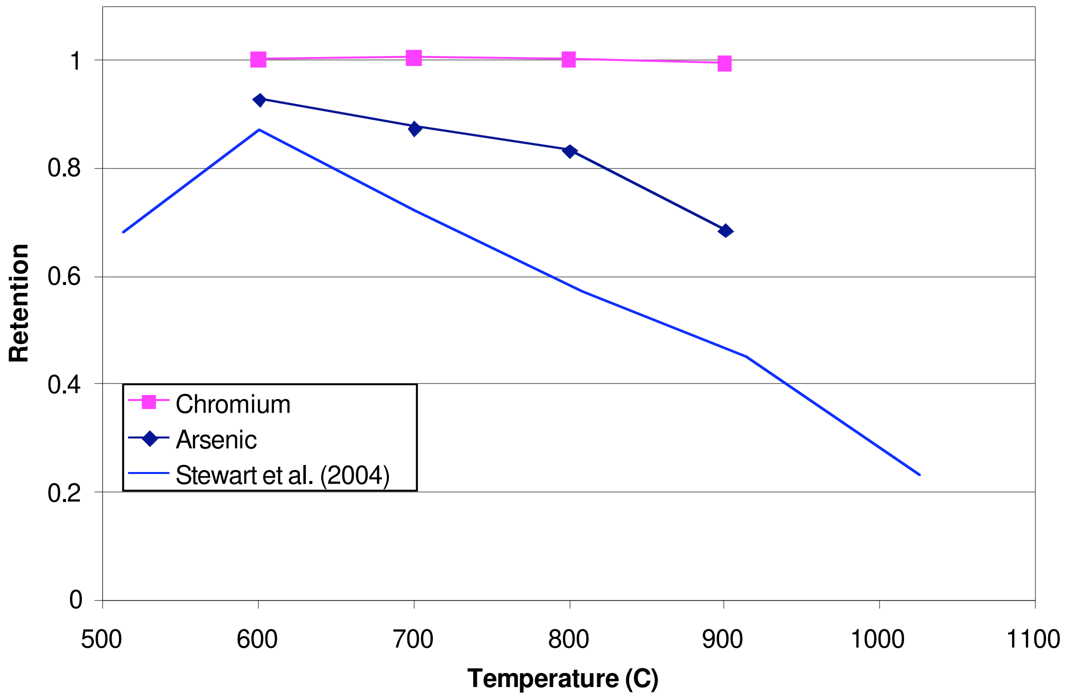


Figure 14: *Fractional retention of arsenic and chromium in wood chip combustion ash, calculated assuming that all copper is retained in the ash.*

2.2.4 Combustion Studies on the Effect of Added Sorbents

2.2.4.1 Addition of dry powder sorbents

The efficacy of a number of potential sorbents, thermodynamically capable of forming thermally stable arsenates (Sections 2.1.3 and 2.1.4), were thoroughly mixed as powders with 1 g of woodchip in an alumina crucible prior to combustion. Molar ratios of sorbent metal to As up to approximately ten were examined for Ca, Al, Fe. K and Mg; this was extended to a ratio of 15 for Ca.

The residence time in the furnace was 11 minutes and the mean wood particle size was 1.1 mm for all experimental runs. The temperature range was 600ºC-900ºC. The combustion experiments were also carried out at 1000ºC and 1100ºC. However, the ash generated at these temperatures could not be digested completely. Therefore, results for these temperatures will not be described here.

Hydrated Lime, $Ca(OH)_2$

Table 8 shows the results of CCA-metal contents that were analysed after the combustion of CCA-treated wood woodchip and $Ca(OH)_2$ along with As/Cu and Cr/Cu ratios for normalisation purposes.

Table 8: *Ash analyses from combustion experiments at different temperatures after addition of dry powder* $Ca(OH)_2$ *to wood chip.*

Temp. (°C)	n_{Ca}:n_{As}	mgAs/ kgwood	mgCa/ kgwood	mgCr/ kgwood	mgCu/ kgwood	As/Cu	Cr/Cu
600	0.00	2689	654	4433	2466	1.090	1.798
	0.82	2801	2313	4503	2505	1.118	1.798
	1.63	2804	4226	4452	2490	1.126	1.788
	2.46	2763	5778	4376	2402	1.150	1.821
	4.08	2939	8914	4524	2521	1.166	1.795
	8.15	2966	16776	4520	2500	1.187	1.808
	12.22	2816	25141	4082	2327	1.210	1.754
	16.29	2919	31136	4377	2452	1.191	1.785
700	0.00	2782	815	4553	2525	1.102	1.803
	0.82	2883	2356	4595	2537	1.136	1.811
	1.63	2901	4284	4543	2526	1.148	1.798
	2.46	2868	5803	4581	2515	1.141	1.822
	4.08	2851	8433	4530	2480	1.150	1.826
	8.15	2785	15792	4377	2393	1.164	1.829
	12.22	2821	23281	4315	2432	1.160	1.775
	16.29	2929	31188	4384	2435	1.203	1.800
800	0.00	2751	677	4877	2683	1.025	1.817
	0.81	2791	2372	4789	2518	1.108	1.902
	1.63	2823	3927	4698	2575	1.096	1.824
	2.46	2821	5994	4563	2475	1.140	1.844
	3.26	2788	7082	4455	2455	1.136	1.815
	4.08	2842	9238	4535	2453	1.159	1.849
	8.15	2787	16475	4474	2464	1.131	1.816
	12.22	2875	23536	4428	2465	1.167	1.796
	16.29	2764	29459	4174	2314	1.194	1.804
900	0.00	2080	696	4395	2419	0.860	1.816
	0.81	2359	2960	4430	2485	0.949	1.783
	1.63	2374	4024	4656	2557	0.928	1.821
	2.46	2474	5636	4436	2438	1.015	1.820
	3.26	2532	6965	4442	2460	1.029	1.806
	4.08	2666	9174	4768	2626	1.015	1.815
	8.15	2731	15933	4483	2501	1.092	1.792
	12.22	2737	24506	4686	2580	1.061	1.816
	16.29	2667	31620	4407	2464	1.082	1.788

Figure 15 shows the results for the relative retention of arsenic in the ash when the wood chip is combusted with added calcium. At all temperatures there is an apparent increase in retention of arsenic in the ash when calcium is added, but the effect is incomplete, even when the molar Ca:As ratio is as high as 20. Indeed, the effect of the added calcium appears to plateau when the molar Ca:As ratio exceeds ~5-10.

Not unexpectedly, the retention of chromium is unaffected by the addition of calcium and remains essentially complete, as shown in Figure 16.

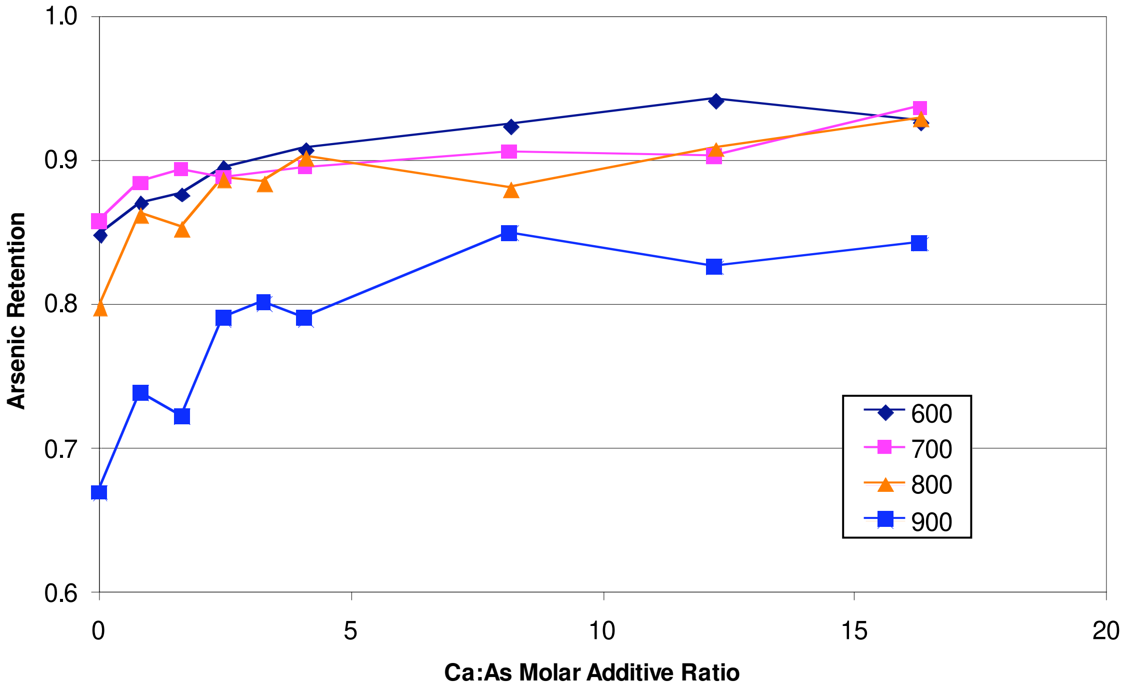


Figure 15: *Retention of arsenic in the ash in the presence of calcium additions. The amounts of sorbent are based on the added amount, ignoring the inherent ash contribution.*

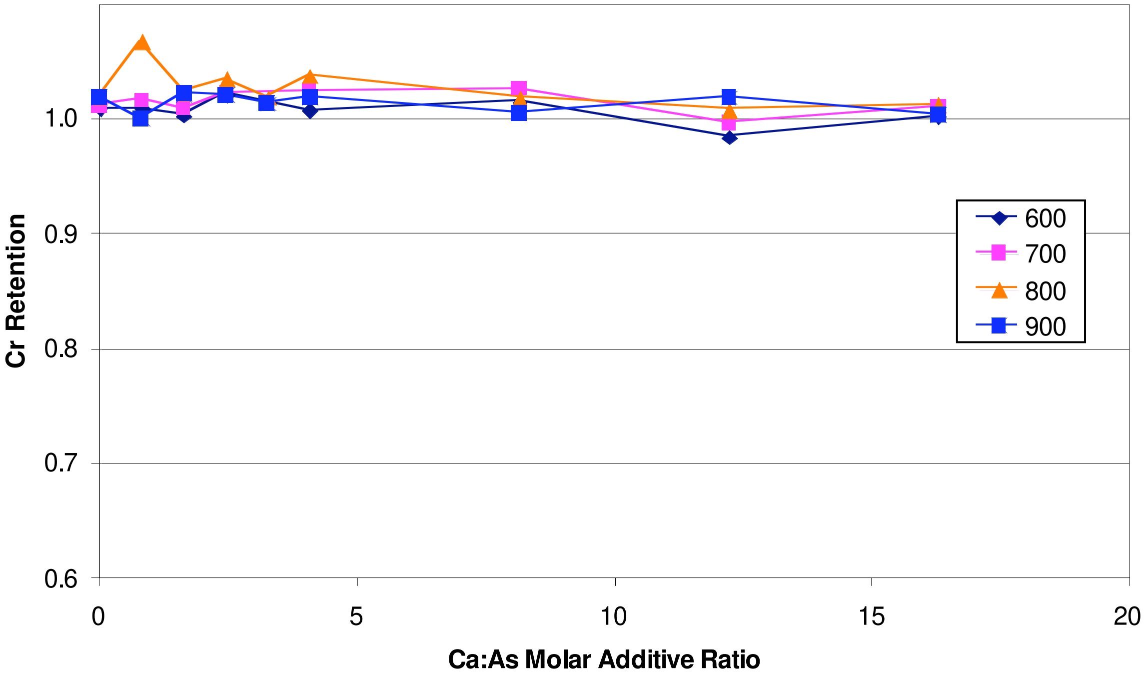


Figure 16: *Retention of chromium in the ash in the presence of calcium additions. The amounts of sorbent are based on the added amount, ignoring the inherent ash contribution.*

Fe, Mg, Al and K based sorbent additions

In addition to Ca, sorbents based on Fe, Mg, Al and K were identified in the thermodynamic equilibrium analysis as being capable of capturing arsenic in the solid phase and improving its retention in the ash. We have examined these sorbents over a range of sorbent metal:As ratios for combustion at 900ºC. The additive compounds employed were Fe_2O_3, MgO, Al_2O_3, and K_2SO_4. Detailed results are tabulated in Table 9.

Table 9: *Summary of ash analyses obtained for combustion of wood chip at 900 ºC after dry powder additions of $Ca(OH)_2$, Al_2O_3, Fe_2O_3, K_2SO_4 and MgO.*

Additive Metal	Molar Metal:As	mgAs/ kgwood	mgCr/ kgwood	mgCu/ kgwood	As/Cu	Cr/Cu
Blank	0	2080	4395	2419	0.860	1.816
Ca as $Ca(OH)_2$	1.62	2374	4656	2557	0.928	1.821
	4.07	2665	4765	2625	1.015	1.815
	8.13	2732	4484	2502	1.092	1.792
Al as Al_2O_3	1.60	1247	3043	1720	0.725	1.769
	4.02	1458	3504	1935	0.753	1.811
	8.03	1573	3524	1924	0.817	1.831
Fe as Fe_2O_3	1.60	1535	3479	1900	0.808	1.831
	4.02	1392	3229	1766	0.788	1.829
	8.03	1442	3416	1824	0.790	1.873
K as K_2SO_4	1.79	1336	3725	2005	0.667	1.858
	4.49	1209	3494	1878	0.644	1.860
	8.96	1457	3616	1911	0.762	1.892
Mg as MgO	1.60	1831	3893	2080	0.880	1.872
	4.02	1887	3758	2002	0.943	1.877
	8.03	2179	4189	2230	0.977	1.878

Results are presented in Figure 17 for arsenic retention and in Figure 18 for chromium retention. The figures include data for calcium additions separate from those presented in Figure 15 and Figure 16 – both data sets are shown here to enable comparison with the other potential sorbents and to illustrate the typical intersample variability that is obtained in these experiments which were separated in time by some weeks. The amount of sorbent added in each run is expressed as the molar ratio of the metallic element in the sorbent to the relevant CCA element (As in Figure 17 and Cr in Figure 18), neglecting contributions from intrinsic ash.

Figure 17 shows that the fractional retention of arsenic is enhanced, apart from by $Ca(OH)_2$, only by MgO additions, with the magnesium being slightly less effective than the calcium. The magnesium has about 60% of the molar efficiency of calcium – the Fact53 database did not include magnesium arsenate but the SGTE database predicted that magnesium would react preferentially to calcium when both were present, but this seems not to be borne out by the results of Figure 17.

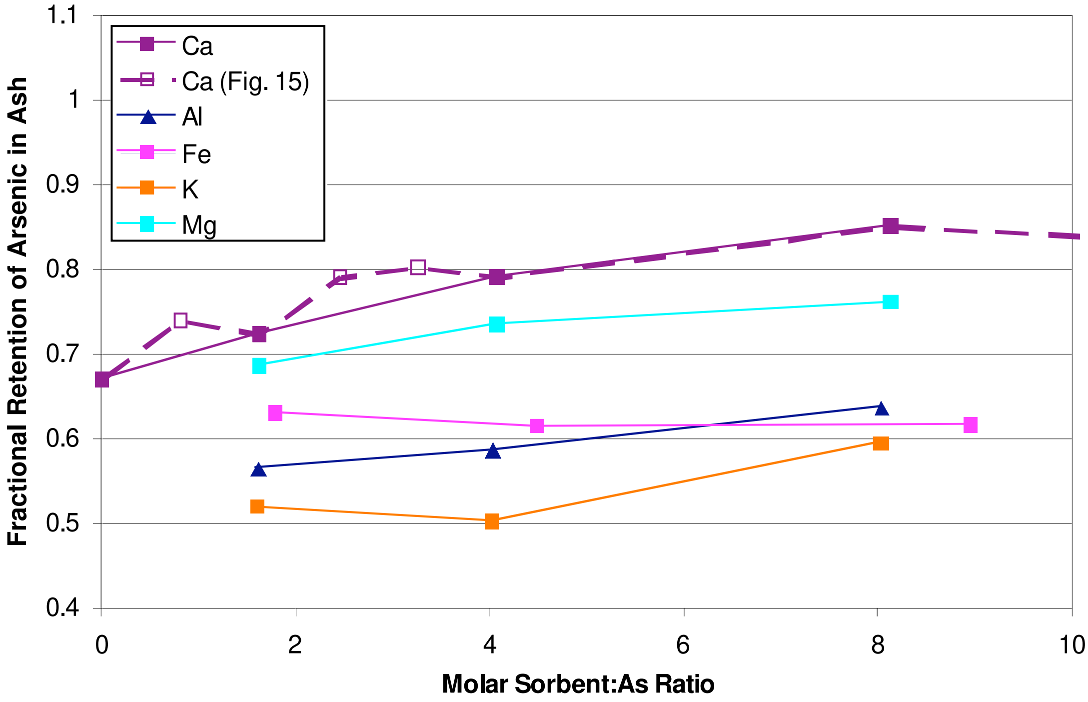


Figure 17: *Effect of different dry powder sorbents on retention of arsenic in ash from combustion of woodchip at 900 ºC. The amounts of sorbent are based on the added amount, ignoring the inherent ash contribution.*

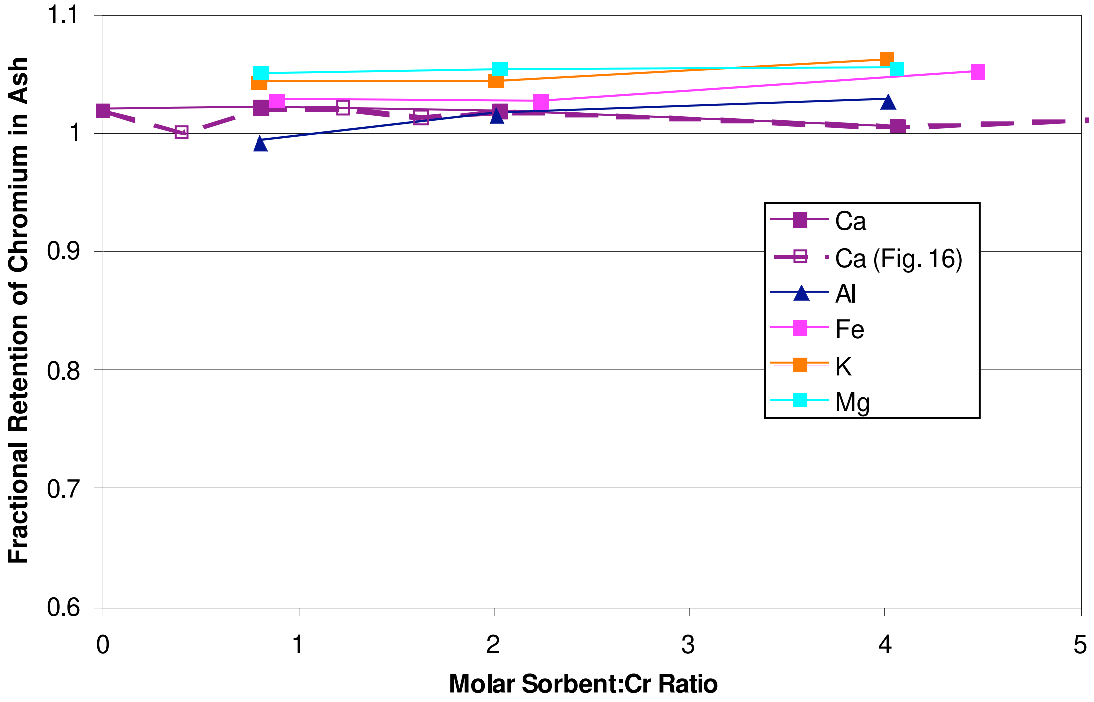


Figure 18: *The effect of different dry powder sorbents on retention of chromium in ash from combustion of woodchip at 900 ºC. The amounts of sorbent are based on the added amount, ignoring the inherent ash contribution.*

The potassium sorbent used in this study actually favoured arsenic volatilisation, probably because it interacted with the inherent mineral matter in the wood ash that would otherwise bind arsenic. Greater amounts of additive do appear to reverse the trend but that effect remains weak. Alumina additions also appeared to cause a small initial reduction in arsenic retention while iron has little effect over the range of addition levels studied.

None of the additives examined has any significant effect on the retention of chromium in the combustion ash. The results (Figure 18) show chromium retention values slightly in excess of 100% but the discrepancy here is within experimental uncertainties.

2.2.4.2 Addition of calcium sorbent by wet impregnation

The previous section has demonstrated that dry mixing of lime with wood chip has a limited effect on arsenic retention in the combustion ash. As will be discussed in Section 2.2.6, electron microscopy techniques (SEM-EDS) and X-ray diffraction (XRD) reveal a relatively weak sorbent-arsenic interaction when the sorbent is mixed as a dry powder. Calcium does inhibit the volatilisation of arsenic, but a large stoichiometric excess is required, presumably because of the poor contact between the dispersed arsenic and the particles of calcium hydroxide. To investigate this further by improving the dispersion of the calcium additive, we have studied wet impregnation of the wood with a calcium salt prior to combustion.

To impregnate CCA-treated timber with calcium, a 2 gram sample of 1.1 mm woodchip was soaked in water to which different amounts of the soluble calcium salt $Ca(NO_3)_2.4H_2O$ had been added, ranging from nil to 400 mg. The wood chip was then drained and dried at 70 ºC and then combusted in the usual way. Results are presented in Table 10.

The results in Table 10 are unusual in that the concentrations are well below the values usually seen for the consolidated woodchip sample (Table 4). The reasons for this are not understood because repeat experiments showed similar trends. Despite this anomaly, we have examined the behaviour of the fractional retention of arsenic and copper in the usual way, as shown in Figure 19 and Figure 20. The results for chromium (Figure 20) are more scattered than found in other experiments but still show remarkable constancy across all the experiments, and the mean value of 1.08, while higher than typical, continues to support the premise that the chromium and the copper are both retained completely in the ash. The results for arsenic (Figure 19) show significant effects of the calcium loading, with higher values of the molar Ca:As ratio giving higher values of retention. The results for retention significantly greater than 100% underline the fact that these experiments have some systematic problems but it remains noteworthy that, experimental scatter notwithstanding, comparison of Figure 19 and Figure 15 (dry powder addition of calcium) suggests that the wet impregnation technique is more efficacious at lower calcium loadings than is dry powder.

Table 10: *Composition of ash from combustion of CCA-timber woodchip that has been wet-impregnated with calcium nitrate.*

Temp. (°C)	Added Sorbent (mg)	mgCa/ kgwood	mgAs/ kgwood	mgCr/ kgwood	mgCu/ kgwood	As/Cu	Cr/Cu
600	0	296	2096	2982	1589	1.319	1.877
	20	1321	2381	3105	1660	1.434	1.870
	50	2607	2558	3203	1687	1.517	1.899
	100	5378	2594	3144	1679	1.545	1.872
	200	8193	2579	2944	1586	1.626	1.856
	400	10878	2389	2705	1427	1.674	1.896
700	0	249	2053	2954	1569	1.309	1.883
	20	1106	1925	2669	1370	1.406	1.948
	50	2492	2230	2970	1512	1.475	1.964
	100	5187	2539	3070	1627	1.561	1.887
	200	9329	2518	2845	1575	1.599	1.806
	400	11692	2384	2642	1375	1.734	1.921
800	0	242	1974	3038	1619	1.219	1.876
	20	1217	2032	2819	1464	1.388	1.926
	50	2890	2262	2869	1544	1.466	1.859
	100	4592	2437	2974	1553	1.569	1.914
	200	7481	2577	2938	1553	1.659	1.891
	400	12000	2665	2963	1552	1.717	1.909
900	0	219	1560	2918	1520	1.026	1.920
	20	976	1620	2419	1283	1.263	1.886
	50	2438	1959	2466	1346	1.455	1.833
	100	4350	2067	2837	1451	1.425	1.956
	200	8426	2146	2816	1462	1.468	1.926
	400	11234	2211	2601	1377	1.606	1.889

In order to assess whether wet impregnation of the CCA timber with calcium would still be effective with larger wood particles, we have repeated the experiments using a series of wood cubes of approximate weight 500 mg. These were soaked in solutions containing various amounts of Ca(NO3)2.4H2O and subsequently dried at 70ºC prior to combustion. The combustion experiments were carried out in the microwave furnace in the usual way, except that the duration of the experiment was extended to 20 minutes in order to ensure complete combustion of the sample. The resultant ash was then digested and analysed in the standard way, with results as shown in Table 11.

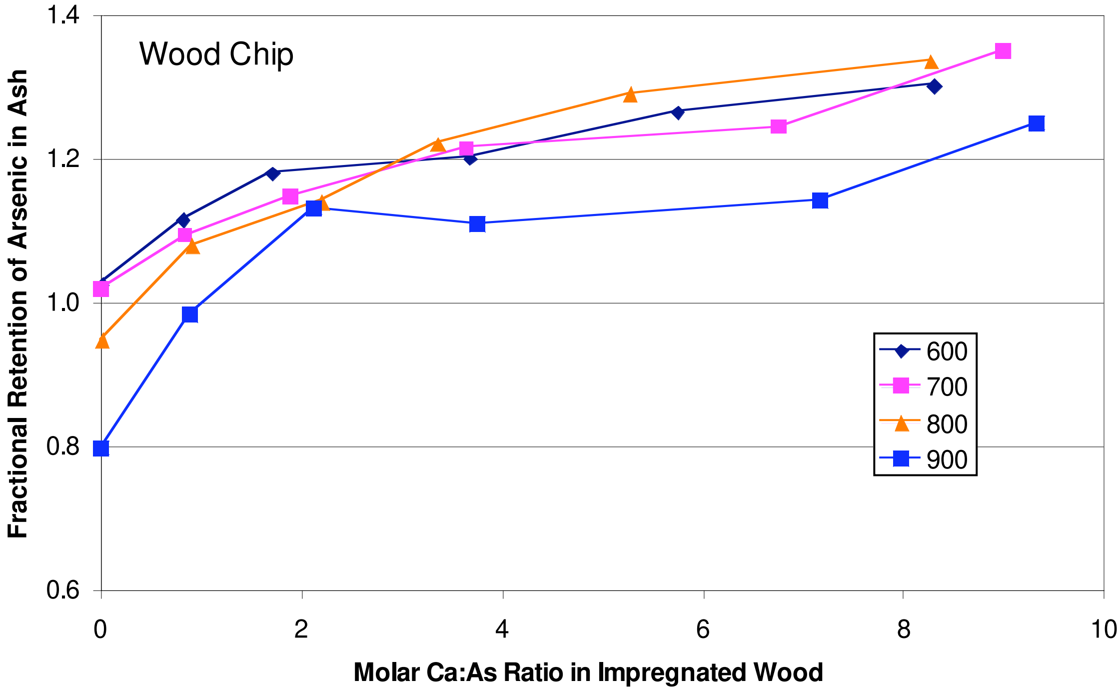


Figure 19: *Apparent fractional retention of arsenic in combustion ash derived at different temperatures from woodchip that has been wet impregnated with calcium salt.*

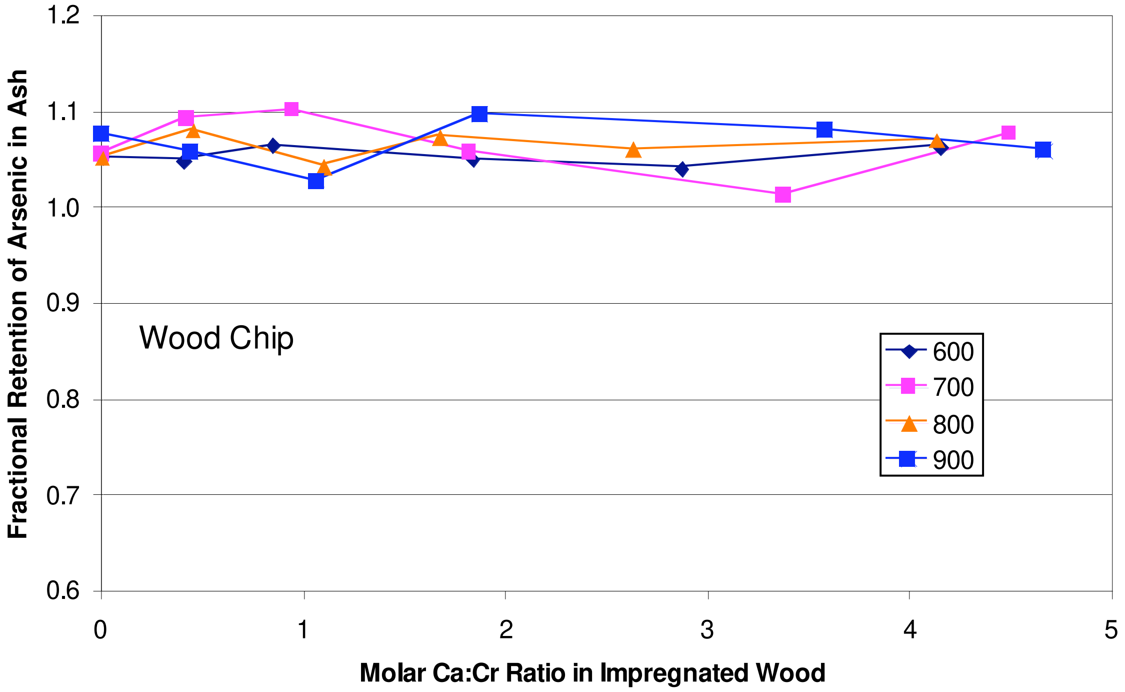


Figure 20: *Apparent fractional retention of chromium in combustion ash derived at different temperatures from woodchip that has been wet impregnated with calcium salt.*

Table 11: *Elemental analysis results of ash generated from* $Ca(NO_3)_2.4H_2O$ *solution immersed wood particles.*

Temp. (°C)	Added Sorbent (mg)	mgCa/ kgwood	mgAs/ kgwood	mgCr/ kgwood	mgCu/ kgwood	As/Cu	Cr/Cu
600	0	29	1808	3706	2389	0.757	1.552
	20	5122	2544	4044	2299	1.107	1.759
	50	13689	2656	3847	2287	1.162	1.683
	100	19209	2719	3721	2155	1.262	1.726
	200	25374	2123	3020	1781	1.192	1.696
700	0	232	3335	5286	3063	1.089	1.726
	20	4032	3861	5102	2918	1.323	1.749
	50	9612	4165	5127	2915	1.429	1.759
	100	15539	3652	4492	2706	1.350	1.660
	200	23184	3133	3880	2197	1.426	1.766
800	0	203	2224	4366	2720	0.818	1.605
	20	3762	2286	3218	2007	1.139	1.603
	50	9492	3293	4359	2641	1.247	1.651
	100	17256	2789	3562	2272	1.228	1.568
	200	22287	2437	2961	1874	1.301	1.580
900	0	115	1503	4618	2763	0.544	1.672
	20	4396	3372	4634	2659	1.268	1.743
	50	9921	4244	5592	3156	1.345	1.772
	100	14844	3743	4767	2757	1.358	1.730
	200	19295	2370	3113	1904	1.245	1.635

The raw results for the CCA content of the various ashes in Table 11 show considerable scatter, as expected for the individual lump samples employed in these experiments. However, the results for the apparent fractional retention of arsenic and chromium, calculated assuming no volatilisation of copper, show consistent trends, as depicted in Figure 21 and Figure 22 for arsenic and chromium respectively.

Figure 21 indicates that arsenic retention is approximately the same for wet impregnation as for dry powder mixing of the calcium sorbent. The results for chromium retention (Figure 22) are entirely typical, remaining constant at a value of the order of 100%

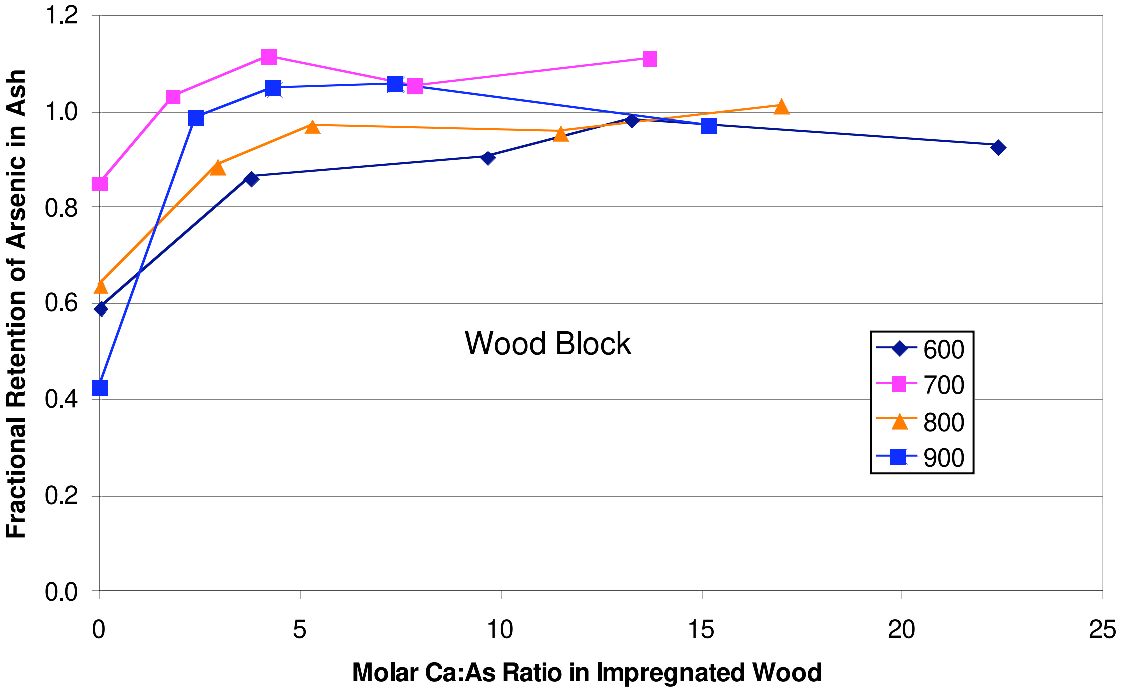


Figure 21: *Apparent fractional retention of arsenic in combustion ash derived from single small wood blocks that have been wet impregnated with calcium salt.*

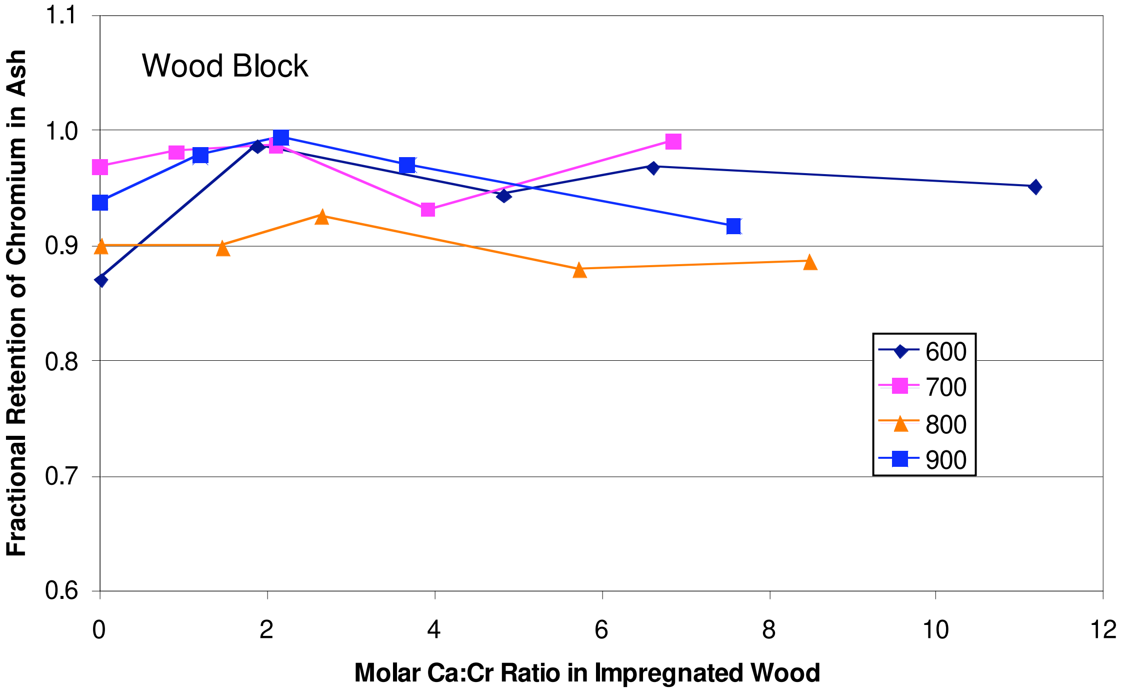


Figure 22: *Apparent fractional retention of chromium in combustion ash derived at different temperatures from single small blocks that have been wet impregnated with calcium salt.*

2.2.5 Ash particle size

The size of the ash produced in the combustion of 1.1 mm wood chip was investigated by light scattering measurements on suspended particles. For these measurements, a Malvern Mastersizer S size analyser with a measurement range from 0.05µm to 900µm was employed. The ash particles were suspended in a water-filled magnetically-stirred measurement cell.

Figure 23 shows the volume mean particle sizes obtained for combustion of wood chip at different temperatures, with and without the addition of calcium that had been added by wet impregnation. Without the additive, the volume-mean particle size is about 140 µm, for temperatures 600 to 800 ºC. The ash generated at 900ºC did not suspend in water and its size distribution could not be obtained. The rapid sedimentation of this ash may have been affected by a number of factors. While the ash particles obtained at higher temperatures appeared (by visual observation) to be finer, they also contain more very dense chromium oxide.

When the wood particles are impregnated with calcium, their combustion leads to larger ash particle sizes. There is little effect of temperature on this trend.

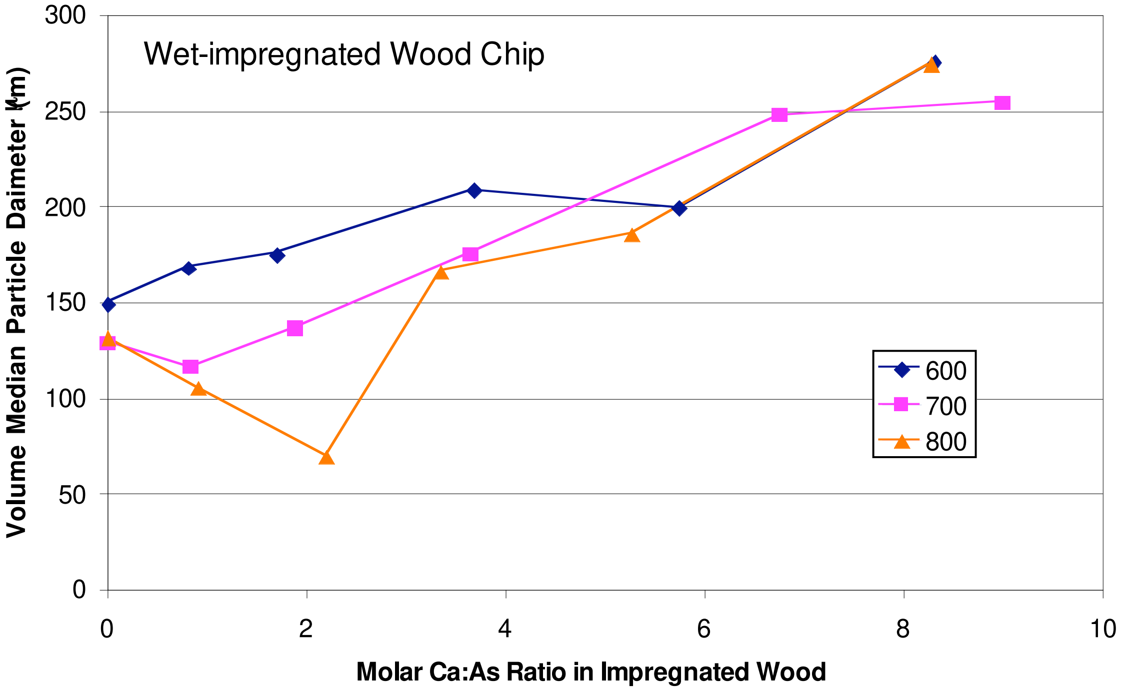


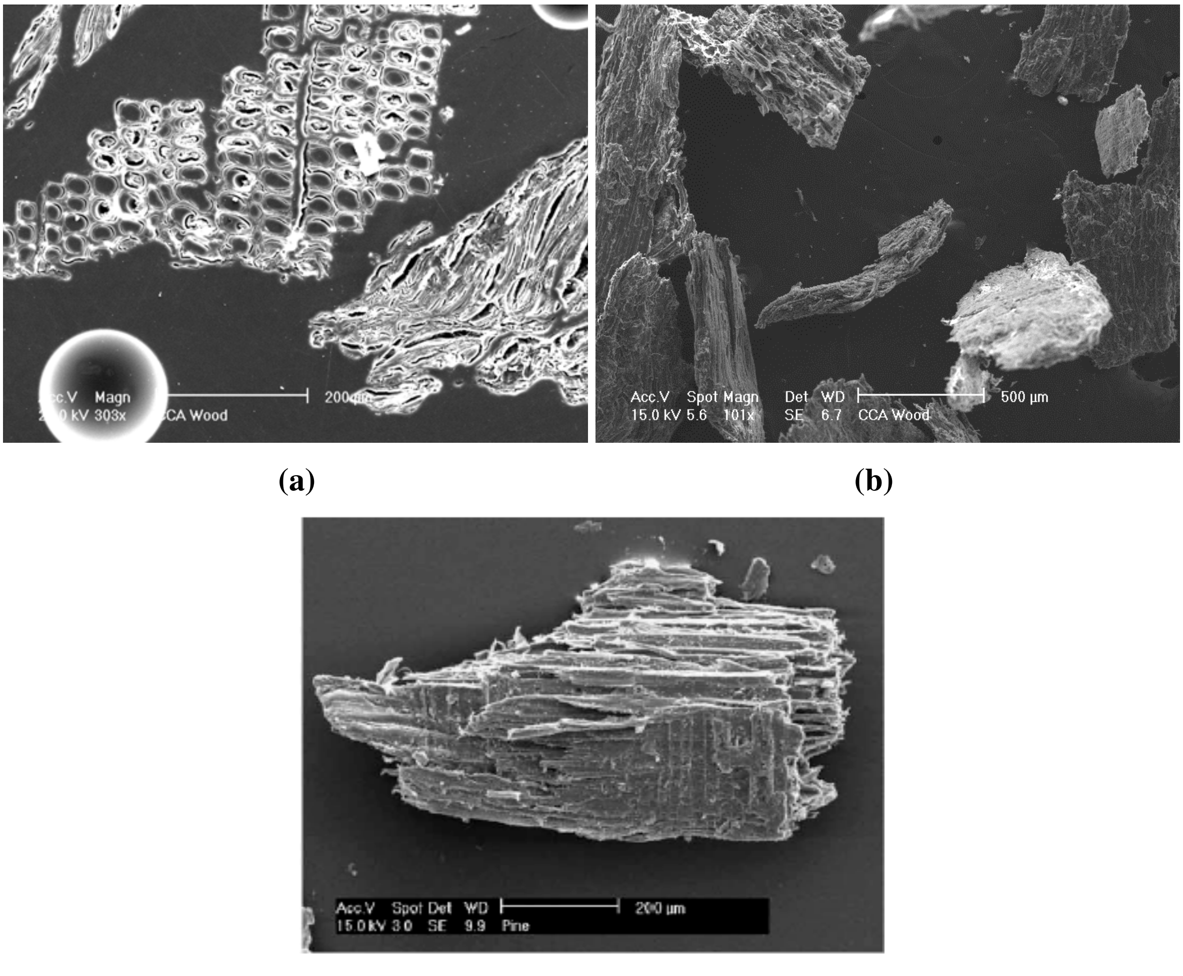
Figure 23: *Particle size analysis of the ash produced at different Ca:As molar ratios. The calcium was added by wet-impregnation of 1.1 mm wood chip.*

2.2.6 Electron Microscospy and Related Analyses of the Ash

This Section describes the chemical and morphological properties of the combustion ash, analysed using various microscopy and electron spectroscopy techniques.

2.2.6.1 Image Analysis

Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS) was done to investigate the morphology and the chemical components of the CCA ash particles. SEM works on a basis of an incident electron beam hitting atoms of the sample and causing secondary and backscattered electron emissions from the surface, from which an image of the irradiated region can be formed. In addition to those emissions, the sample also loses some energy in the form of X-rays as electrons from outer shells drop into the inner shells to stabilise its state. The X-rays emitted from the sample are collected with EDS (energy dispersive spectroscopy) and provide average composition data since each atom has its own characteristic signature in EDS. Figure 24 and Figure 25 respectively show SEM and EDS images of CCA-treated wood before combustion.



(a) **(b)**

(c)

Figure 24: *SEM images of (a) CCA-treated woodchips embedded in epoxy resin for cross-sectional analysis (b) loose CCA-treated woodchips (c) an untreated radiata pine woodchip.*

The SEM images of CCA-treated wood particles are shown in Figure 24. To examine the cross section view of the wood particles, samples were embedded into epoxy resin and polished (Figure 24(a)). Figure 24(b) is the SEM image of the loose CCA-treated woodchip particles showing the surface structure. The CCA-treated pine pole analysed in this study is made by impregnating radiata pine and a particle of untreated radiata pine is therefore shown for comparison in Figure 24(c). The same physical structures that are present in the treated timber sample in Figure 24(a) and (b) are present in the untreated sample - the CCA impregnation process that is performed at high pressure has not affected the particle morphology, and presumably, treated and untreated pines have the similar cell structure, total surface area and porosity. By contrast, the metal content of CCA-treated pine is much higher than that of the virgin pine, giving rise to much brighter back-scattered SEM images because of the higher molecular weight of the metals.

Figure 25 shows the EDS analysis of the wood particle shown at the bottom of Figure 24 (a). The dispersed nature of the metals in the wood means that arsenic, chromium and copper can be identified in a typical EDS spectrum. Also identified are potassium and calcium which form much of the normal ash constituent of wood. It should be noted that the chlorine peaks seen in EDS Spectra originate from the epoxy resin in which the sample is mounted.

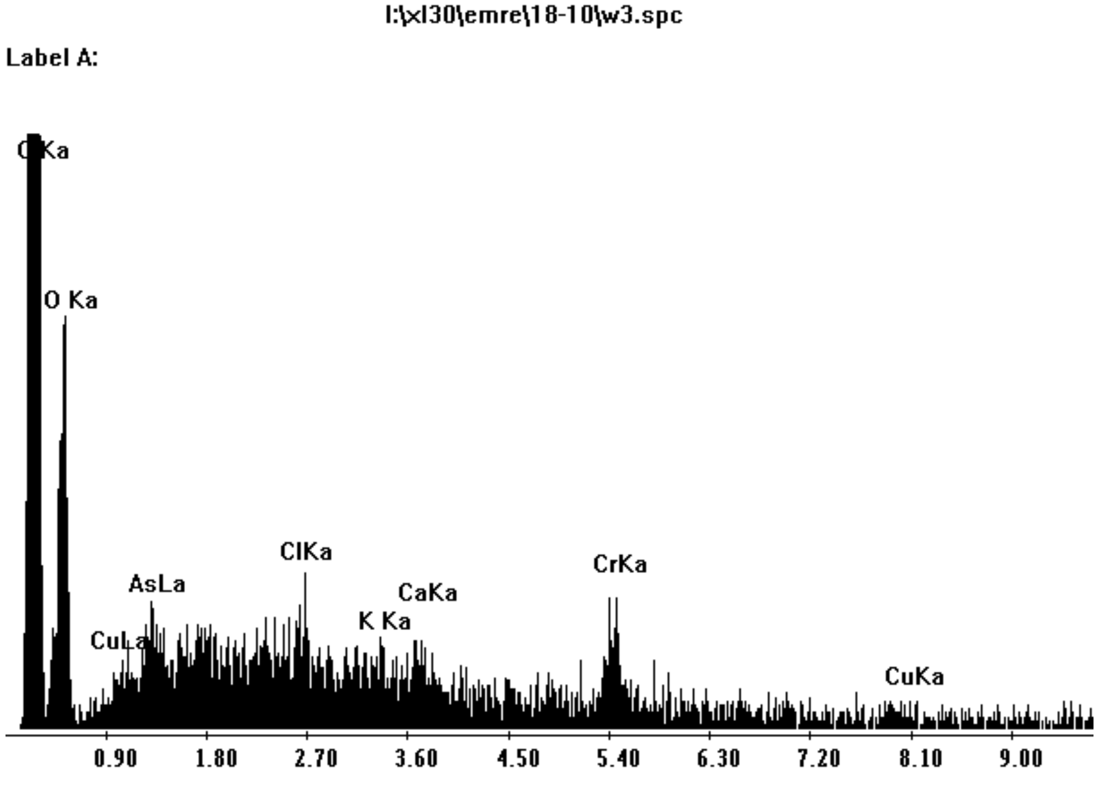
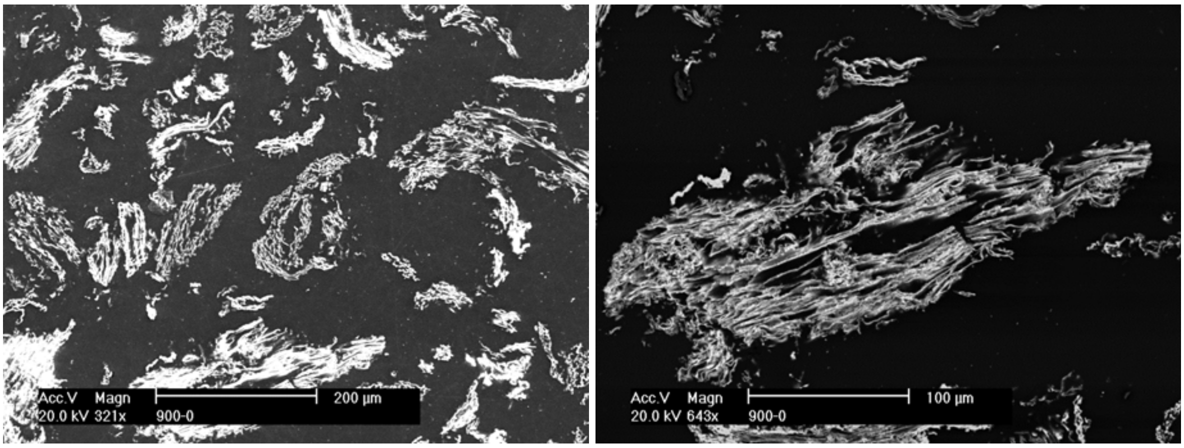


Figure 25: *EDS analysis of the wood particle seen in the bottom of Figure 24(a).*

Figure 26(a) shows cross-sectional SEM images of ash particles generated at 900ºC. The particle at the bottom of this image, partly obscured by the scale bar, is shown at greater magnification in Figure 26(b) and Figure 27 provides the EDS analysis of this particle. In this particle, chromium is the major component followed by copper, arsenic and calcium. This calcium content originates from the original mineral matter content of the wood. The peaks in this spectrum (Figure 27) are much clearer (have a higher signal:background ratio) than those for the unburned wood sample (Figure 25) because the metals are concentrated in the ash sample. The bright (metal-bearing) regions in Figure 26 show signs of the original wood structure in which the CCA-impregnating solution has clearly passed through the longitudinal pores in the wood.



(a) **(b)**

Figure 26: *SEM images of 900°C ash particles. The image in (b) is of the particle at the bottom centre of (a), where it is partly obscured by the scale bar.*

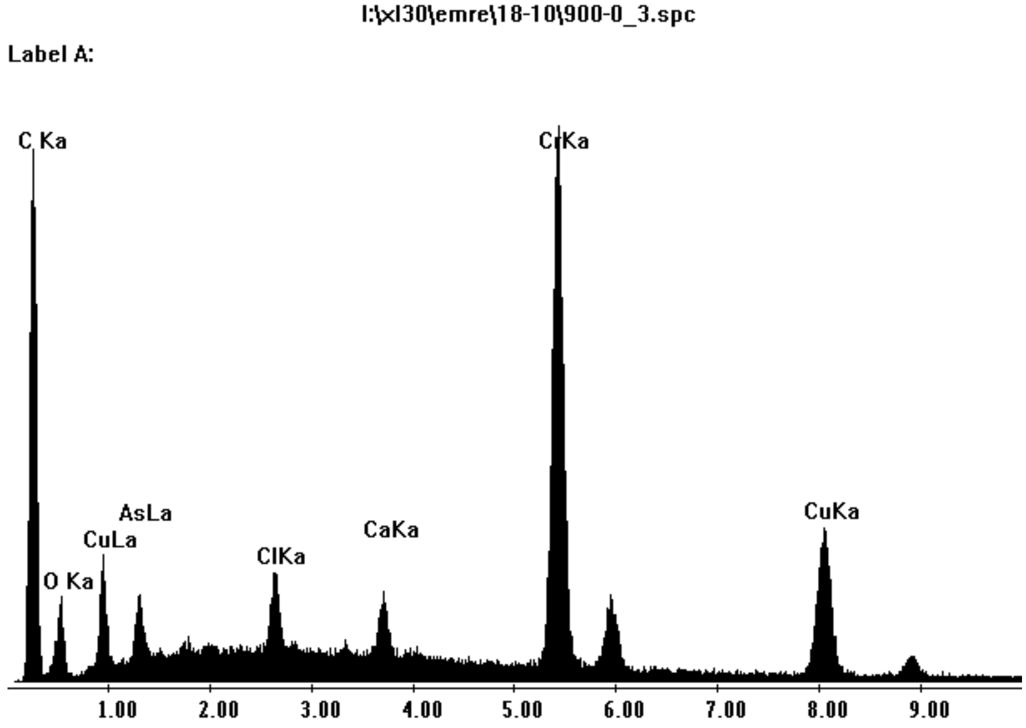
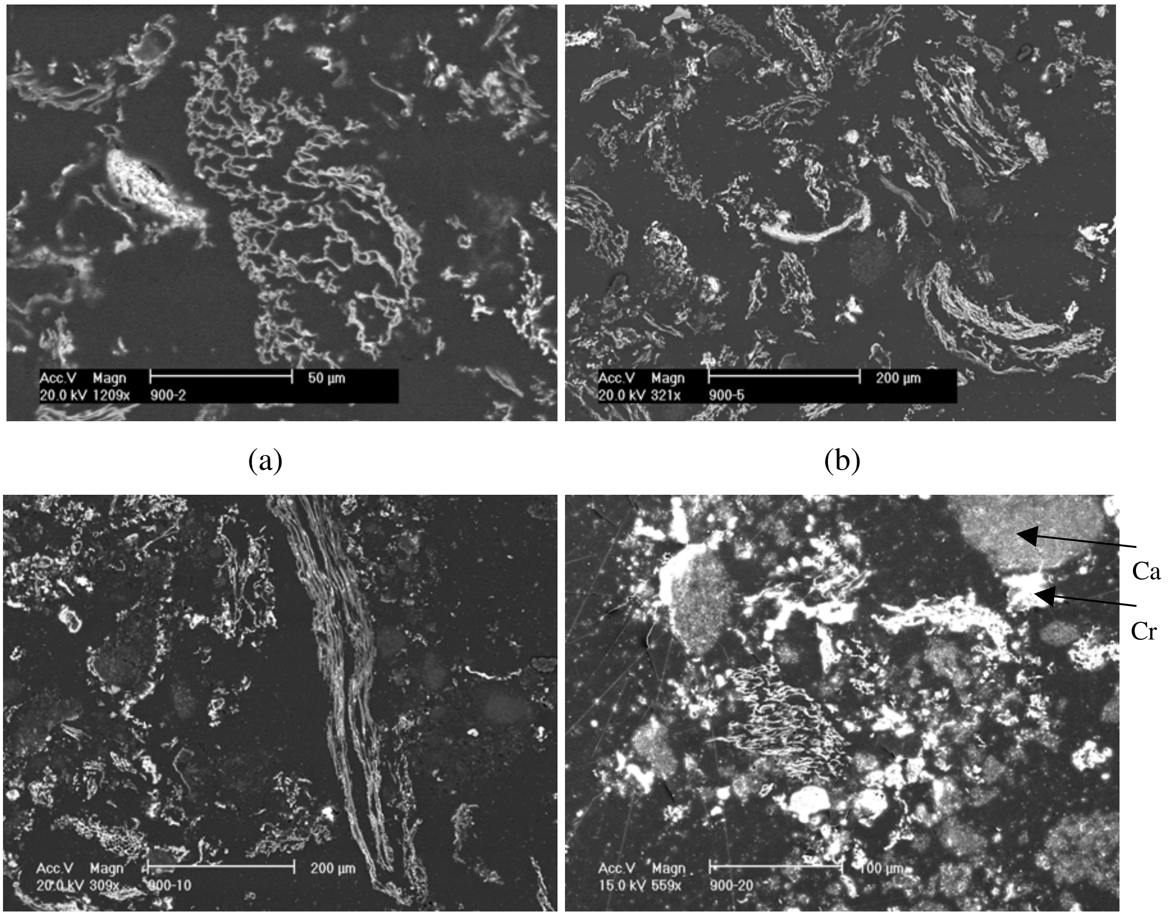


Figure 27: *EDS analysis of the 900°C ash particle shown in Figure 26(b).*

Figure 28 shows SEM images of ashes produced in combustion at 900ºC of wood chip samples mixed with different amounts of dry $Ca(OH)_2$ (see section 2.2.4.1). The heavier CCA metals in the ash residue can easily be distinguished from the rest of the ash by virtue of their greater brightness in backscatter. In particular, the accumulation of the heavy CCA-metals on the sorbent particle surface can also be observed as bright bands on the surface of duller regions, the lower molecular weight of calcium giving rise to less backscatter from its particles. Increasing the Ca:As molar ratio from 1.6 in Figure 28(a) to 16 in Figure 28(d) results in an increasing proportion of unreacted calcium in the ash.



(a) (b)

(c) (d)

Figure 28: *SEM images of ashes generated at 900ºC a) $n_{Ca}:n_{As}=1.6$, b) $n_{Ca}:n_{As}=4$, c) $n_{Ca}:n_{As}=8$, d) $n_{Ca}:n_{As}=16$.*

Figure 29 shows an SEM image with three morphologically distinct ash particles formed in the combustion of CCA wood chip mixed with $Ca(OH)_2$ powder to give a molar ratio Ca:As ~ 8. Regardless of the physical structure formed, these ash particles are all dominated by calcium, arsenic and chromium. This is in good agreement with the equilibrium calculations described in Section 2.1.3 which predicted that that the major products of the CCA-treated wood combustion in the presence of calcium were $Ca_3(AsO_4)_2$, $CaCr_2O_4$ and CuO (see Figure 4).

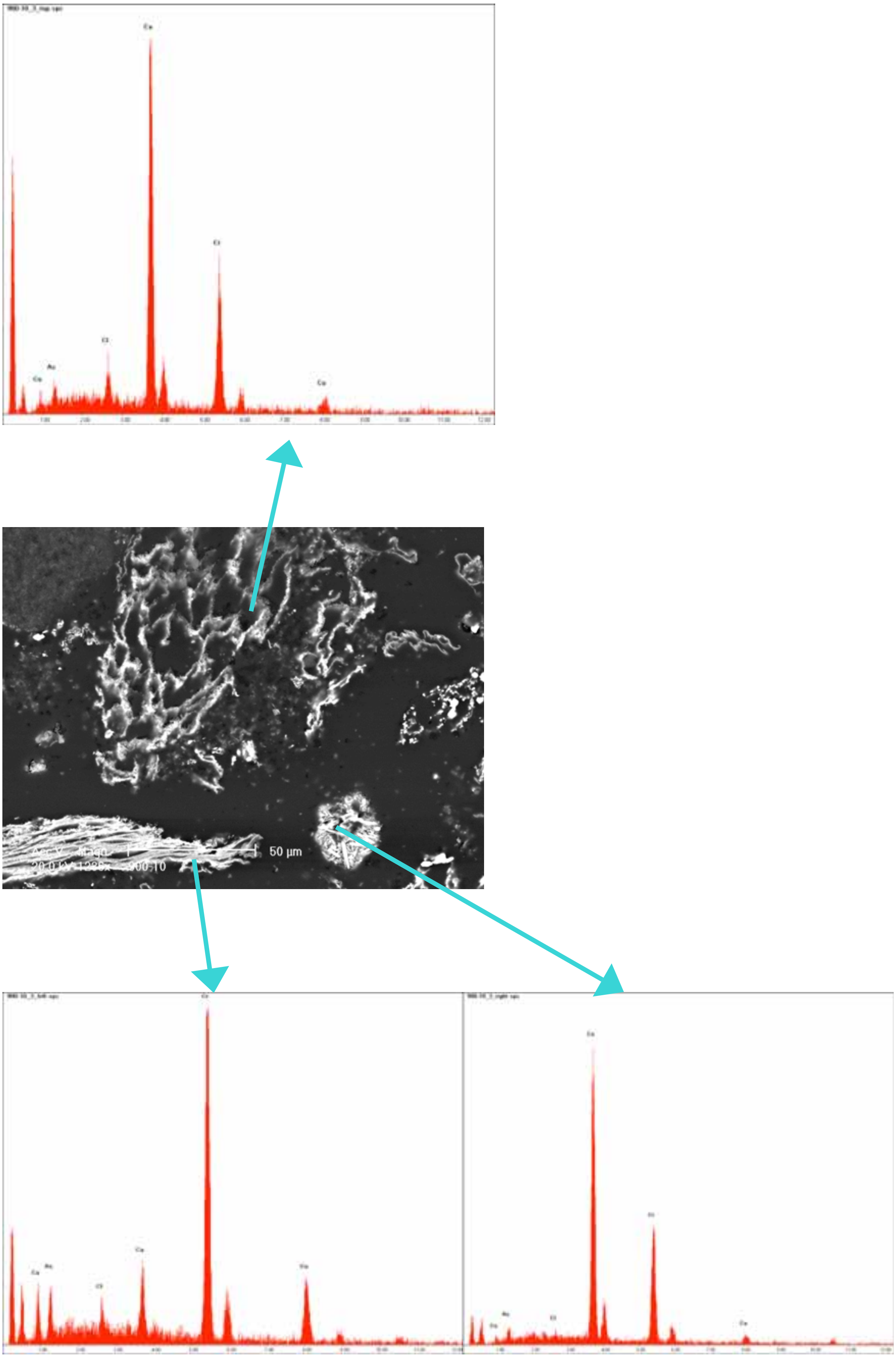


Figure 29: *EDS spectra of different ash particles generated at 900ºC from CCA-timber mixed with* $Ca(OH)_2$ *powder,* n_{Ca}:n_{As}=8.

The combined technique of SEM-EDS mapping which reveals the distribution of specific elements was performed to investigate the added calcium and metal associations in more detail (Figure 30 and Figure 31) when the calcium was added by mixing of dry $Ca(OH)_2$ powder with the wood chip. At 700ºC, the thin bright edge on the particle in the upper right corner of Figure 30(a) belongs to the surface of a calcium particle, as revealed by the calcium distribution in Figure 30(b). Figure 30(d) shows that this bright edge region is due exclusively to chromium which is clearly mobilising and associating with the sorbent to a greater extent than either arsenic or copper.

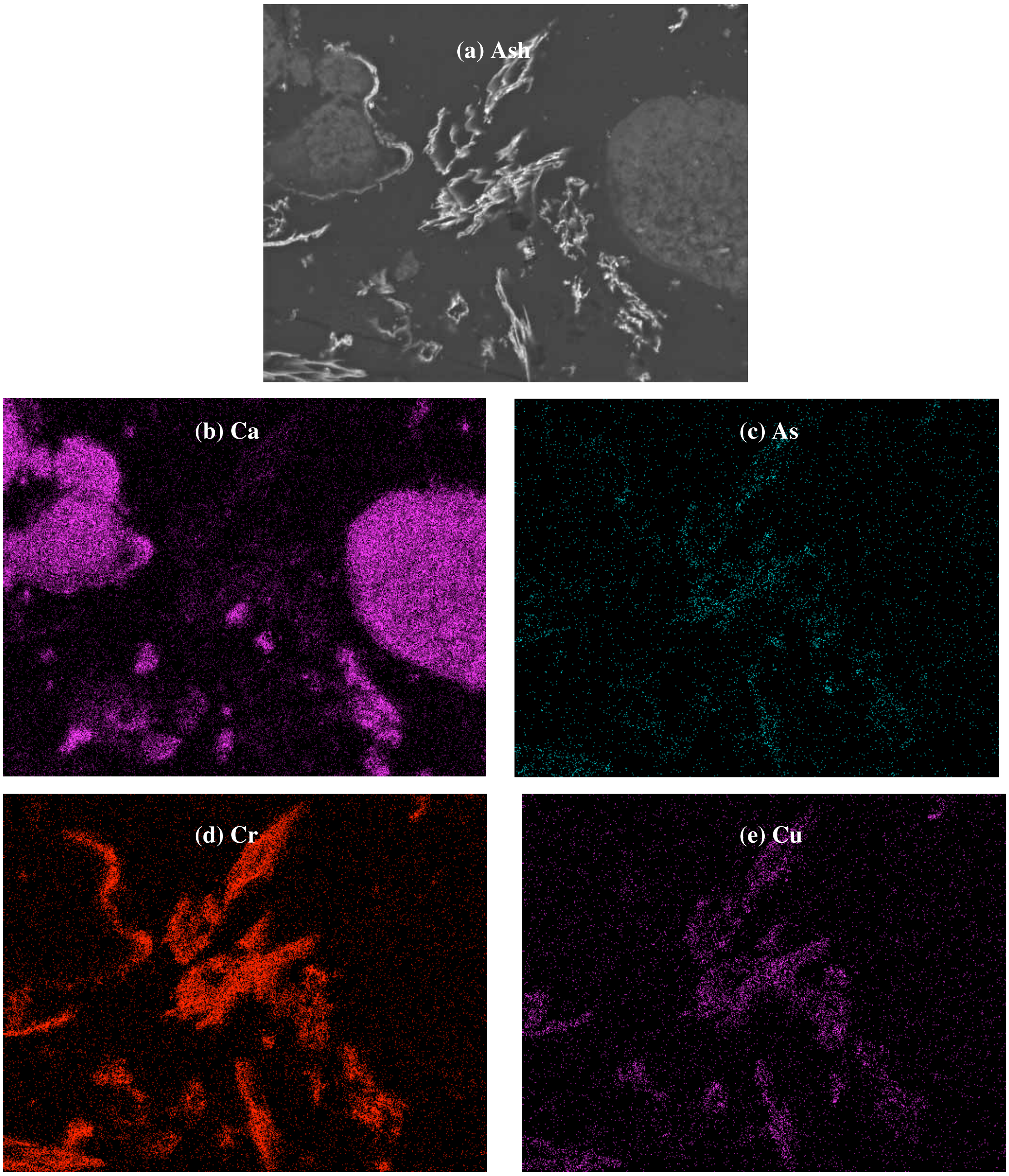


Figure 30: *SEM-EDS mapping of an ash particle (T=700ºC, n_{Ca}:n_{As}=8); (a) Ash particle, (b) Ca, (c) As, (d) Cr, and (e) Cu.*

However, the distribution of much of the chromium remains distinct from that of the calcium – where the chromium is not associated with specific calcium particles, arsenic (Figure 30c) and copper (Figure 30e) are also present, indicating a region of CCA ash from the wood. The effect of calcium additions in stabilizing arsenic in the ash is clearly occurring in finely distributed calcium, rather than in the lumps of calcium that are formed at heavy dosing levels such as depicted in Figure 30. Not surprisingly, therefore, large excesses of additive are ineffective and a more highly dispersed method of addition such as wet impregnation is more effective than dry powder addition.

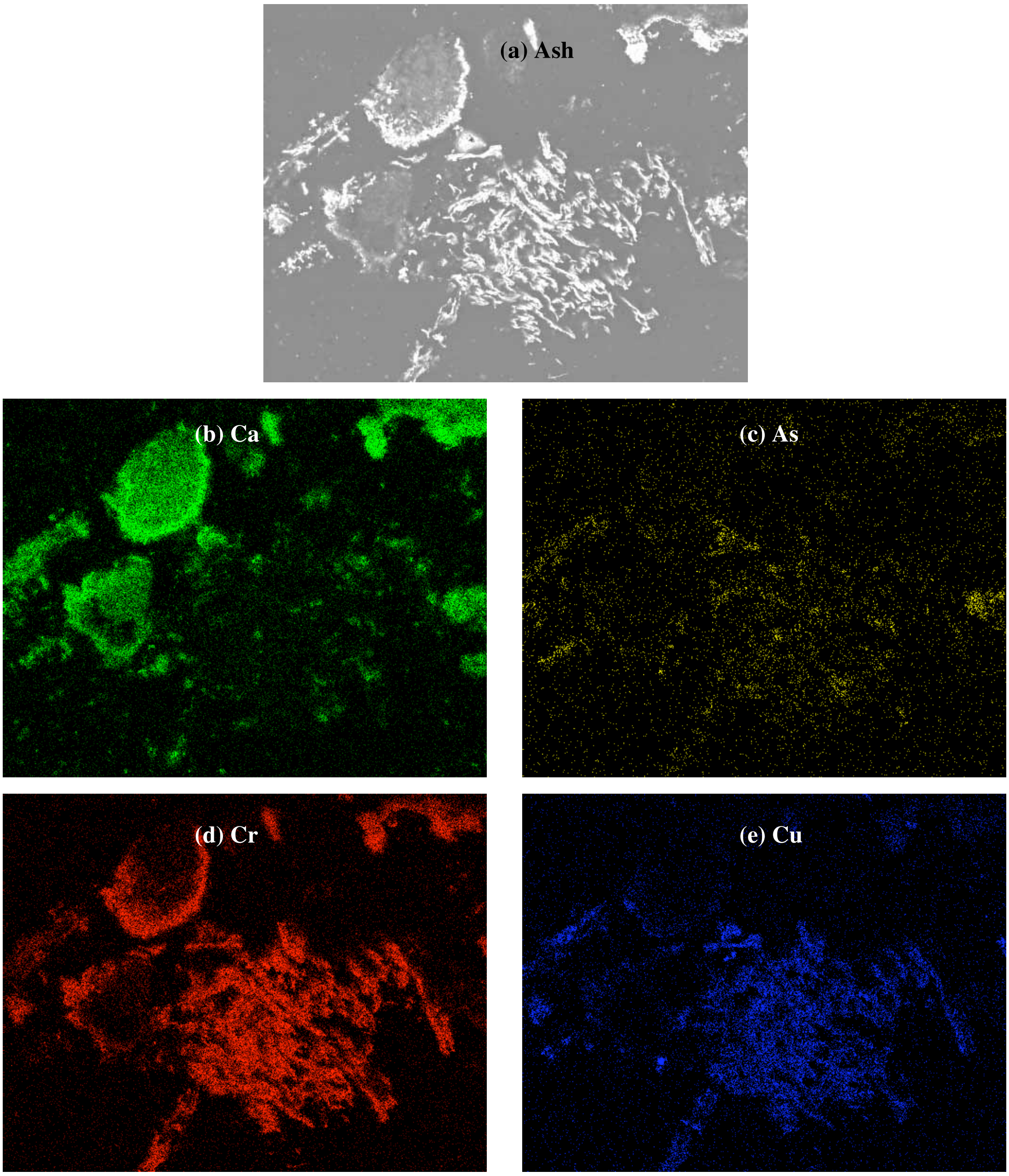


Figure 31: *SEM-EDS mapping of an ash particle (T=900ºC, $n_{Ca}:n_{As}=4$); (a) Ash particle, (b) Ca, (c) As, (d) Cr, and (e) Cu.*

Figure 31 shows SEM-EDS results for combustion at 900ºC with a nominal molar Ca:As molar ratio of 4:1. The particle in the top left of Figure 31(a) is clearly calcium and again shows a concentration of chromium at its surface with an absence of copper and arsenic there. However, the chromium has penetrated much more into the calcium particle than was seen for 700ºC in Figure 30. More significantly, there is more calcium distributed through the CCA-bearing regions and specific evidence now of As-Ca interaction (e.g. in the region at the right-hand edge of Figure 31, about halfway down the image).

2.2.6.2 *X-Ray Diffraction Analysis*

XRD analyses were carried out to identify the crystalline phases formed following CCA-treated wood combustion. FactSage equilibrium calculations were also compared with the XRD spectra produced.

Figure 32 shows an XRD spectrum for ash produced by the combustion of CCA woodchip at 900ºC. Also shown in the figure are the known locations of peaks for reference compounds, blue being for $CuCrO_2$, red for Cr_2O_3, and green for As_2O_3. We therefore conclude that Cr_2O_3 is the most prominent crystalline species in this ash produced. As_2O_3 is the main crystalline form of arsenic while $CuCrO_2$ is the only recognisable copper-containing product detected.

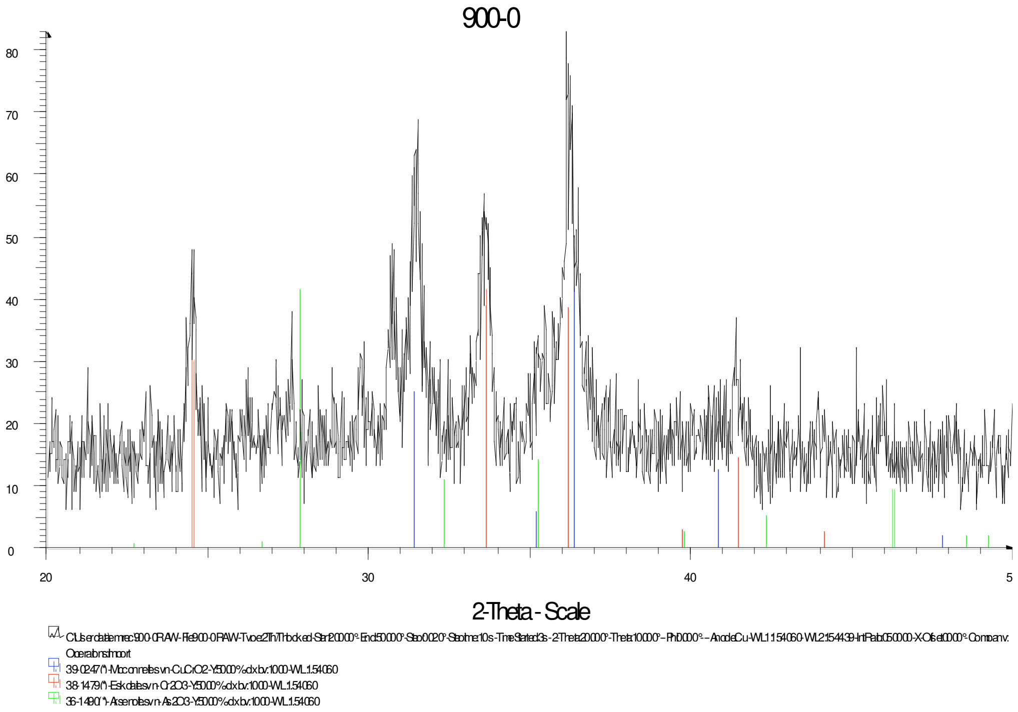


Figure 32: *XRD spectrum of CCA-treated wood ash made at 900ºC. The blue bars show the locations of known peaks for* $CuCrO_2$*; red is for* Cr_2O_3*, and green is for* As_2O_3*.*

Figure 33 shows the XRD spectrum of 900ºC ash generated by CCA-treated wood combustion with $Ca(OH)_2$ admixture at the nominal molar ratio of n_{Ca}:n_{As}=8. The added $Ca(OH)_2$ could also be seen as a major product (blue bars in Figure 33).With $Ca(OH)_2$ addition, the major chromium product is now $Ca_5(CrO_4)_3O_{0.5}$ (red bars) although a small amount of Cr_2O_3 (green bars) could still be identified. It is not possible to come to a decision on possible Ca-As or Ca-Cu associated species from the XRD analysis. The XRD analysis confirms SEM-EDS observation that externally added calcium interacts mainly with chromium.

Other than Cr_2O_3 and As_2O_3, the main CCA-containing species predicted by Factsage thermodynamic equilibrium analysis, including $Ca_3(AsO_4)_2$, $CaCr_2O_4$, $MgCr_2O_4$, CuO, and Cu_2O could not be recognised from the XRD analysis.

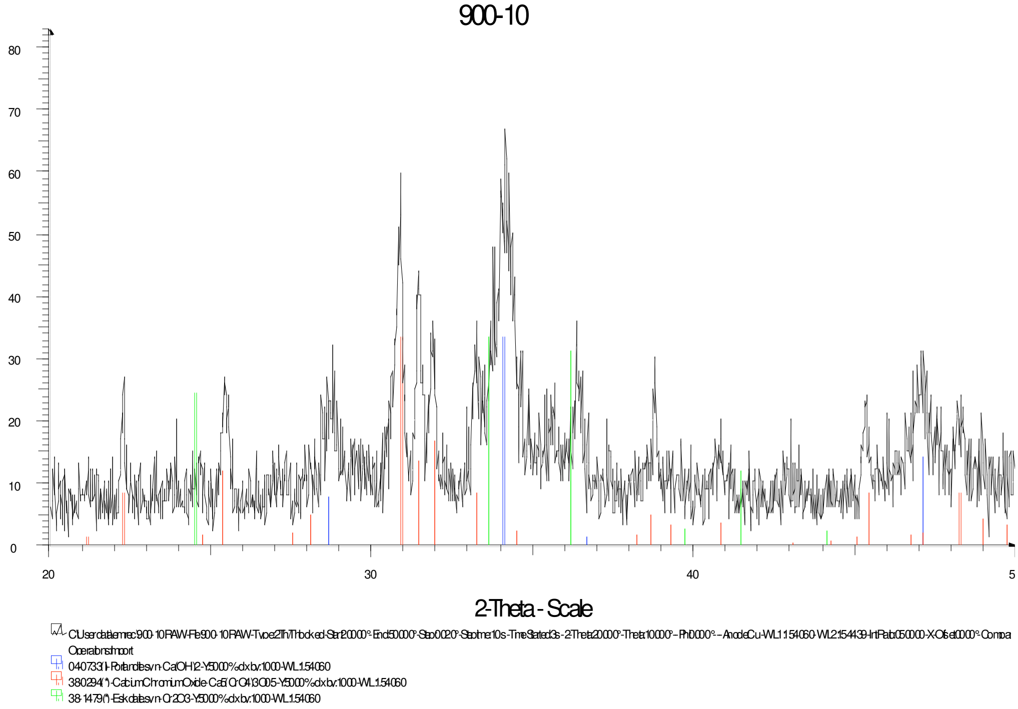


Figure 33: *XRD spectrum of CCA-treated wood ash made at 900ºC with* $Ca(OH)_2$ *addition at the rate of* $n_{Ca}:n_{As}=8$.

2.2.7 Ash Leaching Studies

The ash generated at different temperatures (with and without $Ca(OH)_2$ addition) was analysed using the dilute acetic-acid leach (DAAL) procedure that we developed in earlier work (Stewart *et al.,* 2004). This test uses a 25 mg sample of ash in 25 ml of dilute buffered acetic acid. It avoids the very high pH that occurs when the ash is subjected to TCLP conditions and which was observed to enhance the solubility of some components dramatically in our earlier work (Stewart *et al.*, 2004).

Table 12 lists the results of these tests in terms of the quantities of the CCA metal in the original wood that report to the leachate in the DAAL test. These results are presented in Figure 34 and Figure 35 as fractions of the CCA metal in the wood that report to leachate.

Approximately 20% of the arsenic in the wood reports to the DAAL leachate when the wood is combusted at temperatures from 600 to 900ºC (Figure 34). This drops to about 5% for combustion at 1000ºC, which we believe to be due to the fact that combustion at 1000ºC leads to almost complete volatilisation of the arsenic in the wood, so there is very little left in the ash that could report to the leachate. These results are qualitatively similar to those obtained for combustion of lumps of CCA-treated wood in our earlier report (Stewart *et al.*, 2004), although in that case the plateau values were around 10% before dropping to very low values at high temperature.

Less than 10% of the copper in the wood reports to the leachate after combustion at 600 to 900ºC and at 1000ºC, no copper was found in the leachate. In general we found the high temperature ashes to be extremely difficult to digest completely due to the formation of refractory copper and chromium compounds so it is not surprising that mild leaching conditions fail to mobilise some of these. These results are very similar to those obtained from the combustion of lump samples (Stewart *et al.*, 2004).

The results for chromium show a generally decreasing leachability from the ash as the combustion temperature is raised from 600 to 900ºC, but there is an increase in going to 1000ºC, the highest temperature studied. It should be noted that the combustion of lump samples (Stewart *et al.*, 2004) gave the same decreasing trend as seen up to 900ºC in Figure 34, but that this continued to beyond 1000ºC, in contrast to the present result at 1000ºC.

Table 12: *The quantities of CCA components reporting to the leachate.*

Temp. (°C)	$n_{Ca}:n_{As}$	**As [mg/kgwood]**	**Cr [mg/kgwood]**	**Cu [mg/kgwood]**
600	0	818	789	332
700	0	603	448	227
800	0	569	375	347
900	0	724	350	225
	1.6	1728	295	339
	4	2134	1391	265
	8	2138	1847	302
	16	2851	3182	528
1000	0	35	813	-

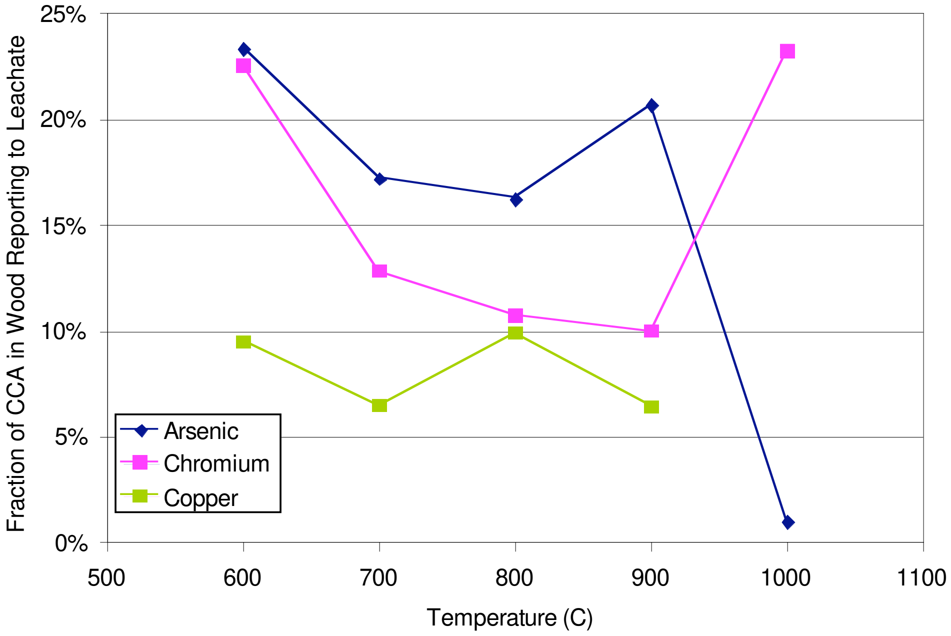


Figure 34: *Fractions of CCA metals in the parent treated timber that report to the leachate in the DAAL leaching test of the ash, as a function of the combustion temperature of the wood.*

The effects of calcium additions (as dry powder $Ca(OH)_2$)on the fractions of the wood CCA components that report to the ash leachate can be profound, as shown for combustion at 900ºC in Figure 35. Even small amounts of calcium enhance the leachability of arsenic and with a molar Ca:As ratio greater than 10, the great majority of the arsenic in the wood ends up in the leachate. The increased capture of As by Ca is clearly accompanied by the formation of species that are relatively soluble, most probably calcium arsenate.

While calcium interaction with chromium is more obvious than it is with arsenic (see SEM-EDS analysis, Section 2.2.6.1), it takes a greater quantity of calcium to have an effect chromium leachability. As seen in Figure 35, beyond a molar ratio Ca:As ~ 2, leachability of chromium is strongly enhanced and essentially all the chromium can be leached if the combustion is carried out with Ca:As > 10. It should be noted that the molar ratio Cr:As = 2.0 in the parent wood, so this high leachability condition is achieved with Ca:Cr >5.

Finally, calcium addition did not affect the copper concentration in the leachate.

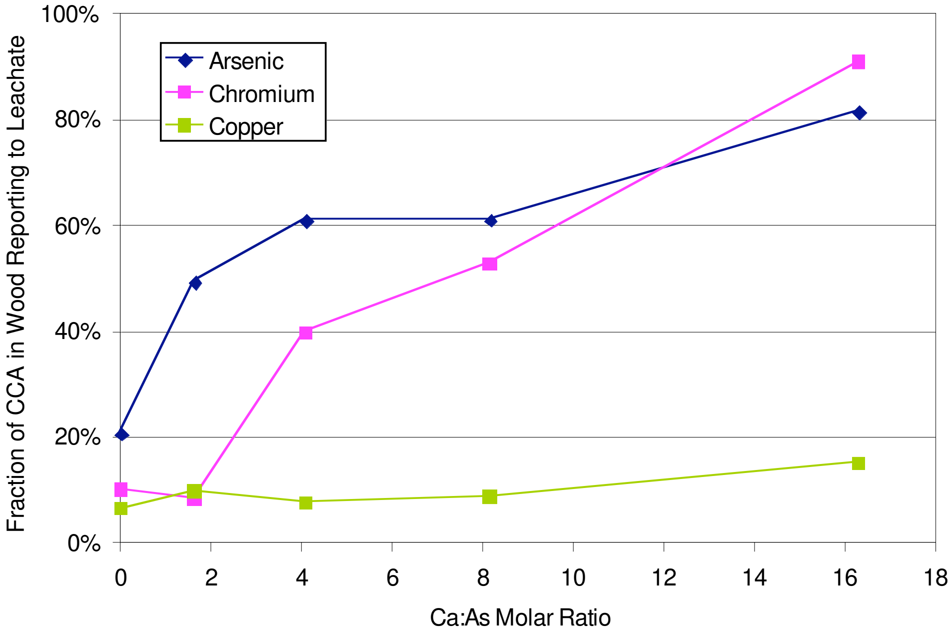


Figure 35: *Fractions of CCA metals in the parent treated timber that report to the leachate in the DAAL leaching test of the ash produced at 900 ºC, as a function of the amount of calcium mixed with the wood as* $Ca(OH)_2$ *powder.*

2.3 Discussion and Conclusions

Equilibrium modelling studies can provide a basic understanding of speciation and physical states of ash products formed during combustion. However, the thermodynamic analysis of ash from CCA-treated combustion proved to be somewhat dependent on the choice of database, with the two pure substance databases, Fact53 and SGTE, each having deficiencies. Even when the two databases had the same species, $Ca_3(AsO_4)_2$ and $Mg_3(AsO_4)_2$, 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 arsenic 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 (Helsen and van den Bulck, 2005). 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. Sorbent addition during combustion is a proven technology to reduce SO_2 emissions from coal-fired boilers. Without sorbents, control of arsenic emissions from large-scale power plant is difficult (Dismukes, 1994; Winter *et al.*, 1994) but this has not to date been a major problem in Australia.

The effect of sorbent injection in reducing arsenic emissions from coal combustion has been studied by various researchers (Gullet and Raghunathan, 1994; Mahuli *et al.*, 1997; Biswas and Wu, 1998; Wu and Barton, 2001; Jadhav and Fan, 2001; Sterling and Helble, 2003; Helsen and van den Bulck, 2005). Sorbents added into the combustion chamber react with the arsenic oxide vapour to create thermally stable species such as calcium arsenate $Ca_3(AsO_4)_2$ in relatively large particles that are easily captured. If arsenic vapour is not captured, it will condense to some extent as the combustion gases are cooled in the heat recovery section of the boiler – this condensation can lead to the formation of submicron particles, which are more difficult to collect efficiently (Venkatesh *et al.*, 1996; Helsen and van den Bulck, 2005).

Our investigations of the use of hydrated calcium oxide to inhibit arsenic volatilisation in the combustion of CCA-treated wood have revealed that a significant increase in the retention of arsenic in the ash can be achieved. Mahuli *et al.* (1997) showed that $Ca(OH)_2$ can effectively capture volatile arsenic oxide to produce calcium arsenate. Jadhav and Fan (2001) found that interaction between arsenic and lime (CaO) results in $Ca_3As_2O_8$ below 600ºC and $Ca_2As_2O_7$ between 700ºC and 900ºC. They suggested that there is a decrease in the efficiency of arsenic capture at temperatures between 700º and 900ºC due to the fact that the reaction product, $Ca_2As_2O_7$, is unstable. While we found the greatest impact of calcium sorbent at 900ºC, it should be noted that the extent of volatilisation in the absence of sorbent was also greatest at this temperature so the effect of the sorbent was more noticeable – in fact, the achievable retention in the presence of calcium was lowest at 900ºC (Figure 15), which is in accord with the suggestion of Jadhav and Fan (2001). On the other hand, Iida *et al.* (2004) reported more or less constant extents of arsenic retention in combustion of CCA-treated wood with $Ca(OH)_2$ between temperatures 600ºC and 900ºC.

Wu and Barton (2001) used thermodynamic equilibrium modelling to conclude that other sorbents might also be effective in trapping arsenic, in the order K>Al>Ca>Mg. Contrary to this suggestion, we find that calcium is the most efficient sorbent for arsenic capture, slightly better than magnesium. Potassium and possibly also aluminium additions actually promote arsenic loss at lower rates of addition, presumably because they upset the natural sorbent behaviour of the ash inherently present in the wood. Although iron oxide (Fe_2O_3) is used in copper smelters to capture vapour As2O3 (see Section 4.3.3), our experiments on Fe_2O_3 additions suggest that it has negligible impact on arsenic retention under combustion conditions, at least up to 900ºC. Retention of chromium (and copper) in the presence of the various sorbents examined experimentally remained complete up to 900°C.

Scanning electron microscopy showed that the added calcium powder actually interacted more intimately with chromium than with arsenic, consistent with the results of Chen and Wey (1996) who showed very strong interaction between chromium volatiles and limestone. 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 a only slight 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.

Ultimately, 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.