REVIEW OF THERMOCHEMICAL CONVERSION PROCESSES AS DISPOSAL TECHNOLOGIES FOR CHROMATED COPPER ARSENATE (CCA) TREATED WOOD WASTE

Lieve Helsen and Eric Van den Bulck
Katholieke Universiteit Leuven
Department of Mechanical Engineering
Division Applied Mechanics and Energy Conversion

Environmental Impacts of Preservative-Treated Wood, February 10, 2004, Orlando, Florida
Overview presentation

• Problem statement

• Literature review: options for managing CCA wood

• Thermochemical conversion processes: observations

• Best available thermochemical conversion technology (BAT)
Problem statement: waste of CCA treated wood

- Chromium (C) as $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{CrO}_3$
- Copper (C) as $\text{CuSO}_4$, $\text{CuO}$
- Arsenic (A) as $\text{As}_2\text{O}_5$

World-wide:
- 30 Mm$^3$ treated wood / year
- 500,000 tonnes preservative chemicals
- 2/3 treated with CCA

HAZARDOUS WASTE?

DISPOSAL ROUTE?
Problem statement: waste of CCA treated wood

Waste abatement, elimination or reduction (= prevention):
• alternative wood preservatives without arsenic
• substitution by other materials
• wood modification treatments
• optimisation of preservation treatment
• designing details that minimise the potential for decay
• service life enhancing technologies
• design to minimise waste during construction

improved disposal end-management practices important
Literature review: options for managing CCA wood

P.A. Cooper, 1999, Presented at the 20th annual CWPA conference, Vancouver.
P.A. Cooper, 2003, Presented at AWPA annual meeting, Boston.

sorting needed? (visual sorting, chemical stains, X-ray systems, laser systems, permanent identification marking system)

industrial treated products ↔ residential lumber (increasing quantities and widespread nature)
Literature review: options for managing CCA wood

General order of preference:

1. Waste abatement or elimination
2. Waste reduction
3. Waste reuse
4. Waste refining for recycling
5. Waste treatment and destruction
6. Waste disposal
Literature review: options for managing CCA wood

General order of preference:

1. Waste abatement or elimination
2. Waste reduction
3. Waste reuse
4. Waste refining for recycling
5. Waste treatment and destruction
6. Waste disposal
Literature review: options for managing CCA wood

General order of preference:

1. Waste abatement or elimination
2. Waste reduction
3. Waste reuse
4. Waste refining for recycling
5. Waste treatment and destruction
6. Waste disposal

end-management options

thermal processes

provide energy and concentrate waste for recycling or disposal
Thermochemical processes: observations

1. Thermogravimetric (TG) experiments with model compounds
   (Kercher and Nagle 2001, Helsen et al. 2003)

As sampling train

gas flow $N_2$, air or He
Main conclusions pure compounds:

- **As$_2$O$_3$** volatilises at temperatures as low as 200°C.
- **As$_2$O$_5$** does not reduce nor volatilise at $T < 600°C$.
- **H$_2$** containing atmosphere (5%) causes As$_2$O$_5$ to volatilise at lower $T$ (425°C).
- thermal decomposition of CuO strongly depends on O$_2$ and H$_2$ content of atmosphere.
- **Cr$_2$O$_3$** does not undergo any significant reaction during heating in N$_2$ or air.
Main conclusions mixtures:

\( \text{CuO} + \text{As}_2\text{O}_5: \)

- part of \( \text{As}_2\text{O}_5 \) volatilises at lower \( T \) compared to pure \( \text{As}_2\text{O}_5 \), remainder reacts with \( \text{CuO} \) to form copper arsenates \( (2\text{CuO} \cdot \text{As}_2\text{O}_5 \text{ and } \text{Cu}_3(\text{AsO}_4)_2) \)
- no decomposition of copper arsenates in air up to 900°C (atmosphere exhibits a strong effect)

\( \rightarrow \) formation of copper arsenates may be a mechanism to limit arsenic loss up to 900°C
Thermochemical processes: observations

Main conclusions mixtures:

Cr$_2$O$_3$ + As$_2$O$_5$:
- free As$_2$O$_5$ is volatilised
- some As$_2$O$_5$ reacts with Cr$_2$O$_3$ to form chromium arsenate (CrAsO$_4$)
- CrAsO$_4$ does not exhibit any temperature range of zero weight loss

formation of chromium arsenate is thus certainly not a mechanism to limit arsenic loss
Thermochemical processes: observations

Main conclusions mixtures:

\( \text{Cr}_2\text{O}_3 + \text{As}_2\text{O}_5: \)

- free \( \text{As}_2\text{O}_5 \) is volatilised
- some \( \text{As}_2\text{O}_5 \) reacts with \( \text{Cr}_2\text{O}_3 \) to form chromium arsenate \( (\text{CrAsO}_4) \) (Pizzi: synthesis by reaction \( \text{CrO}_3 + 3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O} + \text{glucose} \rightarrow \text{precipitate} \))
- \( \text{CrAsO}_4 \) does not exhibit any temperature range of zero weight loss

\[ \rightarrow \text{formation of chromium arsenate is thus certainly not a mechanism to limit arsenic loss} \]
Thermochemical processes: observations

Main conclusions mixtures:

As$_2$O$_5$ + glucose:

- faster decomposition of As$_2$O$_5$ compared to pure As$_2$O$_5$
- the effect is more pronounced the higher the O$_2$ concentration in the purge gas is

→ O$_2$ concentrations up to 10% accelerate the decomposition of both As$_2$O$_5$ and glucose,

but do not reverse the reaction As$_2$O$_5$ → As$_2$O$_3$ + O$_2$
Thermochemical processes: observations

Main conclusions mixtures:

As$_2$O$_5$ + activated carbon:

- for temperatures above 300°C faster decomposition of As$_2$O$_5$ compared to pure As$_2$O$_5$

  reducing environment (presence of H$_2$, glucose, decomposition products of glucose or carbon) favours arsenic release
Thermochemical processes: observations

Main conclusions mixtures:

As$_2$O$_5$ + yellow pine sawdust:

- if the mixture is held for longer time periods at $T$ between 250°C - 370°C,

As volatilisation occurs

the rate of As loss increasing with dwell temperature

CuO + yellow pine sawdust

- reduction of CuO at low temperatures
Thermochemical processes: observations

Conclusion:

thermal decomposition of CCA treated wood results in a reducing environment formed by wood, char, pyrolysis vapours

\[
\text{reduction reaction } \text{As}_2\text{O}_5 \rightarrow \text{As}_2\text{O}_3 + \text{O}_2 \text{ can not be avoided}
\]

zero arsenic release seems to be impossible
Thermochemical processes: observations

2. Thermal decomposition studies with CCA treated wood

% of As volatilised: 8 - 95 %

dependent on T, t, Cl, S, pO₂ and air flow rate, extended period of ash heating, impregnation process, … pressure.

threshold temperature below which zero As release: not > 300°C
Thermochemical processes: observations

Mechanism responsible for As release:

- reduction $\text{As}_2\text{O}_5 \rightarrow \text{As}_2\text{O}_3 + \text{O}_2$
- followed by volatilisation $2\text{As}_2\text{O}_3 \rightarrow \text{As}_4\text{O}_6$

How to avoid or limit As release?

- control the reduction reaction
- once $\text{As}_2\text{O}_3$ is formed, it is released at low temperatures
- $\text{As}_2\text{O}_3 + \text{O}_2 \rightarrow \text{As}_2\text{O}_5$ is known to happen only under pressure
3. Modelling high temperature chemistry
(Sandelin and Backman 2000, Kitamura and Katayama 2000)

Equilibrium model based on minimising $\Delta G$

500-1150°C: $\text{As}_4\text{O}_6$ (g) dominates

1150-1600°C: $\text{AsO}$ (g) dominates

Cu and Cr are unlikely to volatilise (resp. 0.51% and 0.05%)
Mg, Cu and Cr may prevent As from volatilising
reducing conditions (char) may affect the tendency to vaporise
Thermochemical processes: observations

Thermodynamic analyses combined with experimental studies

higher retention of As in charcoal (after pyrolysis in N\textsubscript{2}) compared to ash (after combustion in air)

due to absorption of As in the charcoal

Identification of the vaporised As species:

As\textsubscript{4}, As\textsubscript{2}, As\textsubscript{3}, AsO\textsubscript{2}, AsO, As, As\textsubscript{4}O\textsubscript{7}, As\textsubscript{4}O\textsubscript{6}

do not agree for different modelling studies
4. Arsenic capturing devices


Commercially available? Very few tests on industrial scale!

Additional investments needed: better cleaning systems and control

venturi scrubber or electrostatic filter is insufficient

Industrial experience with other As containing feedstock is helpful

c coal combustion → sorbent injection
5. Characterisation of combustion ash
(Solo-Gabriele et al. 2002, Pohlandt et al. 1993)

- the environmental impact of the ashes (bottom ash, boiler ash, fly ash) is remarkable, none of them meeting the requirements for above-ground disposal.
- leachates concentrations > limit for As and Cr
- in the leachate Cr is present in toxic hexavalent state
- bottom ash from wood mixed with min. 5% CCA wood is characterised as hazardous waste (US)
6. Formation of PCDD/PCDF


- copper is identified as a catalyst of PCDD/F formation
- wood burning is always accompanied by unwanted production of PCDD/F, the amount being dependent on the type of wood and the combustion system
- low carbon burnout and zones with low T support PCDD/F
- grate boiler fly ash > bubbling or circulating fluidised bed fly ash
Thermochemical processes: observations

• avoid PCDD/F formation by
  poisoning: blocking the catalytically active sites of Cu
    e.g. by addition of sulfamide to the fuel
  eliminating 1 of the essential elements (C, H, O, Cl)
    e.g. pyrolysis (absence of O$_2$)
  eliminating favourable working conditions
    e.g. quenching the flue gases to very low T
Best Available Thermochemical Technology

- Slow pyrolysis?
- Flash pyrolysis?
- Incineration?
- Co-incineration?
- Gasification?
Best Available Thermochemical Technology

Slow pyrolysis?

As release $\neq 0$, but $<<$ incineration or gasification

+ As volatilised may be easier captured
+ no PCDD/F formation
+ recovery of metals and charcoal through dry centrifugal method
+ production of secondary fuels (pyrolysis gas, charcoal)

- not yet completely optimised on an industrial scale
Best Available Thermochemical Technology

Flash pyrolysis?

+ storable secondary fuel: pyrolysis oil

BUT

- substantial concentrations (5-18%) of As in the oil
  (ref. Hata et al. 2001)

useless
Best Available Thermochemical Technology

Incineration?

- to avoid As and PCDD/F emission ⇒ extensive gas cleaning equipment and appropriate cooling trajectories
- \( \text{As}_2\text{O}_3 \) dust poses occupational health problems
- no production of secondary fuels, but production of heat that has to be used immediately
- treatment of the ash containing As, Cu, Cr

+ recycling of As containing scrubber solution
Best Available Thermochemical Technology

Co-incineration?
+ economy of scale
+ low investment cost
+ short term solution
+ highly flexible with respect to fuel used
+ As may be scavenged by compounds present in other waste streams if mix of waste streams
+ easier to comply with emission legislation

DILUTION EFFECT
Best Available Thermochemical Technology

Co-incineration?

- more bottom ash with higher water-soluble As concentration
- volatile As has to be removed from larger amount of flue gas
- not allowed in some countries where impregnated wood waste has to be treated as mono-stream (e.g. DK)
**Best Available Thermochemical Technology**

**High temperature gasification?**

- very fast rise to high temperature needed to convert all As to metallic form (expensive grinding and heating)
- all converted As has to be captured by cleaning system

+ which may be easier due to the metallic form
+ higher energetic efficiencies and smaller amount of gas to be cleaned compared to combustion
+ no PCDD/F formation due to cracking of the organic compounds
+ recuperation of slag (Cu + Cr), syngas, pure As
Best Available Thermochemical Technology

CONCLUSION

BAT =

• short term: co-incineration as long as mixing (dilution) is allowed

• long term: SUSTAINABLE SOLUTION

“recycle as much material as possible in a cost-effective way”

to identify the BAT further research is needed to prove the following technologies:

1. low temperature pyrolysis in a moving bed

2. high temperature gasification in a metallurgical furnace
**CONCLUSION**

low temperature pyrolysis in a moving bed

high temperature gasification in a metallurgical furnace

Acknowledgement:

we thank ARCH Timber Protection for the financial support of this research work