

**43<sup>RD</sup> IEA FBC MEETING  
LISBON: November 2001**

**“THE BEHAVIOUR OF TRACE ELEMENTS  
DURING THE CO-COMBUSTION OF COAL  
WITH BIOMASS AND WASTES IN FLUIDISED  
BED COMBUSTORS”**

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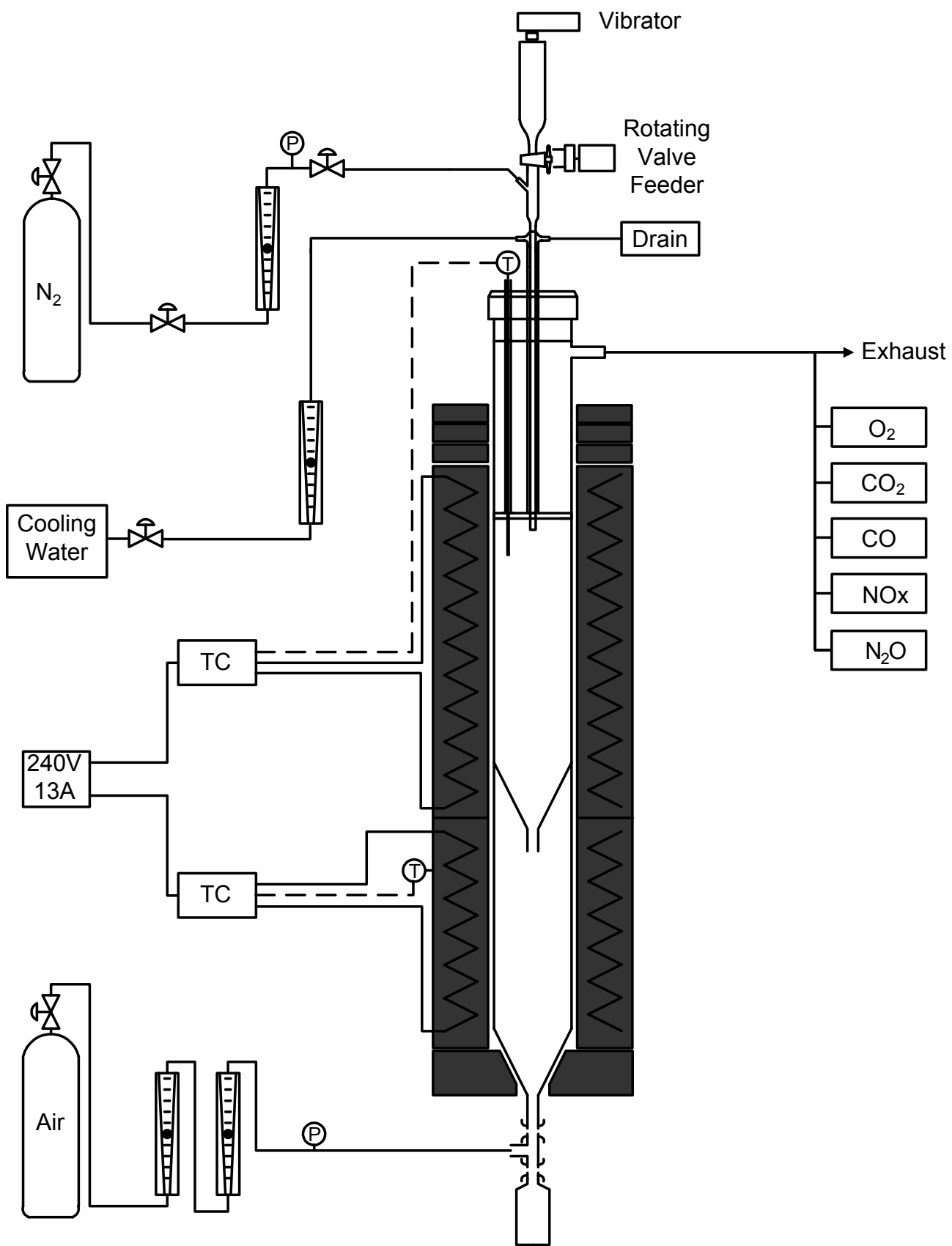
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## Summary

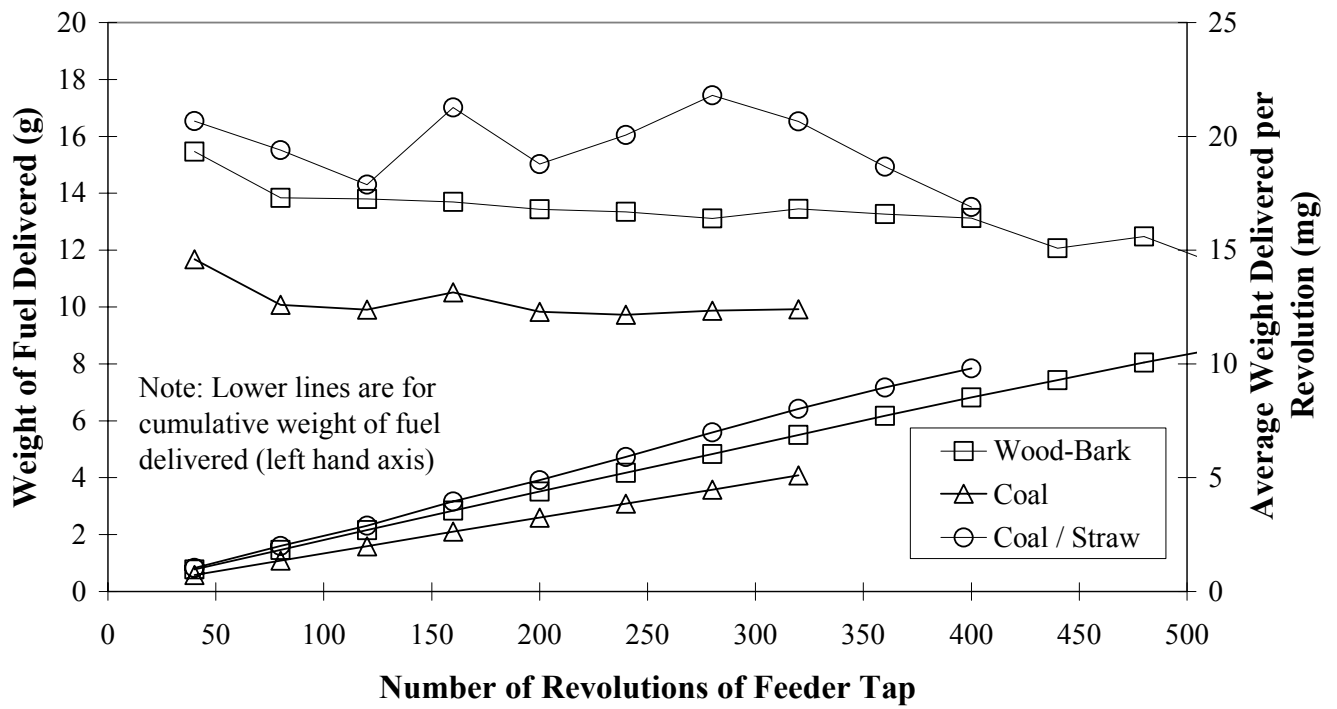
The presentation introduces two novel bench-scale reactors for studying trace element behaviour in combustion systems. The first is a “suspension-firing” reactor designed to monitor trace element release during solid fuel combustion under conditions relevant to fluidised bed combustors. The new design (Figures 1-6) allows the examination of fuel particle combustion in the absence of bed solids. Preliminary experiments presented using two coals, a sample of wood bark and one of straw (Tables 1 and 2). Ash from the reactor walls and base have been analysed separately from ash collected on a sintered disc in the path of exit gas. Trace element concentrations in these samples were analysed by Inductively Coupled Plasma (ICP)-mass spectrometry and ICP-atomic emission spectrometry (AES). The fractions of original trace elements retained by the ash have been reported, together with the relative enrichment in the “sinter-ash” compared to “bottom ash”. Data for a range of elements are presented in Figures 6 – 13). Mercury was almost completely volatilised from all fuels, as was selenium for all except wood-bark. Chromium, manganese and thallium were partially volatilised and nickel mostly retained in all samples. The behaviour of beryllium, lead, molybdenum, vanadium and zinc varied, depending on the fuel sample. Beryllium was released to a greater extent from coal/straw than the other fuels. Vanadium was partially volatilised from wood-bark and coal/straw, while the largest proportion of the zinc released was from the wood-bark. Lead and molybdenum were retained to a greater extent by ‘Colombian coal’ and wood-bark respectively. Evidence of the enrichment of certain trace elements on the finer “sinter-ash” particles has also been observed, e.g. for As, Cd, Pb and Tl during the combustion of the ‘Colombian-coal’. Comparison with data collected by project partners, using pilot and full-scale equipment, is very encouraging. This suggests that the suspension-firing reactor is a promising small-scale device for screening novel fuel blends and mixtures in terms of potential release of trace elements during combustion. (see also FUEL 81, (2002), 159-171).

The second reactor has been designed to study the capture of volatilised trace elements in a range of sorbents, relevant to both combustion and gasification processes. The all-quartz reactor (Fig.01) is made in three parts; a generation section, situated above a high temperature sorbent bed, which is situated, in turn, above an ambient temperature sorbent bed. The upper, generation section is housed within an electric furnace normal run at 1000 °C; here the trace element of interest (either the element or a simple compound – see Fig.02) is volatilised and passed in nitrogen carrier gas through the two sorbent beds in series. The high temperature sorbent bed is located within a second electric furnace; temperatures of 300, 450 and 600°C have been tested. Meta-kaolin and activated carbon have been tested as sorbents for a range of elements including Hg, Se, Cd, Pb, Sb, As and V. The percentage weight of the volatilised element that is captured by the two beds is reported (at three different test temperatures for the high temperature bed) – see Fig.03-06. Significant differences in behaviour are apparent for the various element tested. The kaolin sorbent seems successful for elements such as As and Pb but not for Hg. However, the active carbon was found to be partially successful for Hg. In a second set of experiments (Fig.07), leaching tests were made on sorbent contaminated with various trace elements. This is relevant to understanding of possible disposal options for spent sorbent. Clear evidence of the sensitivity of water leachability to the sorbent bed temperature was evident. The work to date suggests that the novel reactor is a very useful, low cost, device for studying the potential of sorbents for selective capture of trace elements.

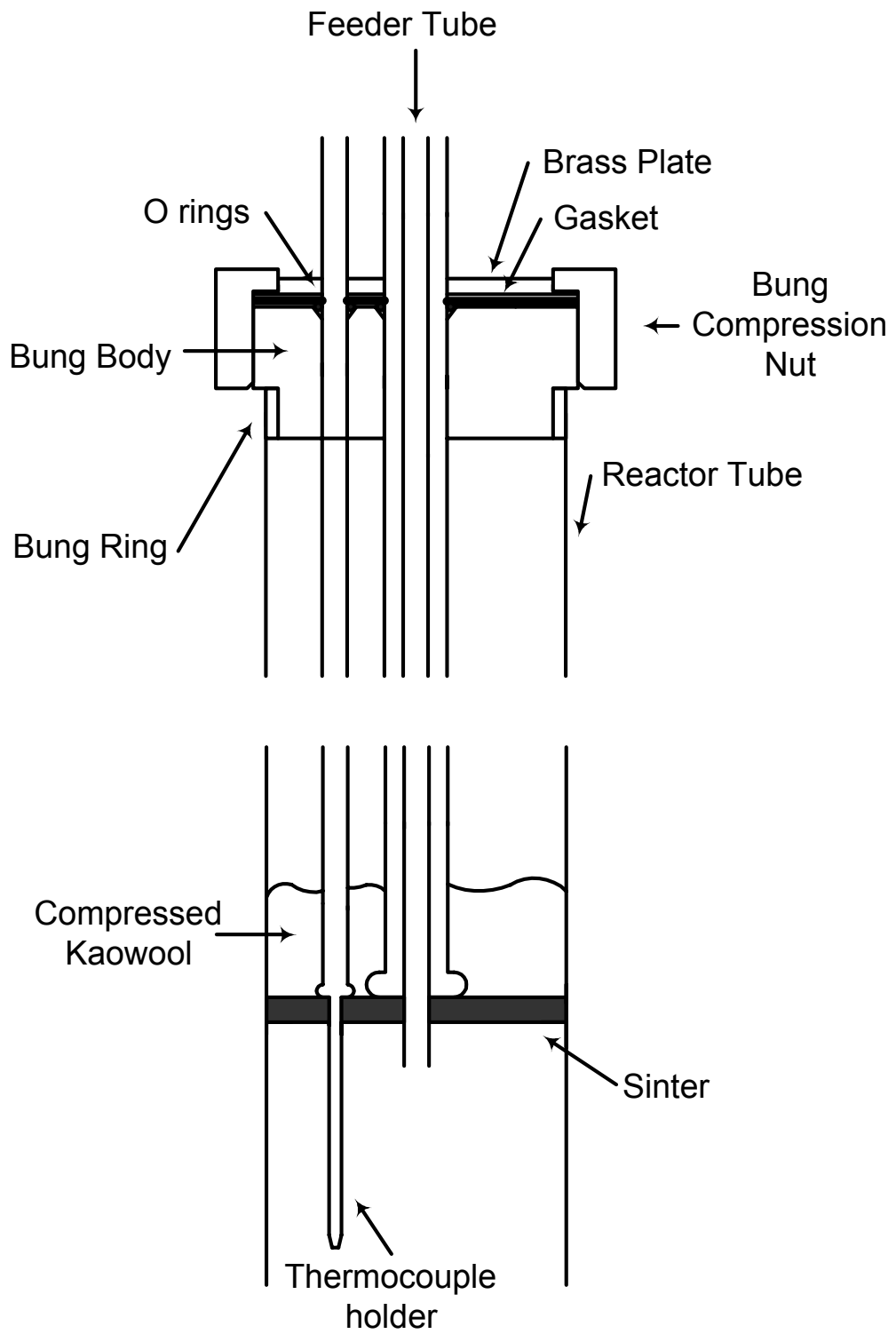
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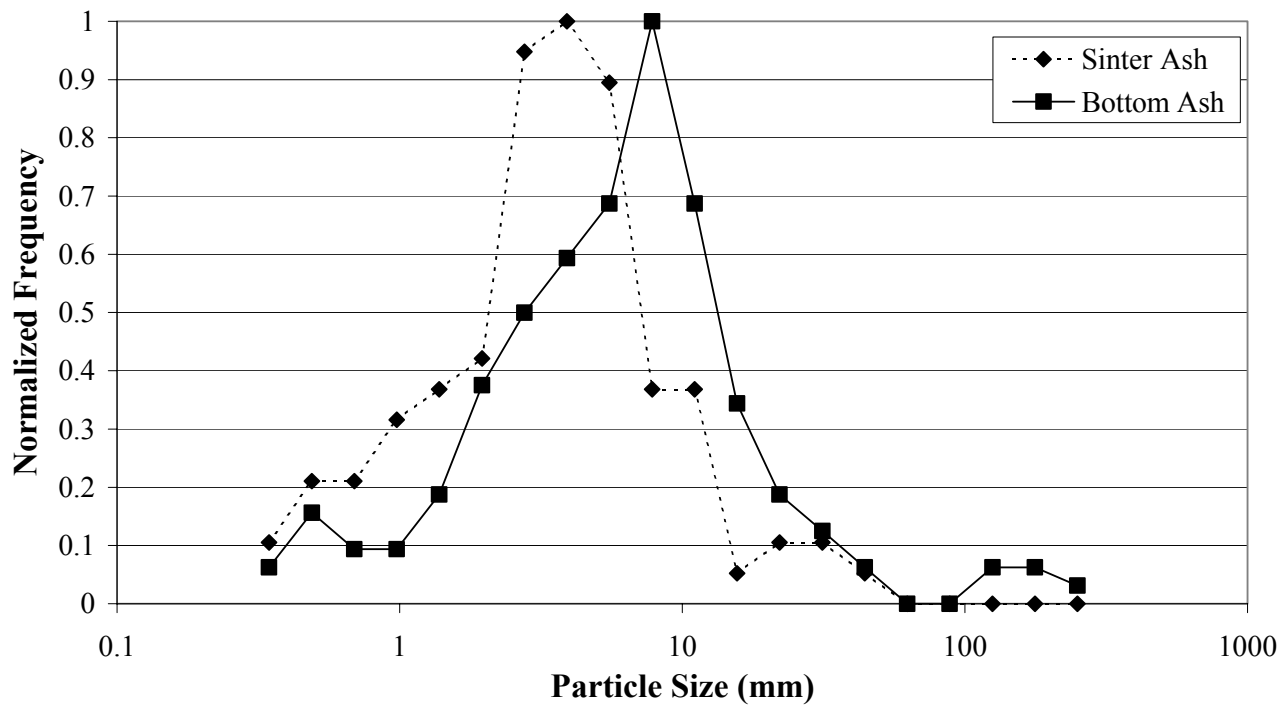
**Figure 1 The suspension-firing reactor**



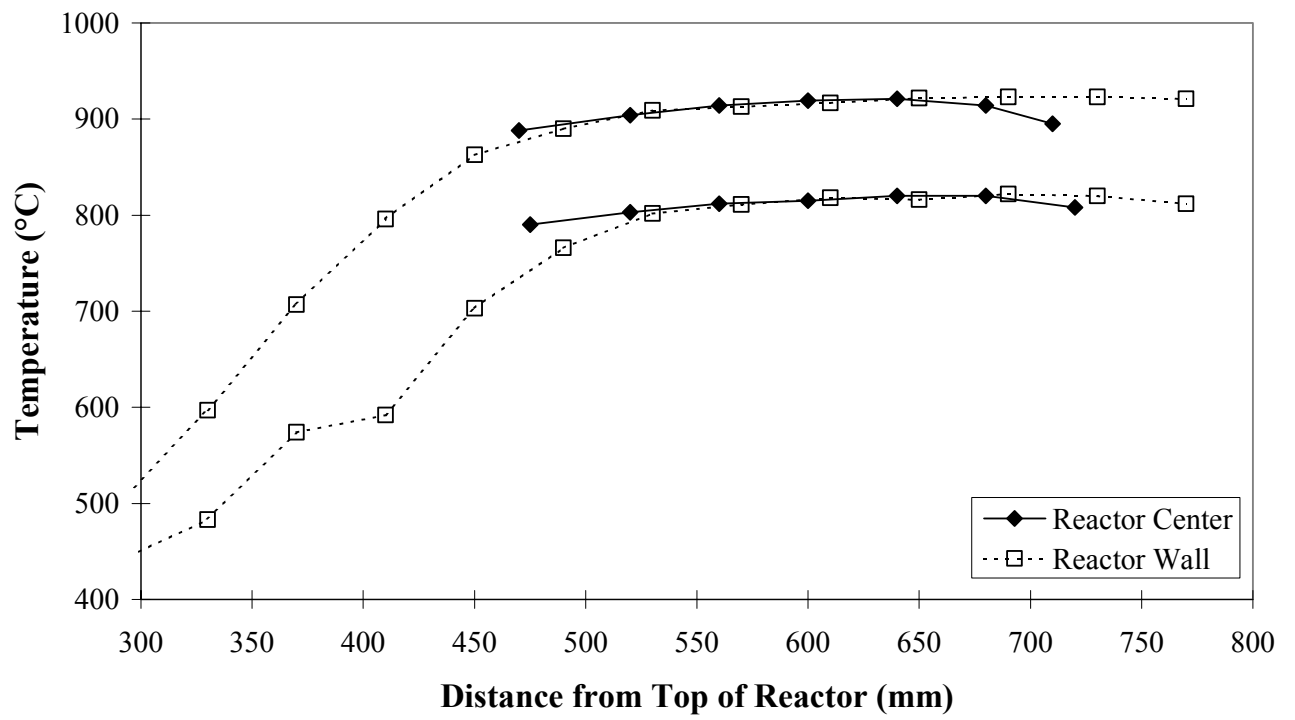
**Figure 2 Calibration of Fuel Feeding System**



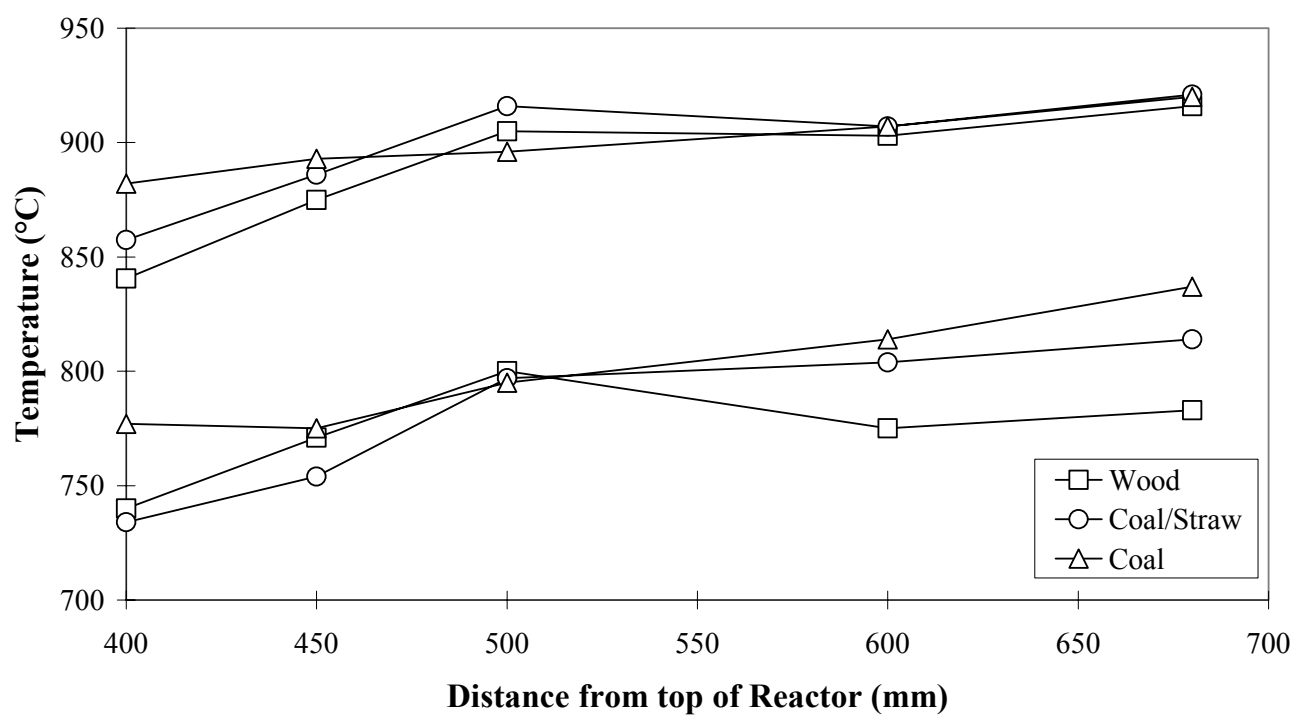
**Figure 3 Sintered Quartz Plate and Top Closure Details**



**Figure 4 Particle Size Distributions of Sinter and Bottom Ash**



**Figure 5 Axial Temperature Distribution at Reactor Centre and Walls, Without Fuel, 800 and 900°C**



**Figure 6 Axial Temperature Distribution inside the Reactor**



**Table 1 Major and Minor Constituents of the Fuel Samples**

	Wood- Bark	Straw	Colombian Coal	Polish Coal
<i>Major Elements</i>				
		% dry ash free		
C	53.1	49.3	80.6	85.0
H	6.0	6.1	5.3	4.8
N	0.5	0.7	1.6	1.2
O ( <i>by diff</i> )	40.3	43.4	11.5	7.9
S	0.07	0.15	0.90	0.84
Cl	0.01	0.26	0.04	0.11
		% as received		
Ash	6.9	2.8	6.2	16.2
Moisture	3.0	8.7	7.9	2.9
<i>Minor Elements</i>		g/kg as received		
Na	1.4	0.1	0.2	0.7
K	2.3	8.9	0.9	2.9
Mg	0.8	0.4	0.5	3.1
Ca	8.0	1.8	0.7	4.9
Al	3.0	0.2	5.7	16.1
Fe	1.5	0.2	2.8	7.5
P	0.04	0.07	0.01	0.02

**Table 2 Raw Fuel Trace Element Contents**

	Wood-Bark	Straw	Colombian Coal	Polish Coal
<i>Trace Elements</i>				
		ppm as received		
As <sup>b</sup>	0.44	<0.10	1.72	1.83
Be	0.07	<0.10	0.40	1.30
Cd	0.20	<0.15	0.30	0.21
Cr	26.0	2.49	11.1	24.3
Cu	87.3	3.16	5.78	24.8
Hg <sup>a</sup>	0.034	0.009	0.031	0.058
Mn	414	20.4	27.2	176
Mo	1.26	0.42	1.51	0.98
Ni	10.0	0.90	6.51	17.3
Pb	3.06	2.64	1.94	33.8
Se <sup>b</sup>	<0.80	<0.20	4.32	2.43
Tl	0.086	0.002	0.11	0.33
V	2.81	0.82	11.8	24.3
Zn	150	30.9	17.6	43.6

a AAS with LECO Hg analyser

b ICPMS of microwave digestion

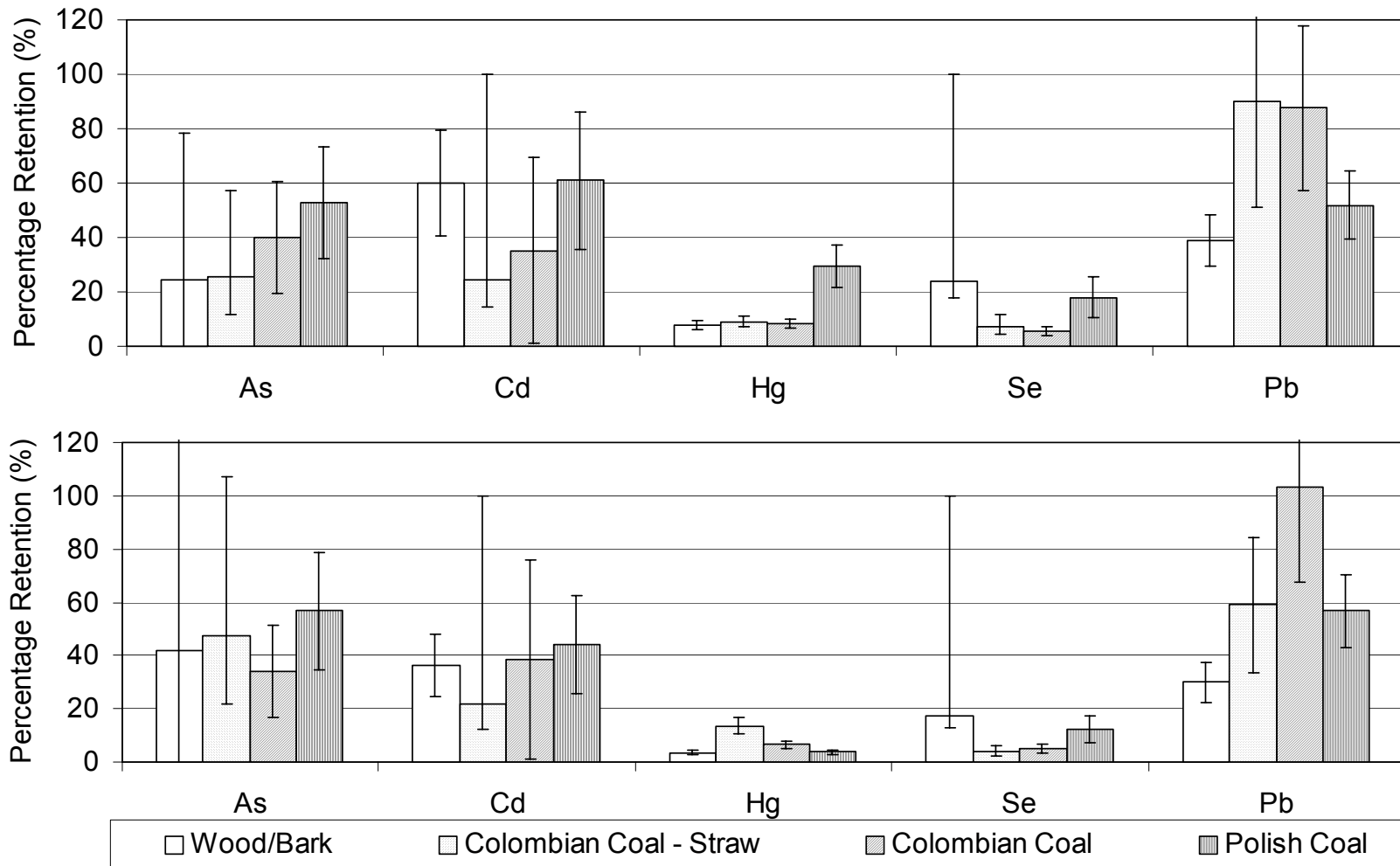


Figure 7 Percentage Retention of As, Cd, Hg, Se and Pb

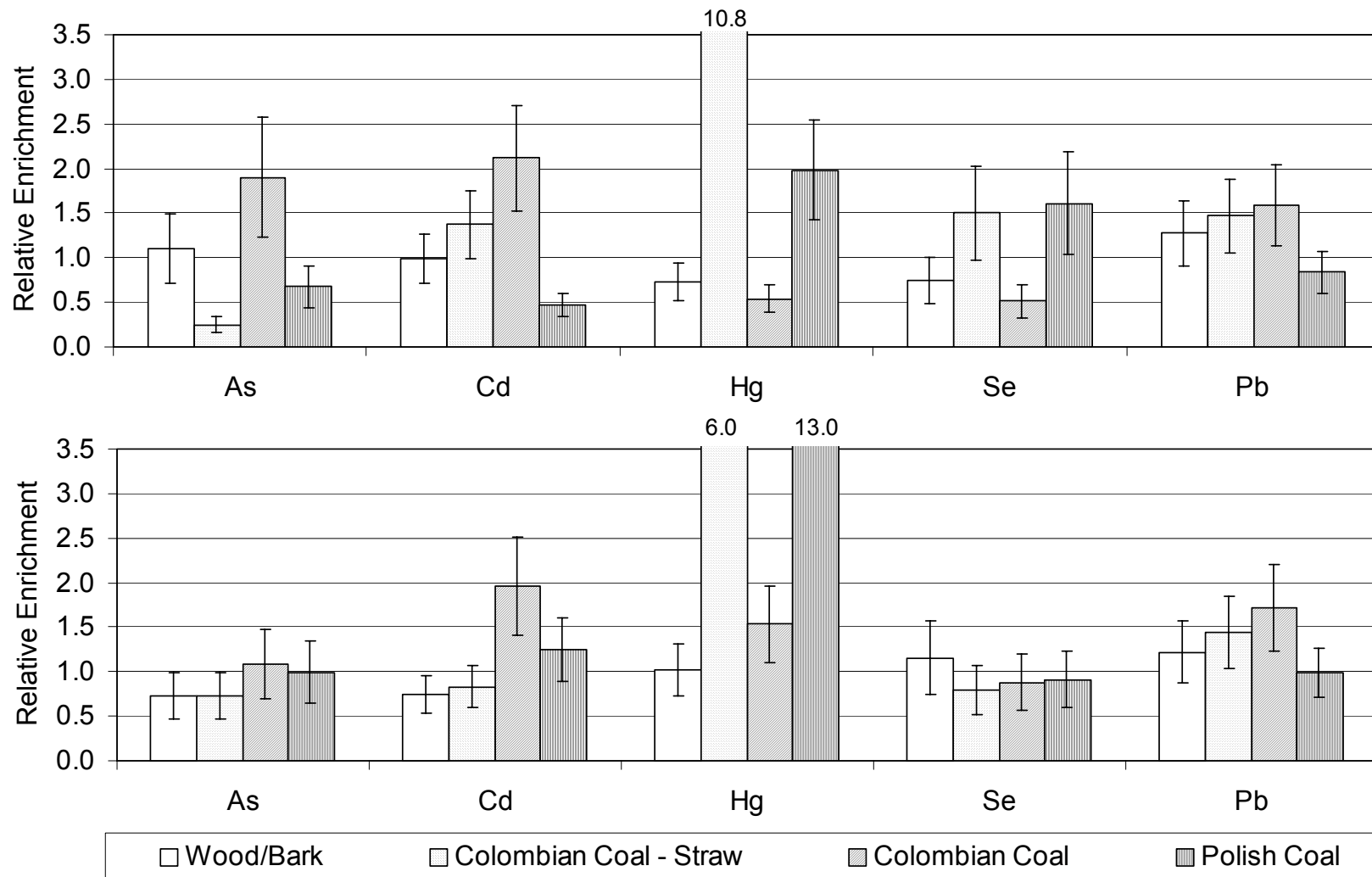


Figure 8 Enrichment of As, Cd, Hg, Se and Pb on Sinter Ash

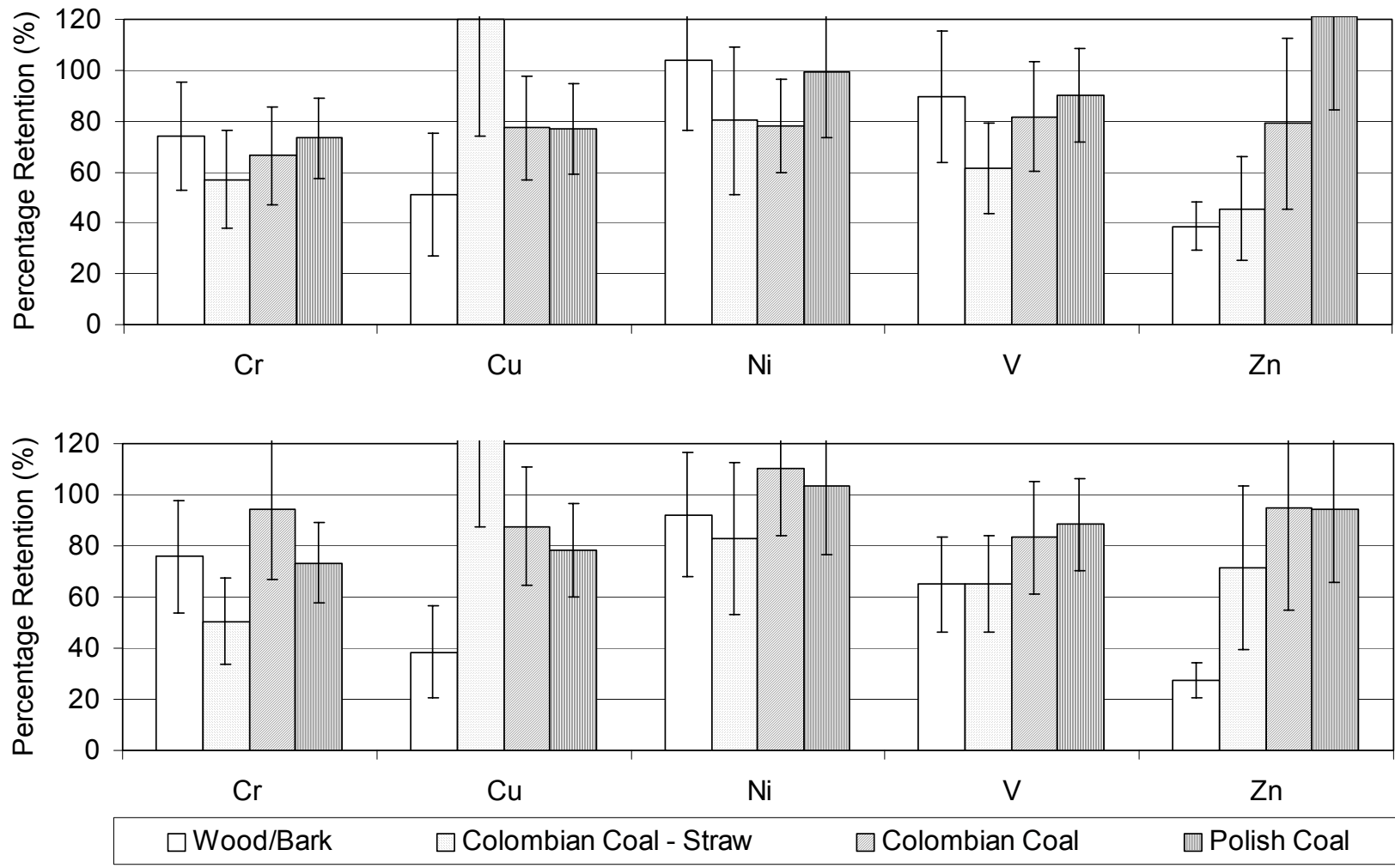


Figure 9 Percentage Retention of Cu, Cr, Ni, V and Zn

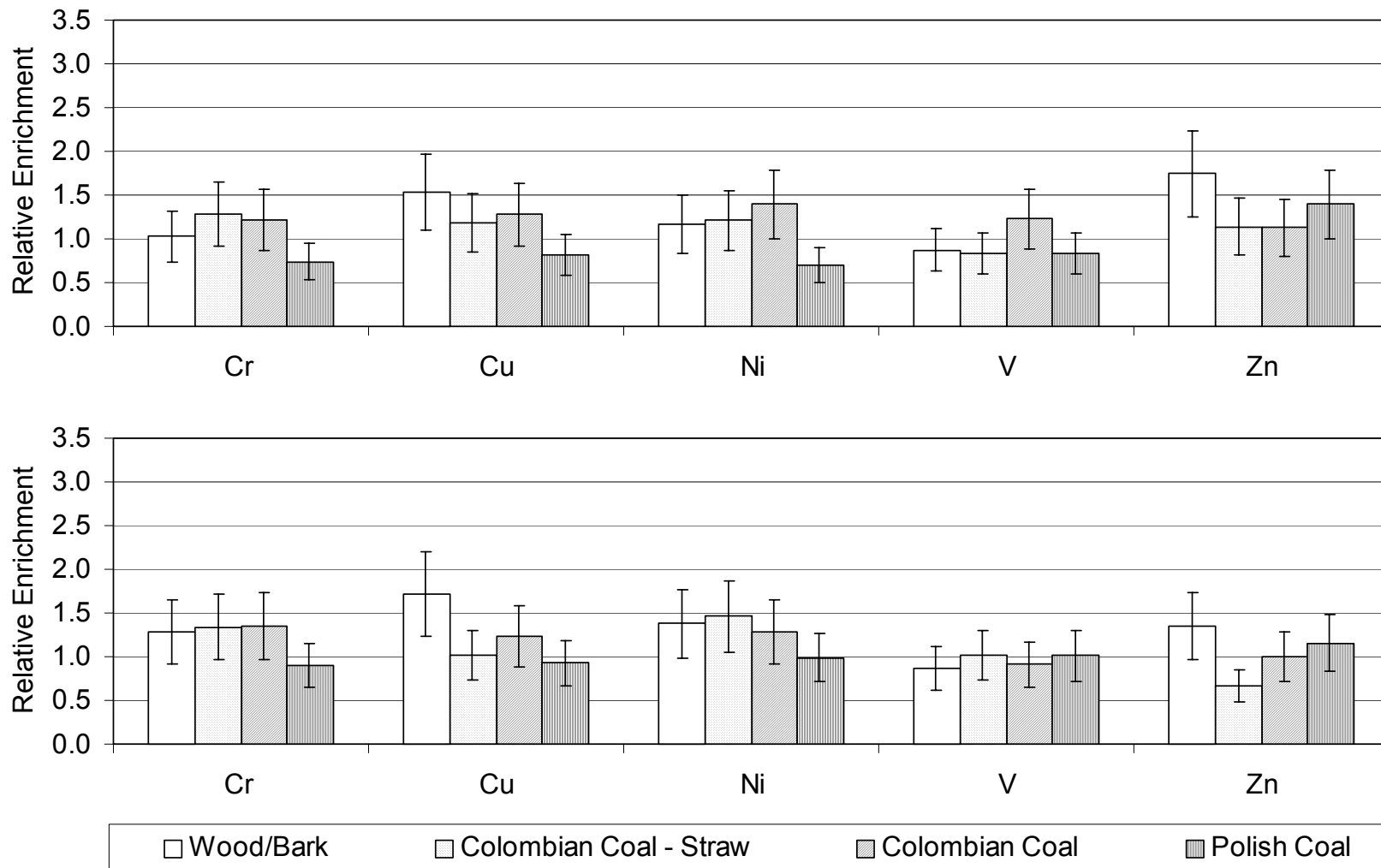


Figure 10 Enrichment of Cu, Cr, Ni, V and Zn on Sinter Ash

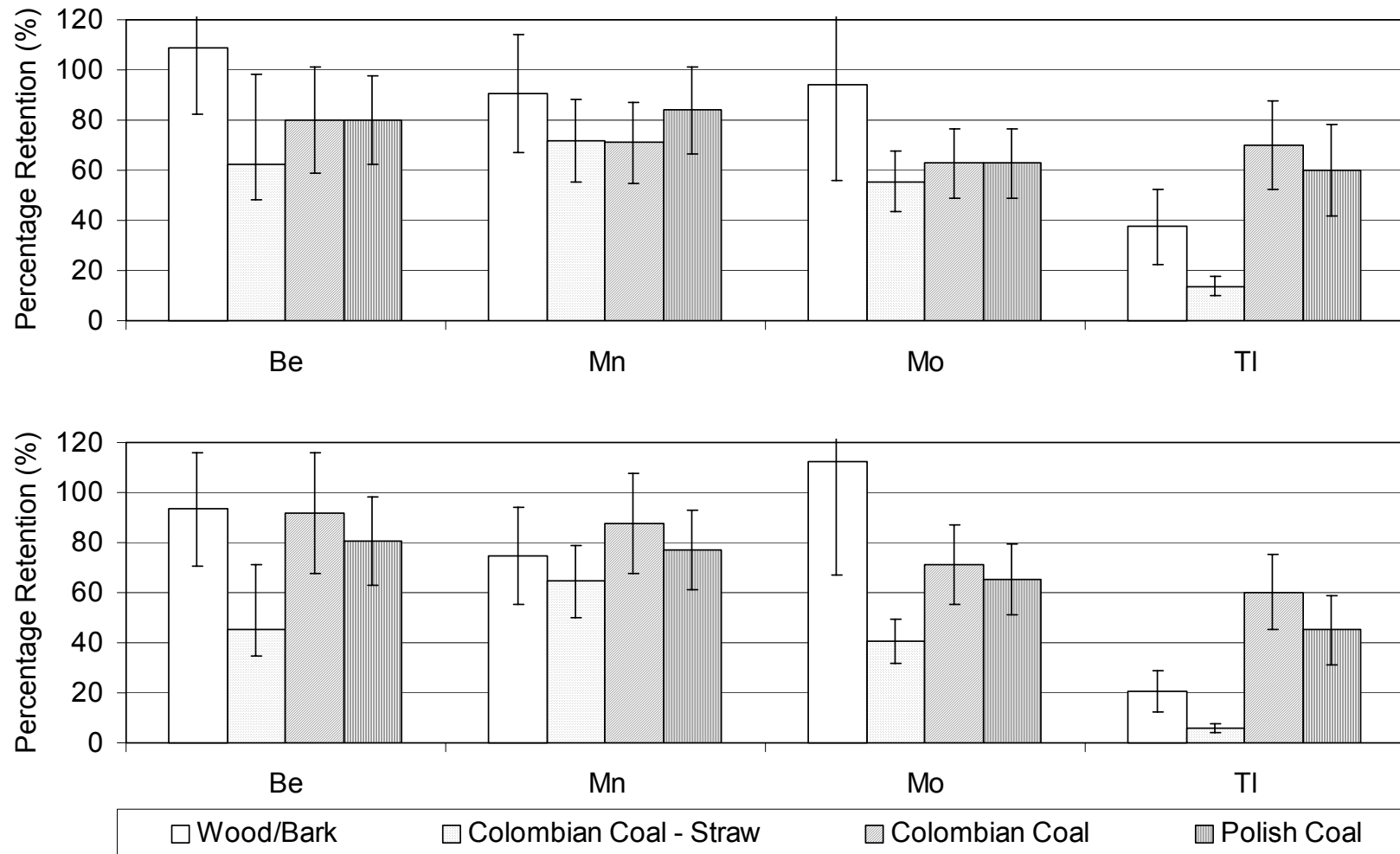


Figure 11 Percentage Retention of Be, Mn, Mo and Tl

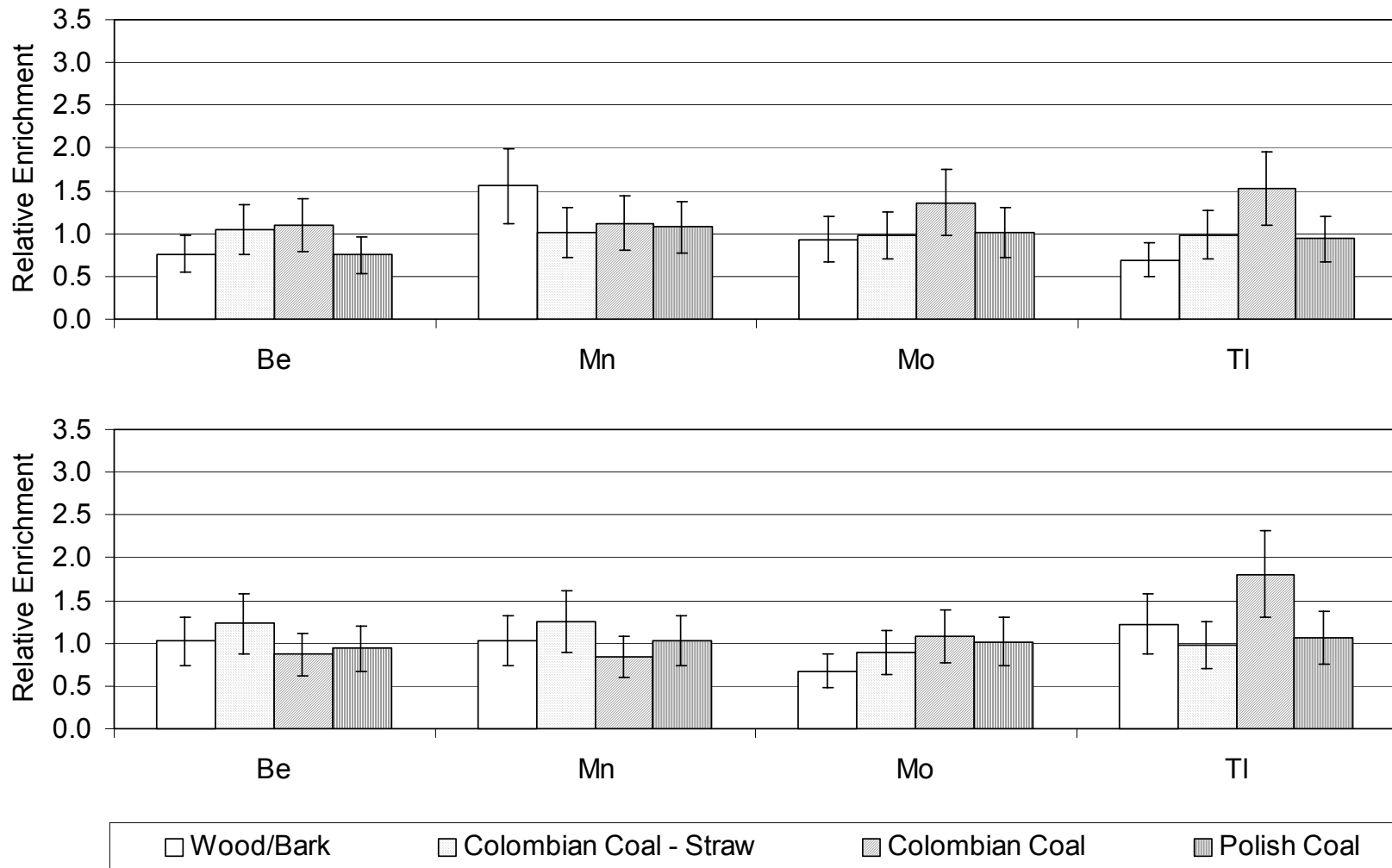
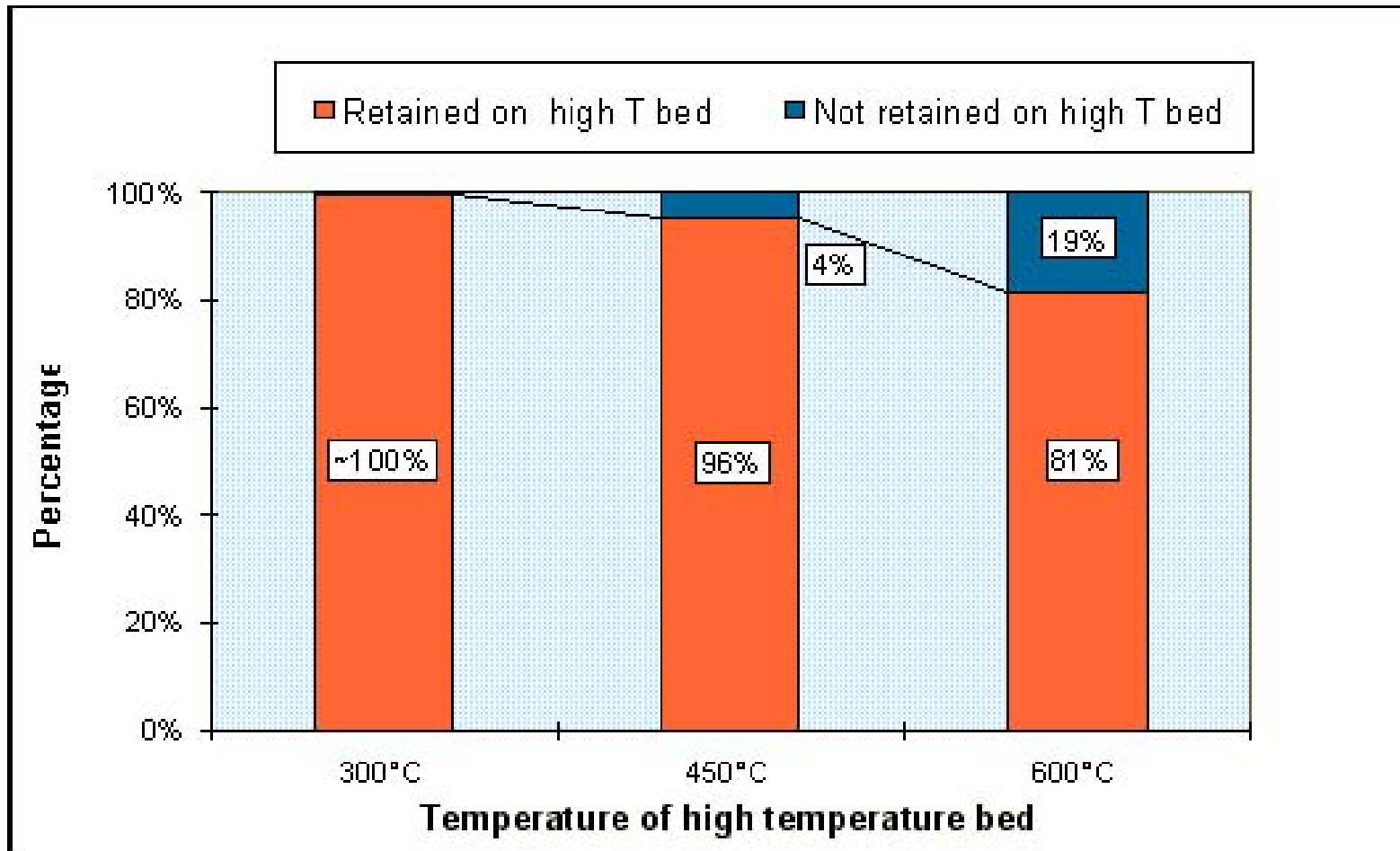


Figure 12 Enrichment of Be, Mn, Mo and Tl on Sinter Ash

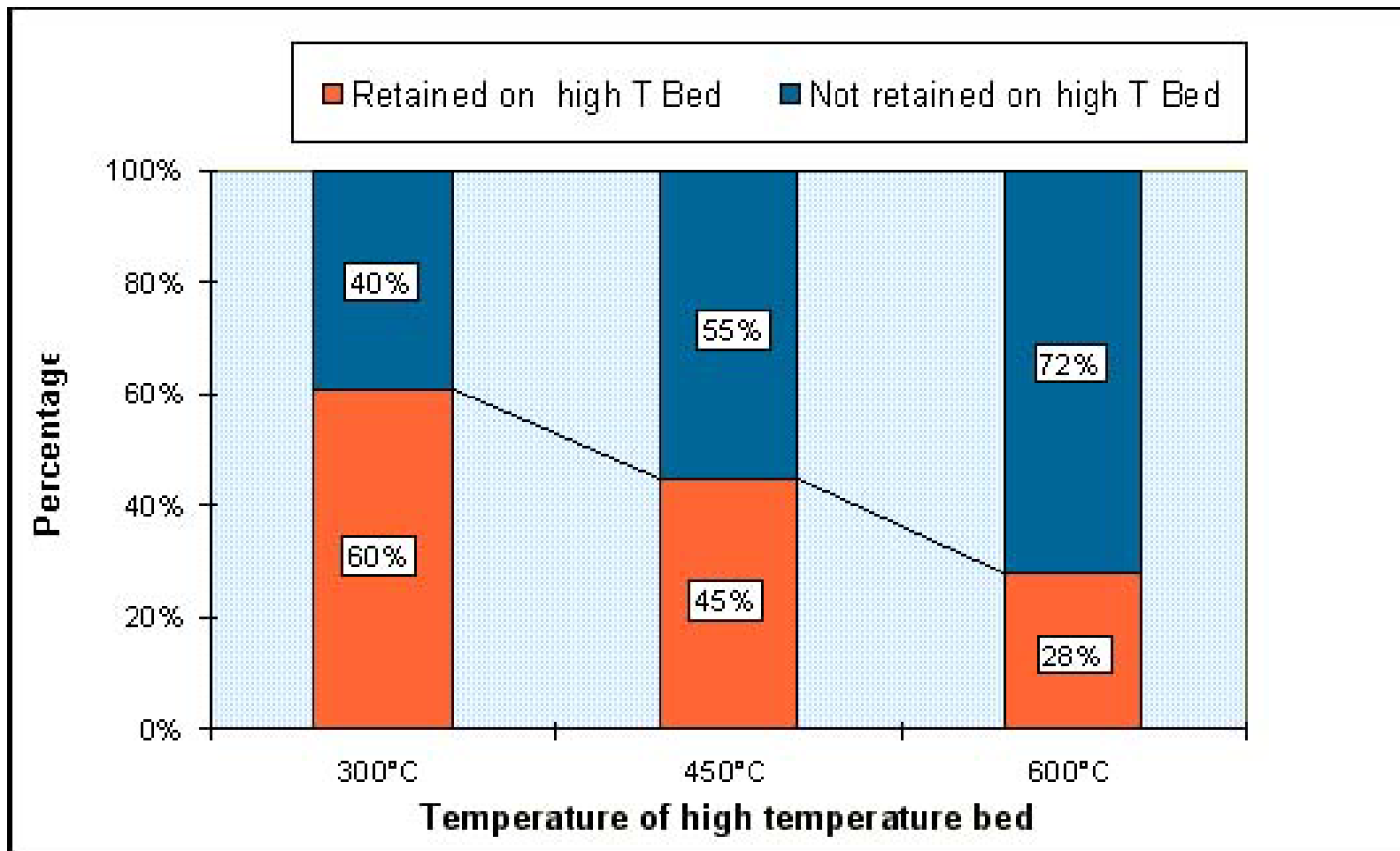


List of compounds selected for each of the elements likely to be formed by heating each compound in the HGCU reactor

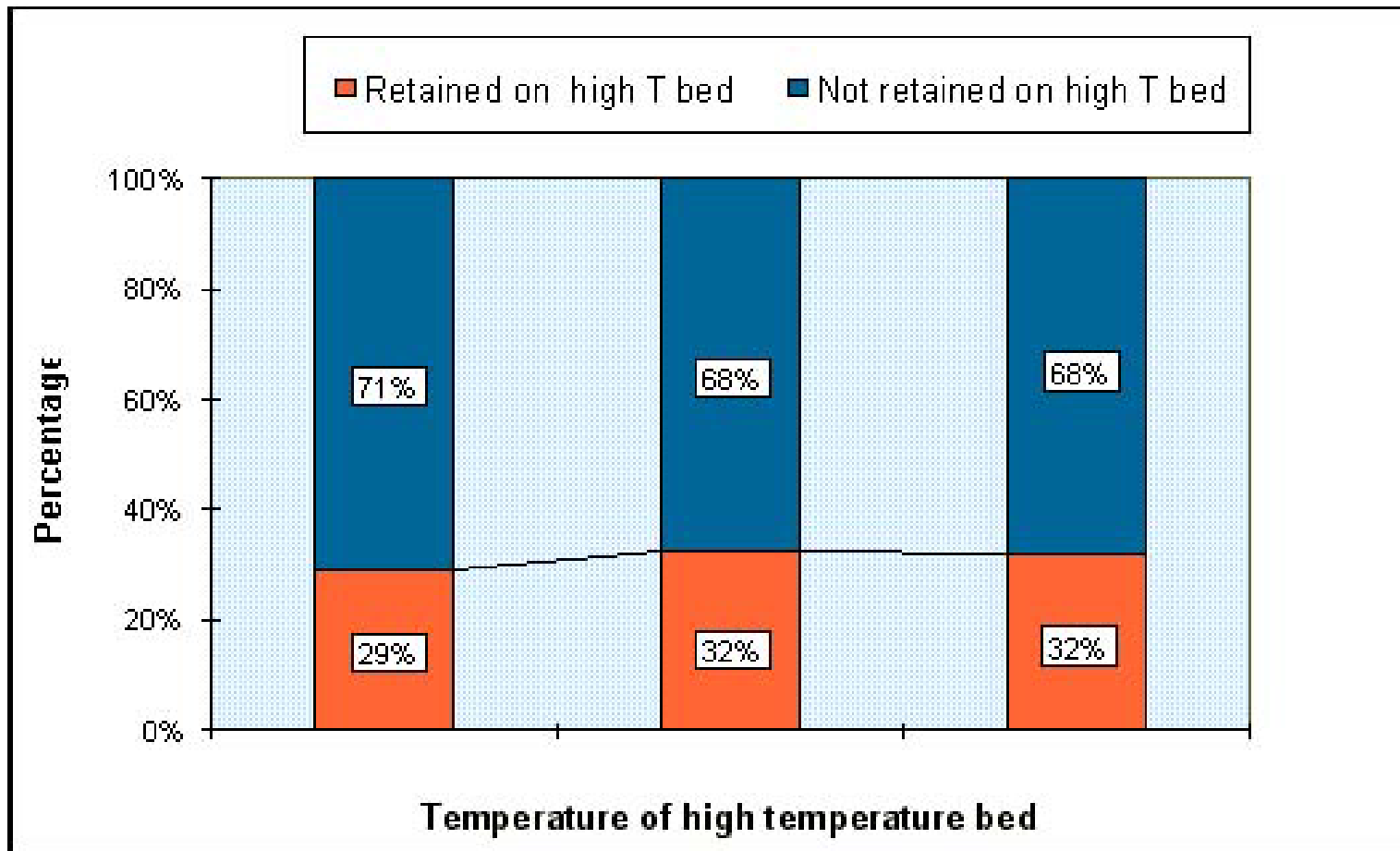
Element	Compound selected	Vapours likely to be formed in the HGCU reactor
Arsenic (As)	As <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>3</sub> (and possibly AsO)
Cadmium (Cd)	CdCl <sub>2</sub>	CdCl <sub>2</sub>
Gallium (Ga)	Ga(NO <sub>3</sub> ) <sub>3</sub> .3H <sub>2</sub> O	Gallium oxides (possibly Ga <sub>2</sub> O)
Mercury (Hg)	HgO	Hg
Lead (Pb)	PbCl <sub>2</sub>	PbCl <sub>2</sub>
Antimony (Sb)	SbCl <sub>3</sub>	SbCl <sub>3</sub>
Selenium (Se)	SeO <sub>2</sub>	SeO <sub>2</sub>
Vanadium (V)	VOF <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> .2H <sub>2</sub> O	V <sub>2</sub> O <sub>5</sub>



Kaolin efficiency to retain arsenic at various temperatures

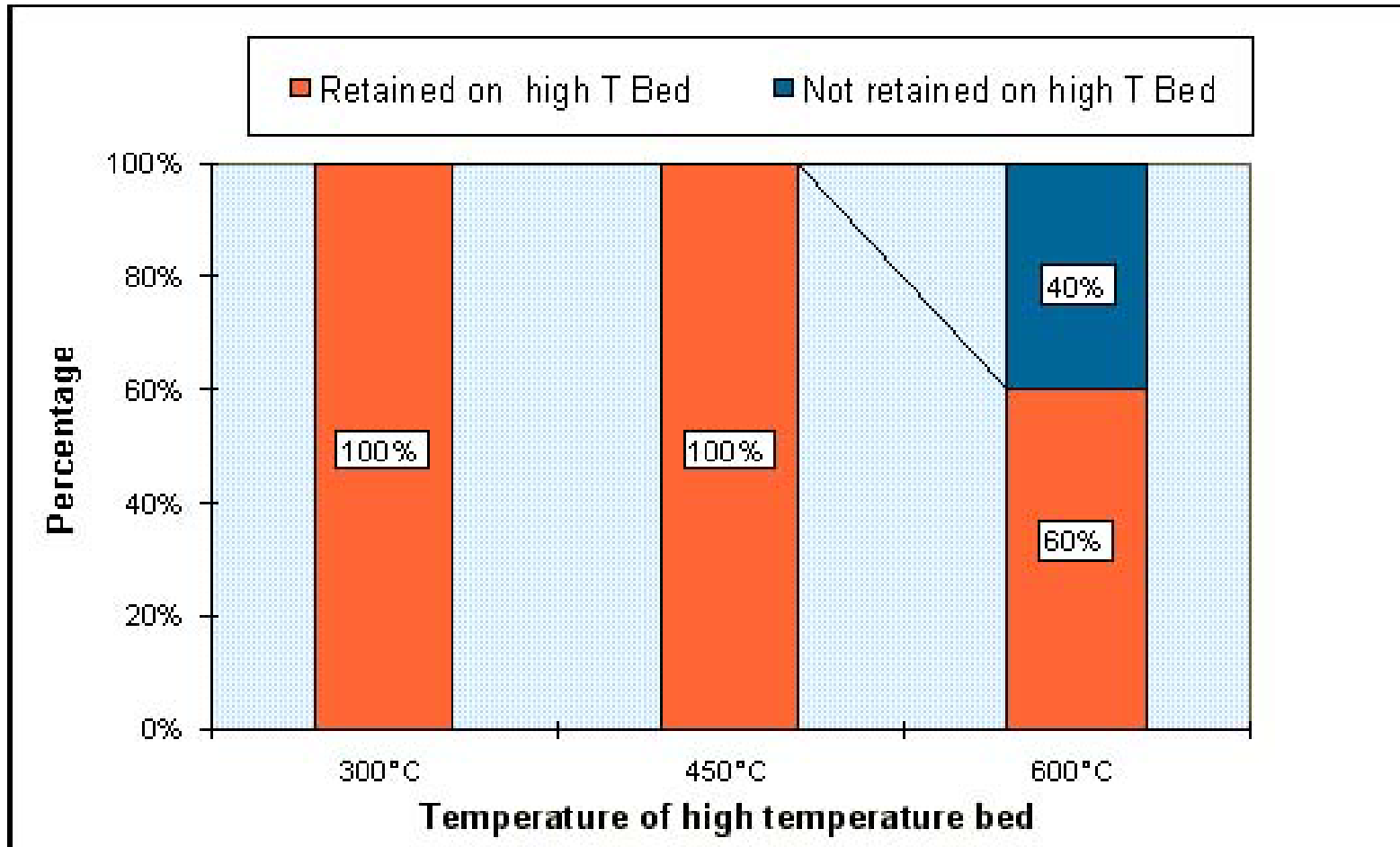


Activated carbon efficiency to retain mercury at various temperatures



Kaolin efficiency to retain mercury at various temperatures

# Arsenic Retention on Carbon



# Arsenic Leachability from Carbon

