



Partitioning behaviour of trace elements in a stoker-fired combustion unit: An example using bituminous coals from the Greymouth coalfield (Cretaceous), New Zealand

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Abstract

In order to understand trace element behaviour during combustion of coals from the Greymouth coalfield, combustion tests were performed on three seam composite samples. The major and trace elements from sub-samples of feed coal, bottom ash, fly ash, and flue gas were analysed by different techniques including inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), wavelength dispersive X-ray fluorescence (WD-XRF), and scanning electron microscopy with energy-dispersive X-ray analyser (SEM-EDXA). To help better understand trace element partitioning in combustion ash, float–sink and sequential leaching experiments were also employed to determine the association of trace elements with mineral matter or organic matter. Instrumental Neutron Activation Analysis (INAA) was also employed to determine trace element content in float and sink fractions of fly ash as well as in three major phases in the bottom ash.

The partitioning behaviour of trace elements, including some that are environmentally sensitive, was also investigated through the use of float–sink tests and direct determination of trace elements in different combustion ash types and phases. Mass balance and partitioning of major and trace elements have been studied to determine the fate of trace elements after combustion. The partitioning of trace elements, especially hazardous air pollutants (HAPs), in different combustion ashes can be summarised as follows:

1. Most trace elements, especially As, Ba, Co, Cr, Mn, Ni, are partitioned in the glassy and refractory bottom ash fractions.
2. A significant proportion of trace elements of As, Se, and Pb are partitioned into fly ash fractions.
3. Some volatile elements (e.g. > 90% of S and Hg and up to 64% of Cl) and, to a lesser extent, B (up to 44%) and Cd (up to 50%) are partitioned in the flue gas fraction.

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4. Although the low ash yield of Greymouth coal seams have the advantage of generating less solid combustion ash, one of the accompanying consequences is that resultant trace elements tend to be enriched in the ash to a greater magnitude than other more clastic sediment influenced coals.

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1. Introduction

With increasing awareness of the environmental impact of coal combustion [US Environmental Protection Agency (US EPA), 1998a,b, 2000] and stringent regulations of hazardous air pollutants (HAPs) in developed countries, the behaviour of trace elements during mining and subsequent utilisation has attracted a great deal of interest. The US Clean Air Act Amendments of 1990 (U.S. Statutes at Large, 1990) specifically identified As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Sb, Se, and U as potential HAPs. Some coals with a high abundance of potentially toxic trace elements, especially HAPs, may become less useable or unusable as stringent compliance on fly ash disposal and flue gas discharge from utilities comes into effect.

Various workers have studied trace element occurrence in coal (Finkelman, 1981, 1995; Swaine, 1990), trace element partitioning in combustion ashes (Querol et al., 1995; Vassilev and Vassileva, 1997; Hower et al., 2000a; Clemens et al., 2000; Vassilev et al., 2001; Karayigit et al., 2001; among others), and the mobility of those trace elements in coal and combustion ashes (Hower et al., 1993; Fernandez-Turiel et al., 1994; Fleming et al., 1996; Querol et al., 1996, 2001; Karuppiah and Gupta, 1997; Gentzis and Goodarzi, 1999). However, the behaviour of trace elements can vary significantly between different coal beds either simply because they have different modes of occurrence or because they are used under different combustion conditions. There are few geochemical rules that apply universally to all coals because of the complexity of trace element occurrence and behaviour upon combustion.

There are numerous studies of trace element partitioning in combustion ashes, but most have been conducted under pulverised combustion regimes characterised by high temperature (1300–1500 °C), fine feed particle size and longer residence time in the boiler, and a ratio of fly ash to bottom ash being roughly

80:20 (Smith et al., 1980; Meij, 1994; Querol et al., 1995; Bool and Helble, 1995; Robl et al., 1995; Hower et al., 1997, 1999a,b,c, in press; Martinez-Tarazona and Spears, 1996; Vassilev and Vassileva, 1997; Senior et al., 2000a,b,c; Yan et al., 1999; Sakulpitakphon et al., 2000, 2004; Ward, 2002; Sloss, 2002; Narukawa et al., 2003; Ren et al., 2004; Pires and Querol, 2004; Mardon and Hower, 2004; Mastalerz et al., 2004; Vassilev et al., 2005a,b; among others). Only a few studies (e.g. Clemens et al., 2000) have been conducted on stoker-fired combustion regimes characterised by lower temperature (1000 to 1200 °C), larger feed particle size, and longer boiler residence time, and a ratio of fly ash to bottom ash being roughly 20:80. Because of the different combustion conditions between the pulverised and stoker-fired combustion regimes, trace element partitioning may not be the same as what has been established in the literature. Many industrial boilers in New Zealand are of the stoker-fired type. Therefore, this study is designed specifically to investigate the behaviour of selected trace elements during stoker-fire combustion regimes. The coal selected is from the Greymouth coalfield and is Cretaceous in age. The study also aims to identify the mineralogical transformations occurring within the combustion chamber in order to gain a better understanding of the factors influencing the partitioning behaviour of trace elements. Understanding of trace element partitioning behaviour allows an assessment of their environmental impact to be made as well as identify any undesirable impacts which then allows potential problems to be avoided or mitigated.

2. Samples and methods

2.1. Location and sampling methods

Three seam composite samples were taken as channel samples in accordance with American

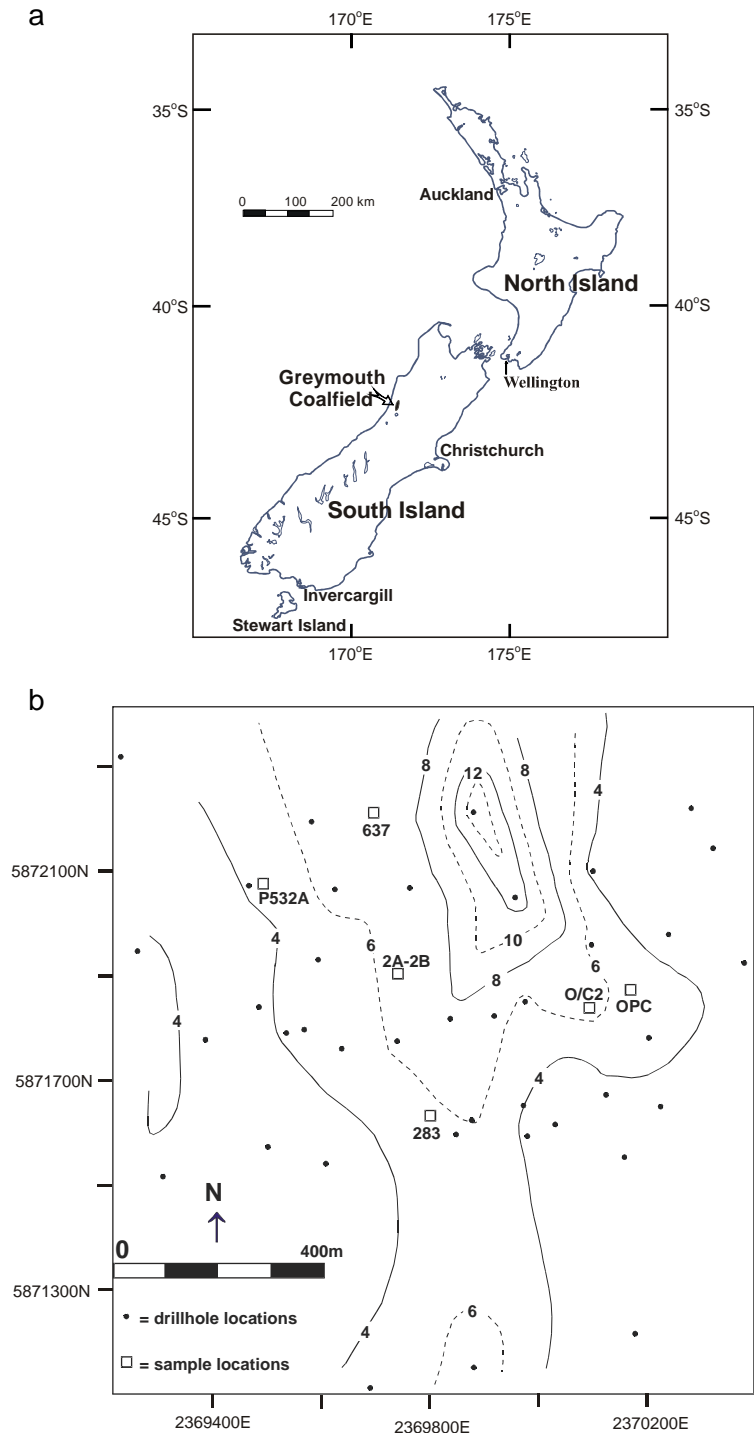


Fig. 1. (a) Index map of New Zealand showing the geographic location of the Greymouth coalfield. (b) Sampled locations and thickness isopachs (in metres) of the E seam, Strongman #2 Mine, based on data from this study and unpublished drilling log data and many hundreds of underground measurements made by Solid Energy Ltd. (J. McNee, personal communication, 2000).

Society for Testing and Materials (ASTM) standard D4596-86 (ASTM, 1995) from two different underground locations (P532A, 2A–2B) in the same seam (“E” seam) from Strongman No. 2 Mine, Greymouth coalfield, New Zealand. The sampling location is given in Fig. 1. The E seam coal occurs in the Rewanui Member of the Paparoa Coal Measures (Fig. 2). Sample P532A was taken from the northwest margin of Strongman No. 2 Mine site and represents the whole seam, whereas 2A and 2B were taken from another underground site close to the centre of the mine. Samples 2A and 2B represent the upper and lower portion of the E seam, respectively. The samples were sent to CRL Energy Limited in Lower Hutt, New Zealand, for combustion testing. The coal was crushed to a particle size of 12 to 30 mm before combustion tests.

2.2. Analysis techniques

The major and trace elements from sub-samples of feed coal, bottom ash, fly ash, and flue gas were analysed by ICP-MS, ICP-AES, WD-XRF, and

SEM-EDX techniques. A float–sink procedure with a specific gravity of 1.6 g/cm³ was also employed to determine the partitioning behaviour of trace elements in the fly ash; INAA was also employed to determine trace element content in float and sink fractions of fly ash as well as three major phases in the bottom ash. The lower detection limits of elements by various analytical methods in this study are given in Table 1.

In order to understand trace element behaviour during combustion, the modes of occurrence of trace elements in the feed coals were investigated by multiple approaches, such as float–sink experiments at specific gravity of 1.3 g/cm³, sequential leaching tests, and SEM-EDX analysis.

The liquids used in the float–sink separation were perchlorethylene with a specific gravity (Sp.G.) of 1.71 g/cm³ and petroleum spirit (Sp.G.=0.72 g/cm³) mixtures. The desirable Sp.G. of the separation medium can be achieved by simply mixing different proportions of the above two heavy liquids. The particle size of feed coal is < 1 mm. After each separation, sink and float fractions were filtered and dried in an oven overnight at a temperature of 40 °C. Whilst a Sp.G. of 1.3 g/cm³ was used in whole coal float–sink separation, a Sp.G. of 1.67 g/cm³ was used to separate fly ash samples because of the higher mineral concentrates.

The sequential leaching procedures used in this study are similar to those described by Palmer et al. (1993). Duplicate 5 g coal samples, with particle size of < 250µm, were weighed into 50 ml polypropylene tubes. Each split was sequentially leached with 35 ml each of 1 N ammonium acetate (CH₃COONH₄), 2 N hydrochloric acid (HCl), concentrated hydrofluoric acid (48 wt.% HF), and 2 N nitric acid (HNO₃). The leaching sequence described above was adopted so that theoretically (1) the first step, CH₃COONH₄, would remove all the exchangeable cations, (2) HCl would remove cations associated with carbonates and monosulphides, (3) HF would remove cations associated with silicates, and finally (4) cations associated with disulphides (pyrite) would be removed by HNO₃. Unleached components may be associated with organic matrix, “shielded” mineral grains encapsulated by the coal matrix, or highly acid resistant phases such as zircon, barite, etc.

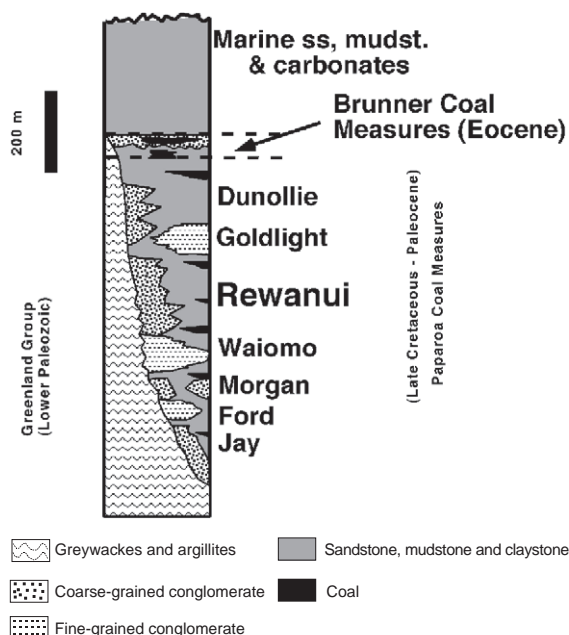


Fig. 2. Generalised stratigraphic sequences in the Greymouth coalfield. The E seam occurs within the Rewanui Coal Measures.

Table 1
Comparisons of lower limits of detection (LLD) for various analytical methods used in this study

Element	ICP-MS ^a (ppb)	ICP-AES ^a (ppm)	INAA ^b (ppm)	XRF ^c (ppm)
Ag	2	0.002	n.d.	n.d.
As	0.1	0.1	0.5	5
B	n.d.	0.1	n.d.	n.d.
Ba	n.d.	0.002	10	10
Be	0.1	0.002	n.d.	n.d.
Bi	n.d.	0.02	n.d.	n.d.
Br	n.d.	n.d.	0.5	n.d.
Cd	0.1	0.002	n.d.	n.d.
Cl	n.d.	n.d.	n.d.	20
Cr	0.5	0.01	0.8	3
Co	0.1	0.01	1	n.d.
Cs	0.1	n.d.	0.05	n.d.
Cu	1	0.01	n.d.	n.d.
F	n.d.	n.d.	n.d.	20
Ga	n.d.	n.d.	n.d.	1
Hf	n.d.	n.d.	0.1	n.d.
Hg	n.d.	n.d.	n.d.	n.d.
Li	n.d.	0.01	n.d.	n.d.
Mn	0.5	0.005	10	n.d.
Mo	0.2	0.05	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	2
Ni	0.2	0.02	10	3
Pb	0.5	0.02	n.d.	1
P	n.d.	0.05	n.d.	n.d.
Rb	0.1	n.d.	4	1
S	n.d.	n.d.	n.d.	100
Sr	0.5	0.002	20	1
Sb	0.5	0.05	0.01	n.d.
Sc	0.1	n.d.	0.1	n.d.
Se	0.1	n.d.	0.1	2
Sn	1	0.01	n.d.	n.d.
Ta	n.d.	n.d.	0.01	n.d.
Tl	0.2	n.d.	n.d.	n.d.
Th	n.d.	0.005	0.1	1
Ti	n.d.	0.005	n.d.	n.d.
W	n.d.	0.01	1	n.d.
U	0.1	n.d.	0.05	n.d.
V	0.1	0.01	n.d.	3
Y	n.d.	0.002	n.d.	1
Zn	2	0.002	2	3
Zr	n.d.	0.05	10	2
<i>Rare earth elements</i>				
La	n.d.	0.002	0.3	4
Ce	n.d.	0.01	0.5	4
Nd	n.d.	n.d.	0.9	n.d.
Sm	n.d.	n.d.	0.05	n.d.
Eu	n.d.	n.d.	0.01	n.d.
Gd	n.d.	n.d.	0.1	n.d.
Tb	n.d.	n.d.	0.02	n.d.
Tm	n.d.	n.d.	0.01	n.d.

Table 1 (continued)

Element	ICP-MS ^a (ppb)	ICP-AES ^a (ppm)	INAA ^b (ppm)	XRF ^c (ppm)
Yb	n.d.	n.d.	0.01	n.d.
Lu	n.d.	n.d.	0.01	n.d.
<i>Major elements</i>				
SiO ₂	n.d.	ppm	%	%
Al ₂ O ₃	n.d.	0.6	n.d.	0.2
TiO ₂	n.d.	0.05	n.d.	0.01
Fe ₂ O ₃	n.d.	0.02	0.02	0.01
MgO	n.d.	0.05	n.d.	0.05
MnO	n.d.	0.005	n.d.	0.01
CaO	n.d.	0.05	n.d.	0.01
Na ₂ O	n.d.	0.2	0.01	0.1
K ₂ O	n.d.	0.05	0.04	0.01
P ₂ O ₅	n.d.	n.d.	n.d.	0.01
SO ₃	n.d.	n.d.	n.d.	0.01

n.d.=not determined

^a Lower limits of detection of ICP-MS (as ppb) and ICP-AES (as ppm) are for leachate solution only (S. Mroczkowski and C. Palmer, personal communication, 2001).

^b Lower limits of detection of INAA (as ppm) are for solid coal samples (N. Eby, personal communication, 2002).

^c Lower limits of detection of XRF (as ppm) for coal samples (S. Brown, personal communication, 2002).

2.3. Combustion experiment

Coal samples were combusted in an underfed stoker unit with approximately 50 kW capacity. The combustion rig was thoroughly cleaned before each combustion run. The rig consisted of a small (200 mm diameter) retort with a ceramic hearth inside a steel furnace chamber (Fig. 3). No overfire air was used. Stack velocities of between 3.7 and 3.8 m/s, corresponding to stack volumetric flows of 65 to 68 m³/h, were obtained and stack-sampling temperatures were between 205 and 209 °C. The flame temperature in the firebox was between 1100 °C and 1250 °C. The furnace exit gases passed over a convective tube bank, which controlled the stack sampling temperature. Particulate matter was removed by a high-efficiency cyclone. Inlet air flow and stack gas flow were measured using orifice plates, and thermocouples were used for temperature measurements.

In order to ensure reasonable combustion, firebox conditions (fuel feeding rate, airflow and temperatures) were maintained throughout each combustion run. The flue gas (FG) was monitored for oxygen, carbon dioxide, carbon monoxide, and methane

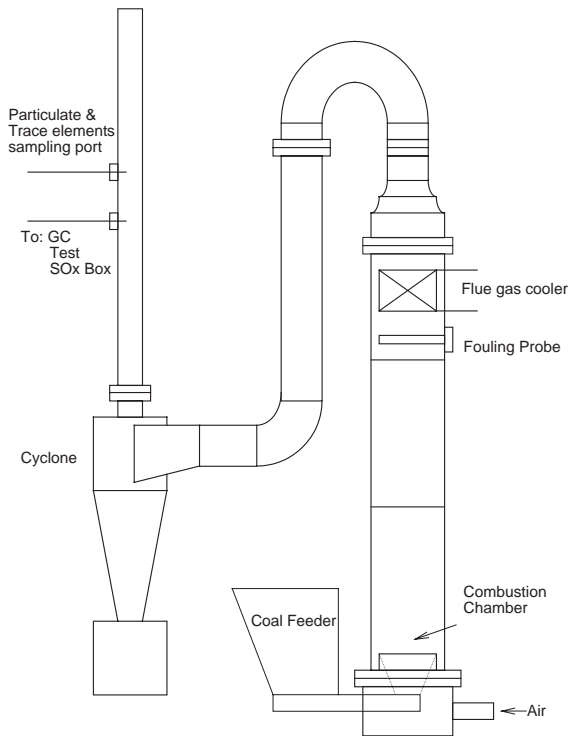


Fig. 3. The diagram of the laboratory coal combustion rig used in this study.

content by withdrawing gas and passing it through a drying tower and into an on-line gas chromatography gas analyser.

After each run, samples of bottom ash and fly ash (FA) were recovered and weighed. The bottom ash (BA) was further divided into small bottom ash (SBA) (deemed to be non-slagging ash and capable of passing through a 1.7 mm sieve opening) and large bottom ash (LBA; that is, bottom ash that is retained on a 1.7 mm sieve opening and deemed to be slag). The ashes were then analysed for major elements by XRF and for trace elements by ICP-MS as described elsewhere (Clemens et al., 2000; Li, 2002).

2.4. Approaches of investigation on trace element partitioning in different combustion ash types

Two common approaches have been used here to study trace element partitioning in different combustion ashes. One approach is to look at concentrations of trace elements in different ashes and different fractions within one type of ash (Querol et al., 1995;

Spears and Martinez-Tarrazon, in press). The other approach is to determine the weight percentages of these trace elements in different combustion ashes or fractions (Meij, 1994; Vassilev et al., 2001).

To determine the trace element partitioning pattern in bottom ash and fly ash, an enrichment factor (EF) has been determined for this study in order to quantify the relative enrichment magnitude of a specific trace element in the combustion ash (e.g. bottom ash and fly ash) fractions relative to feed coal:

$$EF = C_{\text{ash}}/C_{\text{coal}} \quad (1)$$

where C_{ash} represents the concentration of trace elements in combustion ash (either fly ash, small bottom ash, or large bottom ash) and C_{coal} represents the concentrations in the feed coal. Accordingly, trace elements with different enrichment factors (EF) may be categorised into groups.

To quantify trace element partitioning in the different ash fractions, the total input and output of each trace element has to be known. The total input of all the trace elements introduced from feed coal before combustion can be determined from the trace element content and the mass of feed coal. The total output of each trace element can also be calculated by summing the contribution from each ash product.

In order to analyse the partitioning behaviour of trace elements during and after combustion, all ash samples were collected and weighed. The proportion of each combustion ash can be calculated in comparison with the total combustion ash. From the trace element data of each combustion product, the mass balance and contribution of selected trace elements from each ash product (LBA, SBA, FA, and FG) can be calculated.

3. Results and discussions

3.1. Characterisation of the feed coal

Three combustion runs were performed on three underground coal samples taken from Strongman E seam. The coal quality data of these three combustion samples are shown in Table 2.

The major minerals found in the feed coal were clays (mainly kaolinite, illite, and minor smectite), quartz, and carbonates (mainly siderite, ankerite and

Table 2

Coal quality data (% , as received basis) of the feed coal (E seam) for combustion tests

Sample	Moist.	Ash	VM	FC	Total S	Sulfate S	Pyritic S	Organic S	H	C	N	O	MJ/kg
ASTM method	D3172	D3172	D3172	D3172	D4239	D2492	D2492	D2492	D5373	D5373	D5373	D3176	D1989
2B	7.17	3.1	39.26	50.47	0.19	0.02	0.01	0.16	5.8	73.49	1.36	16.06	30.35
2A	6.4	12.5	36.44	44.66	0.21	0.02	0.01	0.18	5.13	65.91	1.33	14.92	27.35
P532A	8.37	9.01	37.18	45.44	0.21	0.01	0.02	0.18	5.34	67.07	1.31	17.07	27.21

Moist.=moisture, VM=volatile matter, FC=fixed carbon, MJ/kg=heat value. ASTM=ASTM (1995).

calcite). The minor minerals include sulphides (pyrite, marcasite) and phosphates (apatite, crandallite, monazite); with trace amounts of sulphates (gypsum), oxides (anatase TiO_2 , hematite, magnetite), chlorides (NaCl, KCl), zircon, and other silicates (biotite). Crocoite (PbCrO_4) was also found in both the Main and E seams (Li et al., 2001b). Detailed

mineralogical investigation of these seams have been reported elsewhere by Li et al. (1999, 2001a) and Li (2002).

All three E seam samples used in the combustion testing were also subjected to the float–sink test (at Sp.G. of 1.3 g/cm^3) in order to determine whether trace elements in the coal are associated with organic

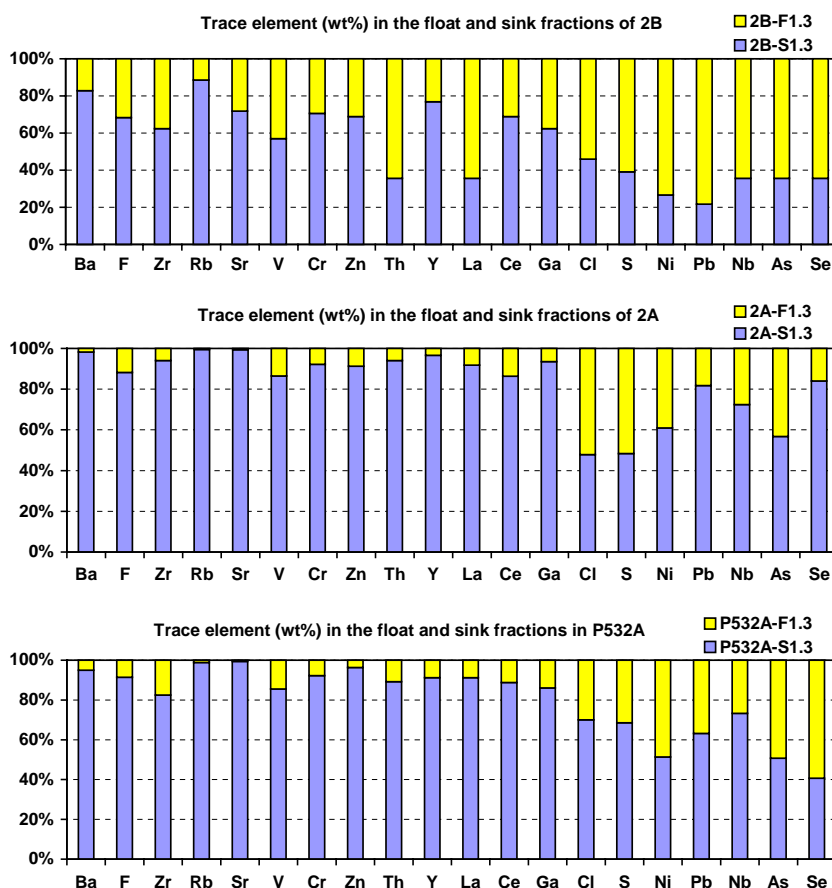


Fig. 4. The wt.% of trace elements in the float and sink fractions after performing a float–sink experiment. Key: 2A-F_{1.3}=float fraction of sample 2A after separation with specific gravity of 1.3 g/cm^3 ; 2A-S_{1.3}=sink fraction of sample 2A after separation with specific gravity of 1.3 g/cm^3 .

matter (e.g. enriched in float fraction) or with mineral matter (e.g. enriched in sink fraction). After float–sink separation, the weight percentages have been determined in both fractions and are given in Fig. 4. Rb, Sr, Ba, Y, Cr, Zn, Zr, Th, and, to a lesser extent, F and REE are associated with mineral matter, such as Cr in crocoite (PbCrO_4 ; see Li et al., 2001b), Zr in zircon, La and Ce in monazite; in contrast, Cl, S, Se, As, and Ni appear to be associated with organic matter, this is especially true for the low ash content sample 2B. However, further investigation reveals that these elements are, in fact, present in silicates (kaolinite and muscovite) either as tiny discrete mineral inclusions (e.g. zircon) or as an elemental replacement within the silicate crystal structure (e.g. sorption of Cr in the clay structure; Li, 2002).

In an attempt to quantify the modes of occurrence of elements in coal, a sequential leaching test, described previously in Section 2.2, was performed on three seam-composite samples of E seam coal. The leached percentages for all elements in each of the sequential leaching steps were previously reported and discussed in detail by Li (2002). The total percentages of leached B, Cd, Br, Se, Ni, and Co are low (5% to 35%) in the sequential leaching tests, with no more than 15% being removed by any one of the acids. This suggests that these trace elements have a close association with organic matter in coal, either loosely bound to the organic matter or as submicron-sized mineral grains intimately dispersed in the organic material. In contrast, a significant proportion (30% to 65%) of the total Cr, Sb, Zr, Rb, Sr, V, and Ba are associated with silicates (Li, 2002). A substantial proportion of Zn (30–70%), Y (30–55%), and Pb (25–55%) were leached by HCl, suggesting a sphalerite (ZnS) occurrence for Zn, a Y-bearing phosphate association for Y, and a crocoite occurrence for Pb (Li, 2002).

3.2. Combustion ashes and ash chemistry

The weights and corresponding percentages of individual combustion ash products are given in Table 3. It is noted that feed coal with the lowest ash (2B) has the highest ash content in the fly ash fraction (6.7%). This can be attributed to the fact that in sample 2B, the ash-forming minerals are predominantly micron- and submicron-sized clays intimately

Table 3

Combustion ash weights and weight percentages in relation to the total combustion ashes

Field sampling no.	2B	2A	P532A
Combustion ref. no.	Expt 40	Expt 39	Expt 38
CRL ref. no.	63/156	63/155	63/157
Bottom ash	kg 0.942	4.168	2.639
Large bottom ash	kg 0.45	2.688	1.376
Small bottom ash	kg 0.492	1.48	1.263
Fly ash	kg 0.068	0.1	0.096
Total ash	kg 1.01	4.268	2.735
Percentage of bottom ash	% 93.3	97.7	96.5
%Large bottom ash	% 44.6	63.0	50.3
%Small bottom ash	% 48.7	34.7	46.2
Percentage of fly ash	% 6.7	2.3	3.5
Fuel weight	kg 30.173	31.539	36.04
Recalculated on whole coal basis: total ash%	3.35	13.53	7.59
on whole coal basis			

dispersed in the coal matrix. When the coal burns, heat flow drives more submicron-sized particulates into the fly ash fraction.

Major element analyses for all combustion ashes are given in Table 4. In general, samples 2B and P532A have similar compositions for most major elements in all three combustion ash types (LBA, SBA, FA). Na_2O in sample 2B is higher in all three ash types, as is SO_3 in the fly ash. In contrast, sample 2A is distinguished by having significantly higher SiO_2 and lower Fe_2O_3 and MnO concentrations (Table 4). However, the major element partitioning has the following characteristics:

- (1) Si and Al are partitioned predominantly into aluminosilicate glass, which often contains minor amounts of K, Ti, Ca, Mg, S, and, in some cases, trace amounts of Na and Cl.
- (2) Fe mainly occurs as Fe-bearing spinel group minerals $[(A, B)\text{O}_3 \text{ and } \text{AB}_2\text{O}_4]$, where $A = \text{Fe}^{2+}$, Mg^{2+} , Ca^{2+} ; $B = \text{Fe}^{3+}$. Fe was also seen in some cases as Fe–S–O glass.
- (3) Ti and Fe were detected as discrete inclusion grains (possibly oxides) encapsulated inside larger quartz or Si–Al glass. Some Ca and Mg were incorporated within aluminosilicate glass. Some Ca, Mg, and Mn were also associated with Fe-bearing spinel minerals. Ca was also present as small CaO crystals ($< 1 \mu\text{m}$ in size).

Table 4

Ash chemistry (by WD-XRF) for the high temperature ash (HTA) of the feed coal and large bottom ash (LBA), small bottom ash (SBA), and fly ash (FA) fractions of the three combustion runs

CRL #	Combustion Run #40, 2B				Combustion Run #39, 2A				Combustion Run #38, P532A			
	63/156	63/570	63/571	63/572	63/155	63/536	63/537	63/538	63/157	63/300	63/301	63/302
Ash type	HTA	BBA	LBA	FA	HTA	BBA	LBA	FA	HTA	BBA	LBA	FA
Fraction%		44.6	48.7	6.7		63.0	34.7	2.3		50.3	46.2	3.5
Ash	3	87.2	79.2	42.6	14	95.94	95.74	53.14	8	94.2	95.26	53.89
SiO ₂	38.14	34.94	44.98	36.48	65.02	68.8	59.8	49.71	47.03	43.48	52.49	45.35
Al ₂ O ₃	17.34	14.45	20.35	16.76	20.13	14.89	25.74	22.46	19.6	18.15	24.7	21.03
Fe ₂ O ₃	33.9	40.55	25.52	32.54	6.64	8.27	5.53	16.34	24.81	26.68	13.84	17.04
MgO	3.07	3.85	2.19	1.12	1.66	1.75	1.67	1.21	2.78	3.14	2.07	1.1
CaO	1.81	2.32	2.25	2.34	1.03	1.35	0.76	1.39	0.91	1.55	1.52	1.61
K ₂ O	2.15	1.57	1.99	2.09	3.56	2.58	4.3	3.75	2.96	3.08	3.17	2.88
TiO ₂	0.68	0.56	0.86	1	0.91	0.69	1.08	1.19	0.83	0.75	1.12	1.23
MnO	0.24	0.3	0.19	0.13	0.05	0.07	0.04	0.08	0.19	0.22	0.1	0.24
Na ₂ O	0.55	0.72	0.77	1.18	0.16	0.1	0.266	0.92	0.12	0.21	0.21	0.38
P ₂ O ₅	0.53	0.53	0.58	0.45	0.62	0.86	0.43	0.33	0.57	0.75	0.59	0.47
SO ₃	1.35	0.005	0.09	1.1	0.18	0.005	0.005	0.15	0.19	0.01	0.01	0.01
LOI	0.57	20.22	12.21	57.4	0.48	4.06	4.46	46.86	0.48	6.3	4.43	46.11
Total	99.76	99.8	99.77	95.19	99.96	99.37	99.62	97.53	99.99	98.02	99.82	91.34

3.3. Combustion ash mineralogy

The mineralogy composition of the bottom and fly ash fractions from the three combustion runs is predominantly quartz, Si–Al silicates, and iron spinels. The main phases of minerals in bottom ash are quartz (identified by XRD), amorphous aluminosilicate glass, mullite, Fe-bearing spinel group oxides (mainly haematite and magnetite), incompletely burned siderite residue, and minor amounts of submicron-sized CaO, sulphate (BaSO₄), phosphates [Ca₅(F, Cl, OH)(PO₄)₃, (La, Ce, Y, Th)PO₄], and chlorides (NaCl, KCl). However, it is often found that K, Ca, Fe, Mg, Mn, and, to a lesser extent, Na and Cl are dissolved in an aluminosilicate glass matrix during combustion.

In addition to the associations listed above, SEM-EDXA observation and analysis revealed that three distinctive glass phases made up the bulk of the bottom ash:

- (1) a Si–Al–O rich phase with minor amounts of K, Ca, Fe, Mg, Na; and
- (2) an Fe–O rich phase with minor amounts of Mg and Mn; and
- (3) an Fe–Ca–Mg–O rich phase.

While the first group of glass (Si–Al–O rich phase) is the result of combustion of silicate

minerals (clays) in the feed coal, the other two groups of glass (Si-free to minor) are related to the siderite and other Fe–Ca-bearing minerals (calcite, ankerite, and Fe-oxides).

The mineral composition of fly ash is very similar to that of bottom ash, although with different proportions of each phase (mineral or glass). The main phases present in fly ash are quartz, amorphous aluminosilicate glass, and Fe-bearing spinel group minerals (haematite and magnetite); with minor amounts of sulphates (BaSO₄), salts (Na_{1-x},K_x)Cl, and copper oxide [CuO,(Fe_x,Cu_{1-x})O].

3.4. SEM-EDXA observation on trace element partitioning in combustion ashes

An attempt was made to locate the hosts of trace elements in the fly and bottom ash fractions through direct analysis of minerals using SEM-EDXA. However, only a few trace elements were detected because most concentrations were below the detection limit (DL) of SEM-EDXA (usually DL is > 0.1 to 0.5 wt.% depending on the individual elements).

Using SEM-EDXA, Ni was detected in Si–Al glass; Cr and Ni was detected in the Fe-rich phase adsorbed on the unburned char particles of the fly ash; and Zr was occasionally detected as zircon in association with quartz in P532A fly ash sample. Cl

and S were detected in association with Cu, Cu–Fe, or Cu–Fe–Ca oxides, most likely as chlorides and sulphates. A small portion of Cl was also present as salts (NaCl, KCl). Ba was associated with S, probably as discrete grains of BaSO₄. Rare earth elements such as La and Ce were associated with REE-phosphate.

3.5. Trace element partitioning in bottom ash

In terms of trace element concentrations, bottom ash has higher Sc, Cs, Ba, Rb, in contrast to fly ash that is enriched in As, Sb, Se, Br, Hg, Mn (except Fe-oxides), Zn and W. Both bottom and fly ash fractions seem to have similar concentration of rare earth elements and other trace elements (Tables 5 and 6).

Bottom ash is mainly composed of quartz, Fe-spinel minerals or Fe-bearing glass, and Si–Al–O rich glass. Trace element concentrations hosted in quartz of feed coal is very low. The temperature in the combustion chamber (1100 °C to 1250 °C) is not high enough to melt the quartz, so there is no obvious mineral transformation expected to take place during combustion. Hence, it is assumed that no significant amount of any trace elements would partition in quartz, and trace elements in bottom ash are mainly partitioned in the aluminosilicate and Fe-oxide phases. In order to determine the exact trace element partitioning in bottom ash, three main phases of bottom ash samples (iron oxide, Si–Al–O rich glass, and Si–Al–Fe–O rich glass) have been identified, as described previously in Section 3.3, and analysed for their respective trace element concentrations by INAA (Table 5). It was found that, except for Mn, As, and Se, the Si–Al–O rich glass has about twice the trace element concentration of the iron oxide phase (Table 5). The iron oxide contains 35 times the Mn (5250 ppm) and three times the As (8.52 ppm) concentrations of the Si–Al glass. But both Si–Al–O glass and Fe-oxide have similar Se concentrations.

In terms of weight percentages of trace elements partitioned in the different combustion ashes, the first group of elements including Ba, V, Zr, Rb, Sr, Th, F, La, Ce, Nb, Ga, Y, and, to a lesser extent, Co, Cr, and Ni are predominantly (> 90%) partitioned into bottom ash fractions (Fig. 5) after combustion. These elements are most likely partitioned in silicates and aluminosilicate glass matrix. This group of elements are associated with mineral matter in feed coal. After

Table 5

Trace element contents (ppm, INAA data) in the three major phases of the bottom ash sample 2A

Sample fraction	2A Bottom ash		
	2A-LA-SA	2A-LA-CARB	2A-LA-FE
	Silicates	Fe-silicate	Fe-oxides
Fe ₂ O ₃ %	1.86	5.86	66.92
Na ₂ O%	0.17	0.14	0.07
K ₂ O%	4.86	4.77	1.64
Br	nd	nd	nd
Sc	19.8	18.9	7
Cr	109.7	98.5	49.5
Mn	151	460	5250
Co	18.9	11.4	11
Ni	nd	nd	nd
Zn	142	125	53
Cs	83.86	81.66	20.9
Rb	248	249	nd
Sr	nd	nd	nd
Ba	835	779	323
La	56.82	53.47	28.65
Ce	109.33	100.59	53.91
Nd	42.55	39.04	19.56
Sm	8.95	8.62	3.82
Eu	1.13	1.09	0.47
Gd	8.42	8.78	2.75
Tb	1.21	1.12	0.43
Tm	0.69	0.59	0.22
Yb	3.96	3.28	1.28
Lu	0.54	0.49	0.18
Zr	268	190	nd
Hf	5.78	5.25	1.72
Ta	2.12	1.88	0.69
Th	20.74	18.41	5.77
U	4.5	3.92	1.53
W	18.3	16.8	11.8
Sb	1.68	1.56	0.67
As	nd	2.55	8.52
Au (ppb)	1.6	1.9	nd
Se	0.65	1.01	0.6
Hg (ppb)	nd	nd	nd

2A-LA-SA=light colour, Si–Al–O glass, resulted from the silicate combustion; 2A-LA-CARB=Fe-bearing silicate glass, resulted from the interaction between clays and carbonates; 2A-LA-FE=dark red coloured Fe-oxides, resulted from the combustion of Fe-bearing minerals. nd=not determined.

combustion, these elements are strongly bonded or encapsulated within aluminosilicate or glass matrices.

3.6. Trace element partitioning in fly ash

In order to determine how trace elements are present in fly ash particles, two fly ash samples

Table 6

Trace element data (ppm, by INAA) for sink–float fractions (at specific gravity of 1.6 g/cm³) of two fly ashes (P532A-FA and 2A-FA)

Sample fraction	2A fly ash			P532A fly ash		
	<u>2A-FA-S_{1.6}</u>	<u>2A-FA-F_{1.6}</u>	EF	<u>P532A-FA-S_{1.6}</u>	<u>P532A-FA-F_{1.6}</u>	EF
	Sink fraction	Float fraction		Sink fraction	Float fraction	
Fe ₂ O ₃ %	26.50	1.73	15.3	21.20	3.17	6.7
Na ₂ O%	0.47	0.21	2.2	0.56	0.30	1.9
K ₂ O%	2.41	1.00	2.4	2.41	1.50	1.6
Br	46.7	60.2	0.8	50.8	72.8	0.7
Sc	9.8	3.9	2.5	15.9	12.4	1.3
Cr	109	30.8	3.5	118.6	66.1	1.8
Mn	2379	126	18.9	1892	245	7.7
Co	59	28.2	2.1	116.3	121	1.0
Ni	nd	nd	nd	nd	nd	nd
Zn	135	56	2.4	208	210	1.0
Cs	38.38	11.71	3.3	23.63	12.88	1.8
Rb	92	29	3.2	113	63	1.8
Sr	nd	nd	nd	nd	nd	nd
Ba	427	148	2.9	531	314	1.7
La	29.43	12.03	2.4	57.52	36.25	1.6
Ce	58.2	22.19	2.6	113.52	73.68	1.5
Nd	24.25	7.71	3.1	41.31	30.07	1.4
Sm	4.38	1.6	2.7	8.53	5.19	1.6
Eu	0.62	0.23	2.7	1.12	0.7	1.6
Gd	3.92	1.64	2.4	7.74	5.33	1.5
Tb	0.63	0.24	2.6	1.24	0.81	1.5
Tm	0.32	0.13	2.5	0.67	0.48	1.4
Yb	1.72	0.72	2.4	3.76	2.85	1.3
Lu	0.29	0.12	2.4	0.49	0.39	1.3
Zr	169	73	2.3	350	258	1.4
Hf	3.34	1.39	2.4	5.85	3.79	1.5
Ta	1.34	0.84	1.6	2.78	2.25	1.2
Th	10.12	4.66	2.2	18.09	12.29	1.5
U	2.5	1.5	1.7	4.02	3.15	1.3
W	15.2	10	1.5	177	89.3	2.0
Sb	1.71	0.76	2.3	2.17	2.29	0.9
As	24.77	7.96	3.1	18.66	9.95	1.9
Au (ppb)	1.1	nd	nd	nd	1	nd
Se	8.08	2.89	2.8	5.01	4.82	1.0
Hg (ppb)	907	424	2.1	433	561	0.8

P-FA-S_{1.6}=sink fraction of fly ash sample P532A-FA; P-FA-F_{1.6}=float fraction of fly ash sample P532A-FA. EF=enrichment factor for the elemental concentration in sink fraction in relation to the float fraction. nd=not detected.

(P532A-FA and 2A-FA) were also subjected to the float–sink experiment in a medium with a specific gravity of 1.64 g/cm³. All trace elements, except Br, generally demonstrate moderate enrichment (1 to 3 times) in the sink fractions in relation to the float fraction of fly ash (Table 6). This result suggests that most trace elements in fly ash are predominantly enriched in the inorganic phases, such as Al–Si glass phases and Fe-bearing phases (Fe-oxide glasses). However, a proportion of most trace elements were

also associated with the float fraction, which consists predominantly of organic-rich, incompletely burned char. The organic association of trace elements suggests some other partitioning mechanism, such as absorption and/or adsorption of the trace elements onto the surface of the fly ash particles, which may play an important role. The electrostatic properties and large surface area presented by the fly ash make this extremely likely and may explain the float–sink behaviour for trace elements in these fly ash samples.

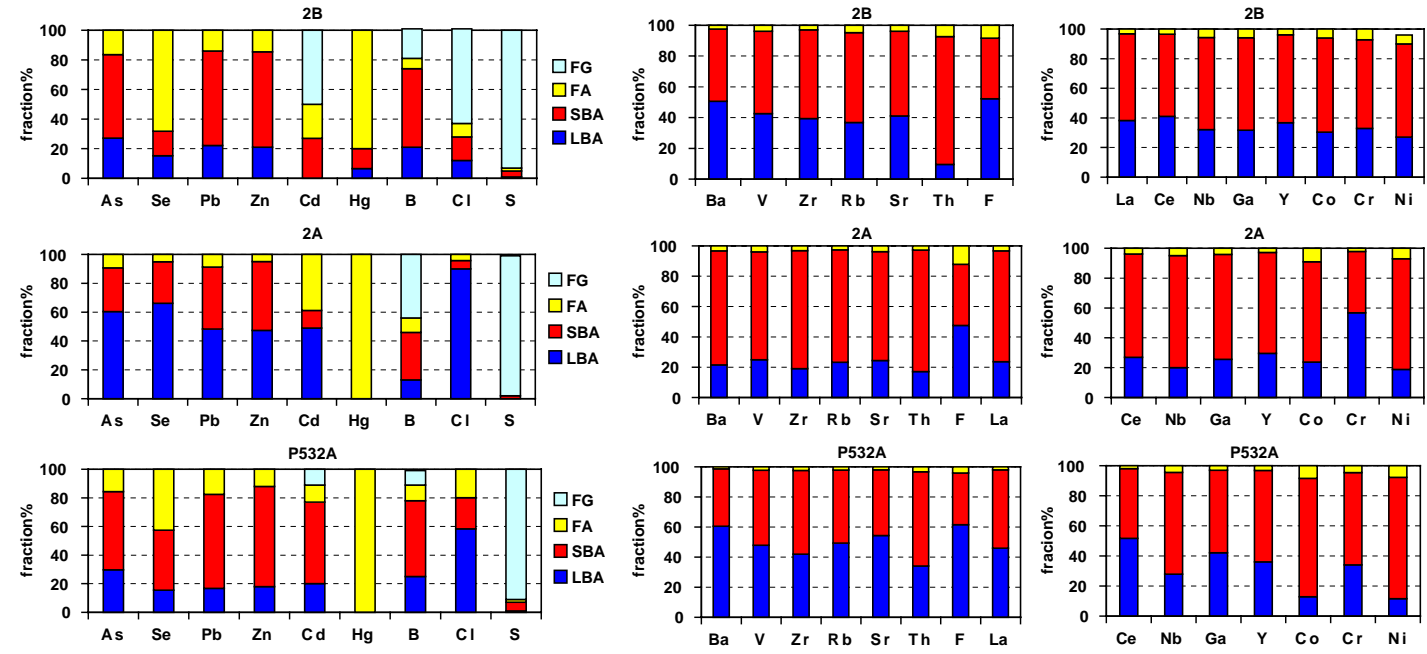


Fig. 5. Proportion (%) of trace elements partitioned in large bottom ash (LBA), small bottom ash (SBA), fly ash (FA), and flue gas (FG) fractions for all three combustion tests P532A, 2A, and 2B.

The depletion of Br in the sink fractions suggests that Br is concentrated in unburned char fragments, which is inherited from an organic association in the feed coal.

Trace elements including As, Se, Pb, and Zn are those with moderate enrichment factors in bottom ash (EF=2 to 16, Table 7) in relation to coal and significant enrichments in fly ash (EF=11 to 25, Table 7). There were significant but generally less than 20% of these trace elements associated with the fly ash fraction, and more than 80% of them were retained in bottom ash, although exact forms were difficult to determine directly because of their low abundance. However, it is more likely that these elements were incorporated into the aluminosilicate melt, oxides, or glass matrix in the bottom ash. In contrast, the proportion of these elements associated with fly ash is thought to be absorbed or adsorbed onto the surface of the fly ash particles because of their large surface area and electrostatic effects.

The total recovered As in the three combustion experiments conducted as part of this study ranges from 22% to 37%. Arsenic often behaves as a volatile element, but in the present study, 84% to 90% of recovered As fails to leave the firebox, with only 10–16% of the recovered As partitioned in fly ash. This As partitioning can be attributed to its association with clay minerals in feed coal which is supported by coal leaching test results. The leaching tests demonstrated that up to 45% of As was associated with silicates (clays) and less than 5% was associated with sulphide. It is highly likely As is present as submicrometer inclusions in clays, because up to 45% of As is not released until the dissolution of clays; After the clay break down during combustion, a large proportion of the As remains trapped within the resulting iron oxide glass.

Interestingly, the partitioning behaviour of Se differs between samples 2B (taken from the bottom of the seam) and 2A (taken from the top). When the sample from the bottom of the seam was combusted, the majority (68%) of the recovered Se escaped the firebox and was recovered in the fly ash. When the top seam sample was combusted, only 5% of recovered Se partitioned in fly ash but the majority (95%) of the recovered Se was associated with bottom ash. The leaching tests indicate that Se is essentially bonded organically. The higher ash, higher Si and K, and

lower Fe in sample 2A may have generated more Si–Al glass during combustion, which may have helped to retain most Se in the bottom ash. In contrast, lower ash, lower Si and K, but high Fe in sample 2B, may have had a very limited capacity of trapping Se in the bottom ash, and let most Se escape to the fly ash fraction.

3.7. Trace element partitioning in flue gas

In contrast to the other elements, this group of trace elements including Hg, B, Cd, Cl, and S is characterised by not only a significant enrichment (EF=10 to 40) in fly ash and with moderate enrichment (EF < 10) in bottom ash, but also with a significant proportion partitioned in both flue gas (up to 97%) and fly ash fractions. This group of elements is known to be highly volatile. As expected, these elements vaporized and escaped from the firebox during combustion, and chiefly partitioned in flue gas and fly ash either by absorption, adsorption, or condensation after reaching cooler parts of the combustion rig. More than 90% of total Hg and S, up to 50% of Cd, up to 64% of Cl, and up to 44% of B were found partitioning in flue gas fractions; and a significant proportion of these elements also partition in fly ash fractions.

It should be noted that the total recovery for this group in all three combustion runs is not high (Cd 7–51%, Hg 5–10%, B 21–36%, Table 8). However, within the total recovery of this group of trace elements, around 80–100% Hg and up to 40% Cd have partitioned into the fly ash (see Fig. 5). The balance of those trace elements recovered have partitioned in the bottom ash.

Hg is well known as a highly volatile element. In the two fly ash samples (P532A-FA and 2A-FA) analysed by INAA, the fly ash has 424 to 900 ppb of Hg, but no Hg was detected in the respective bottom ashes. It suggests that no appreciable amount of Hg is partitioned in the bottom ash, hence most Hg probably was vaporized. However, only part of total Hg (< 10%) (see Table 8) was recovered after combustion. Given the fact that both the high volatile nature of the Hg in the combustion and the low detection limits used in this study, the low Hg recovery after combustion was most likely a result of the ineffectiveness of the impinger solution.

Table 7

Trace element concentrations (ppm) and enrichment factors (EF) in large bottom ash (LBA), small bottom ash (SBA), and fly ash (FA) relative to feed coal

	Combustion Run #40, 2B							Combustion Run #39, 2A							Combustion Run #38, P532A						
	Concentrations				EF			Concentrations				EF			Concentrations				EF		
	Coal (ppm)	LBA (ppm)	SBA (ppm)	FA (ppm)	LBA	SBA	FA	Coal (ppm)	LBA (ppm)	SBA (ppm)	FA (ppm)	LBA	SBA	FA	Coal (ppm)	LBA (ppm)	SBA (ppm)	FA (ppm)	LBA	SBA	FA
As	1.6	7.9	15	31	5	9	19	4.3	11	10	46	3	2	11	1.4	2.4	4.8	18	2	3	13
B	95	470	1100	1000	5	12	11	48	28	130	560	1	3	12	37	100	230	610	3	6	16
Pb	1.8	11	29	45	6	16	25	7.5	18	29	88	2	4	12	3.4	5.6	24	84	2	7	25
Zn	11	31	87	140	3	8	13	18	60	110	170	3	6	9	15	26	110	250	2	7	17
Cd	0.06	0.03	0.12	0.72	0	2	12	0.016	0.031	0.014	0.66	2	1	41	0.03	0.09	0.28	0.78	3	9	26
Hg	0.04	0.01	0.02	0.63	0	0	18	0.05	0	0	1.1	0	0	22	0.018	0.005	0.005	0.53	0	0	29
Se	1	1	1	29	1	1	29	5.8	19	15	39	3	3	7	0.74	0.28	0.82	11	0	1	15
Co	5.7	73	140	94	13	25	16	5.8	9.3	48	95	2	8	16	5.3	18	120	170	3	23	32
Cr	3.3	42	70	60	13	21	18	24	76	100	77	3	4	3	8.4	48	94	93	6	11	11
Ni	15	170	360	250	11	24	17	15	21	150	210	1	10	14	14	38	290	370	3	21	26
V	8	132	152	77	17	20	10	20	22	114	92	1	6	5	19	178	202	116	9	11	6
Nb	1	13	23	15	20	35	23	5	6	41	40	1	8	7	4	22	58	50	6	15	13
Zr	7	219	294	106	31	42	15	38	41	303	179	1	8	5	28	331	477	272	12	17	10
Ba	54	1654	1404	506	30	26	9	116	114	722	471	1	6	4	104	1423	975	458	14	9	4
La	2	53	74	29	27	37	15	9	10	56	37	1	6	4	7	94	116	57	13	17	8
Ce	6	126	156	69	22	28	12	16	18	84	70	1	5	4	16	179	175	99	11	11	6
Ga	2	15	27	18	9	16	11	6	7	35	30	1	6	5	3	24	34	25	7	10	8
Rb	1	66	96	56	132	192	112	35	40	232	123	1	7	4	15	149	160	91	10	11	6
Sr	15	228	280	140	15	19	9	30	34	181	144	1	6	5	31	429	377	217	14	12	7
Th	1	1	8	5	2	16	10	1	2	17	9	2	17	9	0	10	20	14	40	80	56
Y	2	23	34	16	12	17	8	6	7	29	18	1	5	3	5	25	46	32	5	10	7
F	16	190	131	197	12	8	13	39	42	65	288	1	2	7	41	181	110	174	4	3	4
S	2990	3925	9491	44133	1	3	15	2849	2929	594	39686	1	0	14	3479	1608	8735	33180	0	3	10
Cl	2468	909	1115	4406	0	0	2	2055	2232	257	2839	1	0	1	2339	767	309	3758	0	0	2

Trace elements were analysed by ICP-MS, ICP-AES, and XRF except Hg by cold vapour atomic absorption (CVAA).

Table 8

Proportions for trace element partitioning in large bottom ash (LBA), small bottom ash (SBA), fly ash (FA), and flue gas (FG) fractions for all three combustion tests

	Combustion Run #40, 2B					Combustion Run #39, 2A					Combustion Run #38, P532A				
	Proportion in different ashes					Proportion in different ashes					Proportion in different ashes				
	Recov. (%)	LBA (%)	SBA (%)	FA (%)	FG (%)	Recov. (%)	LBA (%)	SBA (%)	FA (%)	FG (%)	Recov. (%)	LBA (%)	SMA (%)	FA (%)	FG (%)
As	27	27	56	16	n.d.	36	60	30	9	n.d.	22	30	55	16	n.d.
B	29	21	53	7	20	21	13	33	10	44	36	25	53	11	10
Pb	41	22	64	14	n.d.	42	48	43	9	n.d.	38	17	66	17	n.d.
Zn	20	21	64	15	n.d.	60	47	48	5	n.d.	37	18	70	12	n.d.
Cd	7	0	27	23	50	34	49	12	39	n.d.	51	20	57	12	11
Hg	5	7	13	80	n.d.	7	0	0	100	n.d.	10	0	0	100	n.d.
Se	10	15	17	68	n.d.	42	66	29	5	n.d.	9	16	42	43	n.d.
Co	63	30	64	6	n.d.	58	24	67	9	n.d.	101	13	79	8	n.d.
Cr	58	33	60	7	n.d.	48	57	41	2	n.d.	64	34	61	5	n.d.
Ni	60	27	63	6	3	63	19	74	7	n.d.	90	12	81	8	n.d.
Cu	106	7	21	71	1	184	26	27	48	n.d.	787	5	13	81	n.d.
Nb	91	32	62	6	n.d.	48	20	75	5	n.d.	75	28	68	4	n.d.
V	60	43	54	4	n.d.	38	25	71	4	n.d.	76	48	50	2	n.d.
Zr	119	39	58	3	n.d.	48	19	78	3	n.d.	107	42	56	2	n.d.
Ba	90	51	47	2	n.d.	39	22	75	3	n.d.	86	61	38	1	n.d.
La	103	38	58	3	n.d.	40	24	73	3	n.d.	112	46	52	2	n.d.
Ce	81	41	56	3	n.d.	35	27	69	4	n.d.	84	52	46	2	n.d.
Ga	42	32	62	6	n.d.	41	26	70	4	n.d.	67	42	55	3	n.d.
Rb	536	37	58	5	n.d.	42	23	74	3	n.d.	80	49	49	2	n.d.
Sr	55	41	55	4	n.d.	39	24	72	4	n.d.	99	54	44	2	n.d.
Th	31	10	83	7	n.d.	100	17	80	3	n.d.	448	34	63	3	n.d.
Y	47	37	59	4	n.d.	32	30	68	3	n.d.	56	36	61	3	n.d.
F	35	52	39	8	n.d.	20	47	40	12	n.d.	27	62	34	4	n.d.
S	11	1	4	2	93	14	0	2	0	97	13	1	6	2	91
Cl	2	12	16	9	64	10	90	6	4	n.d.	2	58	22	20	n.d.

Recov.= % of the element recovered from all combustion products after combustion; LBA=proportional % of the total recovered element partitioned in the large bottom ash (LBA) fraction; SBA=proportional % of the total recovered element partitioned in small bottom ash (SBA) fraction; FA=proportional % of the total recovered element partitioned in fly ash (FA) fraction; FG=proportional % of the total recovered element partitioned in the flue gas (FG) fraction; nd=not detected.

Therefore, it is concluded that Hg probably did partition predominantly into the flue gas (> 90%). The small amount (< 10%) captured by the fly ash probably did so by dry deposition or absorption onto the surface of particles when the flue gas reached the cooler part of the combustion rig. This is consistent with results reported elsewhere (e.g. Huang et al., 1996). More recent studies (Hassett and Eylands, 1999; Hower et al., 2000a,b; Sakulpitakphon et al., 2000) indicate that Hg adsorption on fly ash particles is a function of the form and amount of carbon, surface area, as well as the flue gas temperature.

Carpi (1997) and Galbreath and Zygarlicke (2000) concluded that emissions of Hg from coal combustion sources are approximately 20–50% elemental Hg⁰ and

50–80% divalent (Hg⁺²), which may be predominantly as HgCl₂. The partitioning of mercury in flue gas between elemental Hg and divalent forms may be dependent on the concentration of particulate carbon, HgCl₂, and other pollutants in the stack emissions. Because of the high organic-associated Cl content in the Greymouth coals and also because both Hg and Cl vaporize easily during combustion and form HgCl₂ in the flue gas, it is very likely that HgCl₂ is the dominant form of Hg. HgCl₂ formation may have a detrimental environmental impact if concentrations are high.

The behaviour of B is of particular interest, especially in New Zealand coals. Rafter (1945) noted high B contents (up to 1.5% B in Waikato

coals) in many New Zealand coals. In this study, it was found that 44% of the recovered boron was associated with the flue gas fraction of sample 2A (Table 8). Only 10% and 19% of recovered boron was associated with flue gas for samples P532A and 2B, respectively. This B partitioning behaviour is very different from previously observed partitioning in Ca-rich (up to 55% CaO in ash) subbituminous Waikato coals (Clemens et al., 1999, 2000), in which > 90% B and 60% of As is retained in bottom ash by the formation of borosilicate, $\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$, and formation of calcium arsenates. However, for the combustion tests of the Greymouth coals, the coal ashes are: (a) comparatively low in calcium, (b) contain no calcium borosilicates among the heating products of low-temperature ashes, and (c) the boron and arsenic retention levels remain fairly high. This suggests that the stoker combustion regime itself—a static bed, long retention times, large coal particles and moderate temperatures—is the major reason for the high retention of trace metals traditionally regarded as being highly volatile. Another possibility, of course, is that the elements are originally present in the coal in forms that survive the temperatures within the firebox during combustion.

Both S and Cl are regarded as highly volatile. S is significantly enriched (EF=10 to 15) in fly ash but depleted in bottom ash. Chlorine is only moderately (EF=2) enriched in fly ash but uniformly depleted in all bottom ash samples. It was found that 91% to 97% of the total S and up to 64% of the total Cl were partitioned in the flue gas fractions (Table 8) in the Greymouth coal.

4. Environmental significance of trace elements in combustion products

In the present study, most trace elements (including As, Co, Cr, Ni, Pb, and Zn, etc.) are found to be at relatively low concentrations and mostly partitioned in the glassy and refractory bottom ash fraction, particularly with silicates or Al-silicate glass phases. The elements partitioned in bottom ash are (1) fixed or encapsulated into the glassy phases; and (2) at relatively low concentrations. Therefore, the trace elements partitioned in the glassy and refractory

bottom ash are difficult to mobilise and are of little concern to the environment.

In contrast to bottom ash, trace element partitioning in the fly ash (1) generally contain at least two (or more) times concentration of most trace elements (such as As, Be, Cr, Hg, Pb, etc.) than bottom ash and (2) tends to be in more loosely bonded forms, chiefly absorbed/adsorbed on particles, hence they have a greater potential toward mobilisation under typical natural conditions. The mobilisation of those trace elements, especially HAPs, may or may not be of concern for the environment and human health, depending on the amount and species of HAPs being mobilised. Fortunately in the present case, because of the relatively low trace element concentrations in fly ash compared to other overseas fly ashes (see Li, 2002), there is little concern that would arise from the combustion of the Greymouth coals, although a few trace elements (B and S) may need to be treated with caution during the utilisation or disposal of fly ash of this coal.

One of the accompanying consequences of the low ash Greymouth coals is that trace elements including environmentally sensitive elements can be greatly enriched in the fly ashes. For example in combustion test of a relatively low ash sample (2B, with 3.3% ash), the B concentration in the small bottom ash and fly ash have been enriched to 1100 ppm and 1000 ppm, respectively. The B in the fly ash of the other two combustion tests 2A and P532A also have been enriched to 560 ppm and 610 ppm, respectively. This high B content in combustion ash, especially in fly ash, may cause toxicity to plants (Holliday et al., 1958; Cope, 1962; Hodgson and Holliday, 1966; Wilkinson, 1985; Wright et al., 1998) and the environment (Cox et al., 1978; Aitken and McCallum, 1988). Many studies (Bradford, 1963; De Lanuza, 1969; Smidt and Whitton, 1975) have stated that although B tolerance by plants varies with species and stage of growth, B levels greater than 200 ppm are enough to produce toxicity symptoms in some plants, such as radiata pine, and B toxicity symptoms may become progressively severe and irreversible necrosis occurs at B levels greater than 1000 ppm.

There may also be environmental consequences from S, Cl, and Hg. Sulphur and Cl concentrations in the fly ash are higher than in fly ash reported from overseas (Li, 2002) with concentrations of 4.41% and 2000 ppm, respectively. Therefore, careful manage-

ment is needed to deal with the disposal of the fly ash derived from this coal.

In summary, because of the generally low concentration of most trace elements in comparison with other coal combustion ashes from around the world, it is not expected that significantly undesirable environmental impacts will arise from combustion of the Greymouth coal studied here. Some trace elements (e.g. B) may pose some need for thoughtful disposal of combustion ash. It is the fly ash fraction though that may need special attention in its disposal as it contains some elevated levels of potentially toxic trace elements. Disposal under acidic conditions where these trace elements are especially mobile should be guarded against.

5. Conclusions

The behaviour of some environmentally sensitive trace elements in float–sink tests and their partitioning in different combustion ashes have been quantitatively studied based on the respective proportion in different ash types generated from the laboratory-scale combustion runs. The mineralogical transformation during coal combustion has been investigated in relation to the trace element partitioning in bottom and fly ash. The partitioning mechanisms of those trace elements during stoker-fired combustion has been determined and discussed and is summarised below:

1. Most trace elements including As, Ba, Co, Cr, Mn, Ni are predominantly partitioned in the glassy and refractory bottom ash fractions.
2. A significant proportion of As, Se, and Pb are partitioned in fly ash fractions.
3. Some volatile elements (> 90% of the S and Hg, up to 64% of the Cl) and, to a lesser extent, B (up to 44%) and Cd (up to 50%) are partitioned in the flue gas fraction.
4. Although the low-ash Greymouth coals have the advantage of generating less solid combustion ash, one of the accompanying consequences is that combustion ash can be enriched in trace elements. For example, B, S, and Cl have been enriched to environmentally undesirable levels of 1100 ppm, 4.4% and 2000 ppm, respectively, and these will need to be managed upon disposal.

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