

FATE OF TRACE ELEMENTS IN UK COALS DURING GASIFICATION PROCESSES

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ABSTRACT

Five UK coals were selected to cover the range of mineral matter and ash contents typically encountered in UK bituminous coals. Trace element analysis was performed on both the whole coals and size separated fractions using ICP analysis for 21 trace elements, including Be, Cr, Co, Ni, As, Cd, Sb, Hg, and Pb, elements deemed to be the most environmentally hazardous.

Small quantities of each coal were gasified in a laboratory gasifier in an atmosphere of N₂ containing 15% O₂. Samples of bed ash, cyclone ash, and a fine gas-filtered ash were collected and analysed to determine the partition of the trace elements between the gasification products. Mass balance calculations showed that the recovery of the trace elements varied from 20 to 97%, the low recovery of some trace elements highlighting the difficulties of collecting representative samples from a laboratory system.

A parallel study on samples taken from a pilot plant gasifier showed significantly higher recovery rates, indicating the value of larger scale trials.

INTRODUCTION

The gasification of coal, and in particular the development of integrated gasification combined cycles systems (IGCC) holds the promise for coal conversion processes with both higher efficiencies and lower gaseous emissions. While such systems may meet the anticipated legislation for NO_x, SO_x and particulate emissions, it is essential that the fate of the trace elements and the heavy metals which are present in all coals is well established, since these elements may yet present further environmental hazards.

Coals contain most of the naturally occurring elements with widely varying concentrations depending on rank, geological origin and history. Coal combustion has been reported as being the main source of Hg, Ni, Sn and V emissions, and the second largest source of Cd, Se, and Tl (1). The 1990 US Clean Air Act identified eleven trace elements, namely Be, Cr, Mn, Co, Ni, As, Se, Cd, Sb, Hg and Pb as being the most environmentally hazardous. These elements are all found in coals at concentrations ranging from a few ppb for elements such as Sb and Hg, to several hundred ppm for Mn. The majority of the trace elements are associated with the mineral matter in the coal. This mineral matter consists primarily of clays (aluminosilicates) and quartz, with smaller amounts of carbonates, sulphides, sulphates and oxides. Trace elements may also be associated with the macerals, reflecting the inorganic species present in the vegetation from which the coal was formed. The exchange of ions between mineral matter and macerals following the coalification process gives added complexity to establishing the distribution and mode of occurrence of the trace elements in a coal.

The occurrence of trace elements has been extensively studied and reported by Swaine (2), with recent reviews by Clarke and Sloss (3), and Davidson and Clarke (4). These reviews have concentrated on the origins of the trace elements in coal and on the wide range of analytical techniques which are now available for their determination. Pyrite in coal is generally accepted as being a major source of many of the trace elements, and in particular those of environmental concern.

During combustion or gasification of a coal the trace elements partition between the ash residues and the gaseous emissions. The actual distribution will depend on the combustion or gasification conditions and the mode of occurrence of the trace elements in the coal. Trace elements may conveniently be divided into three groups depending on their volatility and the vapour pressure of simple compounds such as oxides and chlorides. Group I elements are the least volatile and remain with the ash residues. Group II elements are more volatile and partition between the residual ash and the gaseous phase, with condensation of vapour species on the surface of the fine ash particles as the gases cool. Group III elements have a high volatility and show little or no tendency to condense from the vapour phase. Many of the environmentally sensitive elements fall into groups II and III, highlighting the current concern. Dale (5) reported on the trace element partitioning in the stack emissions from pf fired power stations, stressing the importance of monitoring flue gas discharges which may contain some of the environmentally sensitive elements. Other studies, notably those carried out by KEMA in the Netherlands (4) have shown that, with the exception of Hg and Se, 95% or more of the trace elements may be recovered from the bottom ash and the electrostatic precipitators at a power station. Concern remains that the fine particulate matter, with surface enrichment in trace

elements, may escape the gas cleaning process.

Much less work has been reported on the fate of the trace elements during gasification processes. Here the conditions are much more reducing and thus the volatile species may be different from those which form in a combustion process. Benson et al (6) reported that elements such as As, Cd, Se and Pb all showed increased volatility as the C:O ratio decreased in a laboratory gasification study of three US coals. Bushell and Williamson (7) gave the results of a trace element survey for a selection of UK bituminous coals. This showed that the elements with the strongest mineral associations were Ba, Co, Cr, Cu, La, Pb, Zn, and Zr, while those elements with a strong maceral association were Be, Sr and V.

This paper gives further details of the fate of the trace elements during gasification of coals from both a laboratory study and a pilot scale gasification process using UK coals.

EXPERIMENTAL

Five UK bituminous coals were selected from the UK Coal Data Bank, currently managed by CRE Group Ltd, Stoke Orchard. The coals provided the range of ash contents and mineralogy found in UK coals. Coals were supplied as partially washed <212 μ m coals. A high temperature ash (HTA) was prepared in a muffle furnace at 815°C and the major oxides and the trace elements present were analysed using a lithium borate fusion, followed by ICPS analysis. The elements As, Sb and Bi were determined by a hydride generation technique, and both the coals and ashes Hg was determined by a cold vapour generation process followed by ICPS.

A low temperature ash (LTA) was prepared in an O₂ plasma which left the mineral matter in a largely unaltered form. Mineral matter was identified by x-ray powder diffraction analysis of the LTA, and a quantitative estimate of the proportions of the minerals present was made by a normative analysis procedure, using the ash composition and the minerals known to be present.

Samples of each coal were ground to <38 μ m and then density separated into mineral-rich and coal-rich fractions using bromochloromethane ($\rho = 1.99\text{ g cm}^{-3}$). Each fraction was analysed for the trace elements and enrichment factors calculated, i.e. the concentration of an element in the separated fraction / concentration of the element in the original coal, to determine how the trace elements were partitioned between the macerals and the mineral matter.

Each coal was also separated into eight size fractions using a Gilsonic Siever with mesh sizes at 180, 150, 125, 106, 75, 53 and 38 μ m. Size fractions were high temperature ashed and the trace elements in each fraction determined to assess the distribution of the trace elements between the various size ranges.

The coals were gasified in a laboratory gasifier where 10 x 1g samples of coal were introduced into a pre-heated bed of fluidised sand at 950°C where the fluidising gas was 15% O₂ in N₂. After gasification, samples of the bed ash, cyclones fines and fine gas-filtered particulates (10-0.1 μ m) taken from the gas stream were analysed for the trace elements.

The fate of the trace elements in the laboratory gasifier were compared to that in a pilot plant scale gasifier. Coal and ash residues were obtained from the air-blown gasifier (ABG) operated by British Coal at the Coal Research Establishment at Stoke Orchard. This gasifier operates at temperatures up to 1000°C and 20 bars pressure, with coal feed rates of 200-300 kg hr⁻¹. Some 70-80% of the coal is converted into a low calorific gas, with ash and char being continuously removed from the base of the reactor to a circulating fluidised bed combustor (CFBC), where the remaining char conversion takes place. Limestone may be added to the coal as a sulphur sorbent to retain the sulphur in the bed ash. Samples of coal feed, bed ash and ash from the primary cyclone were provided for analysis of the major oxides and the trace elements.

RESULTS AND DISCUSSION

The ash composition and the trace element concentrations in each of the coals used for the laboratory gasification studies are shown in Table 1. To a first approximation, the concentration of most of the trace elements is related to the amount of mineral matter in the coal and thus high ash coals showed higher concentrations of the trace elements. The coals all contained mixtures of clays (kaolinite and illites), quartz and pyrite in different proportions, and variable but smaller amounts of calcite, dolomite, ankerite, rutile and apatite. Trace element concentrations were noticeably higher for coals with larger amounts of pyrite. Ash contents ranged from 3.9 wt% for the Daw Mill coal to 19 wt% for Longannet. Since Longannet has the lowest iron content, although the ash content is high, the trace element levels are still comparable with the other coals.

In general the ash contents of the size separated coals increased as the size range was reduced. The one exception to this was the Longannet coal, where the mineral matter was uniformly distributed across all the size ranges, and thus relatively uniform trace element concentrations were observed for each size fraction of the coal.

Samples of the bed ash, cyclone fines and the fine particulate ash filtered from the gas stream of the laboratory gasifier were analysed and a mass balance calculation performed to determine the distribution of the trace elements during the gasification process. The results with the Daw Mill coal (3.9 wt% ash) are shown in Table 2. With the exception of Cd and Zn, where virtually no recovery was recorded, 30 - 90% of most of the trace elements which entered the gasifier could be accounted for. Most of the trace elements were found in the cyclone fines, where the major oxide ash composition was close to that of the whole coal. A few percent of the trace elements were retained in the bed ash or found with the fine particulates filtered from the gas stream. This suggests that at the gasification temperatures most of the trace elements remain with the decomposed mineral matter, which is elutriated from the bed as the char is oxidised. Some trace elements may be volatilised under gasification conditions, to then recondense on the surface of the ash particles in or before entering the cyclone separator.

Similar results were obtained with the Longannet coal (19.0 wt% ash) as shown in Table 3. The mass balance calculations showed a higher recovery of the trace elements in the gasifier residues, with again the majority of the trace elements appearing in the cyclone fines. Significant amounts of Zn and La were found in the gas-filtered fines, which suggested that condensation of the Zn had occurred on the surface of the finest ash particles from the cooling vapours, while in addition the elutriation of very small La enriched particles (clays) from the fluidised bed may be a possible explanation of the high value for the La.

The results from the laboratory study were nevertheless disappointing, with substantial amounts of many of the trace elements unaccounted for in the mass balance calculations. The most likely source of error in the experimentation would appear to be in the sampling of the bed ash, since this is where many of the low volatile elements should appear. The difficulties in taking representative 1-2g samples from a 200g bed of sand are formidable when one realises that it may be just a few mineral grains, rich in trace elements, which are distributed somewhere in the bed. This raises the whole question of the problems and the suitability of laboratory studies for this type of research.

Residues from the British Coal air-blown gasifier consisted of a bed ash containing approximately 50% char, and fines collected from the primary, secondary and tertiary cyclones. Bed ash and primary cyclone fines constituted the bulk of the inorganic material introduced into the gasifier. Table 4. shows the distribution of the trace elements between the bed ash and the primary fines when Daw Mill coal was used as feedstock for the gasifier. An ash analysis showed that the primary fines were enriched in Fe, indicating possible preferential elutriation of fine particles of pyrite from the bed. Trace element analysis and mass balance calculations showed that 95% or more of the trace elements introduced into the gasifier could be accounted for. The trace elements partitioned relatively uniformly between the bed ash and the fines. The more volatile elements such as Be, Co, Cr, Cu, Mo, Ni, Pb, and V showing an enrichment in the fines, while the more refractory elements such as Ba, Sc, Y and Zr showed a slight preference to remain in the bed ash. The high levels of trace elements found in the cyclone fines from both the laboratory studies and the pilot scale gasification process suggests that the physical and chemical association of the trace elements with the decomposed mineral matter is perhaps as much, if not more important, than the volatility of the elements. Thus establishing the mode of occurrence of the trace elements in a given coal may be key factor in determining the fate of the trace elements on gasification.

CONCLUSIONS

Trace element concentrations in UK coals have been found to be closely related to the amount of mineral matter in the coal. In particular, many of the trace elements would appear to be associated with the pyrite. On gasification the trace elements are distributed between the residual ash and a cyclone ash, with condensation of the more volatile species on the surface of the finest ash particles. Pilot scale gasification has provided better mass balance data than the laboratory studies.

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Table 1. Ash content, trace element concentrations and mineral matter in each coal used for laboratory gasification studies.

Coal	Kellingley	Longannet	Daw Mill	Thoresby	Nadins
ash content (wt%)	4.2	19.0	3.9	4.2	9.4
SiO ₂	33.7	52.3	30.3	36.3	28.6
Al ₂ O ₃	19.5	39.7	25.9	25.3	15.7
Fe ₂ O ₃	23.9	1.4	14.4	25.5	26.4
MgO	0.8	0.5	3.2	0.7	2.9
CaO	9.6	0.9	13.7	2.1	10.6
Na ₂ O	3.6	0.2	0.8	5.6	0.3
K ₂ O	1.3	0.6	0.4	1.6	1.5
P ₂ O ₅	5.0	0.9	0.3	0.2	0.7
TiO ₂	0.8	1.5	1.0	0.9	0.6
MnO	0.2	0	0.5	0	0.3
Trace elements (ppm)					
Ag	1	0	0	0	0
As	5	1	7	12	31
Ba	67	160	150	67	64
Be	1	3	0.6	2	4
Bi	0.1	0.4	0.2	0.2	0.1
Cd	0	0	0	0	0
Co	6	11	5	3	14
Cr	10	57	11	11	28
Cu	23	61	6	24	15
Hg	0.04	<0.01	0.07	0.07	0.1
La	4	43	4	5	6
Li	6	76	7	11	15
Mo	3	4	3	4	4
Ni	13	46	11	14	52
Pb	8	21	8	21	56
Sb	1	0.4	0.3	1.8	2.4
Sc	2	-	1	2	5
Sr	53	581	35	34	44
V	16	45	15	29	25
Zn	62	27	3	13	29
Zr	10	58	8	11	11
Mineral matter content of coals (wt%)					
kaolinite	28	85	54	38	34
illites	27	11		33	
quartz	5	3			9
pyrite	28		20	29	34
calcite			14		7
apatite	12				
rutile		1			
ankerite					16
dolomite			12		

Table 2. Distribution of trace elements between bed ash, cyclone ash and gas-filtered fines from the laboratory gasification of the Daw Mill coal.

	Input to gasifier (μg)	% elements recovered	Distribution of trace elements			
			Bed ash	Fines	Filter	Balance
Ag	1.1	86	5.5	80.7	0	13.8
Ba	1413	33	2.9	29.1	0.5	67.5
Be	5.5	35	2.3	32.6	0	65.1
Cd	5.7	0	0	0	0	100
Co	44	37	2.0	35.0	0	62.9
Cr	99	34	3.3	30.4	0	66.3
Cu	80	35	3.0	31.7	0.1	65.2
La	31	43	5.7	37.7	0	56.6
Li	47	47	5.6	41.4	0	52.9
Mo	30	31	2.5	28.3	0	69.3
Ni	97	33	2.0	31.2	0	66.8
Pb	80	100	7.0	72.3	20.6	-
Sr	288	43	4.4	38.7	0.3	56.6
V	146	40	2.3	37.4	0.1	60.2
Zn	296	0.3	0	0	0.3	99.7

Table 3. Distribution of trace elements between bed ash, cyclone ash and gas-filtered fines from the laboratory gasification of the Longannet coal.

	Input to gasifier (μg)	% elements recovered	Distribution of trace elements			
			Bed ash	Fines	Filter	Balance
Ag	8.3	36	5.7	27.9	2.0	64.4
Ba	1263	67	20.9	45.7	0	3.4
Be	26	56	5.7	49.8	0.7	43.8
Cd	7.2	52	11.0	39.7	1.0	48.3
Co	91	57	2.4	53.9	0.7	43.1
Cr	387	56	3.7	51.5	0.9	43.9
Cu	502	56	4.0	50.9	0.8	44.3
La	305	84	3.3	50.6	30.7	15.5
Li	642	68	17.1	50.4	0.4	32.2
Mo	31	48	5.2	41.5	1.7	51.6
Ni	384	63	11.0	50.7	0.8	37.5
Pb	154	64	12.1	47.1	5.0	35.8
Sr	4392	67	14.3	50.7	1.9	33.2
V	442	60	5.4	54.5	0.5	39.7
Zn	160	54	11.4	35.0	7.9	45.7

Table 4. Distribution of trace elements between bed ash and primary cyclone fines using Daw Mill coal in the pilot scale air-blown gasifier

Trace element input ($\text{mg}\cdot\text{hr}^{-1}$)		Output of trace elements ($\text{mg}\cdot\text{hr}^{-1}$)			Distribution of trace elements	
		bed ash	Fines	Unaccounted	Bed ash (%)	Fines (%)
Ag	0.16	0.03	0.04	0.09	40	60
Ba	97	57	48	0	54	46
Be	0.25	0.05	0.11	0.09	32	68
Cd	0.17	0.05	0.04	0.08	51	49
Co	1.3	0.42	0.82	0.09	34	66
Cr	4.3	1.2	2.3	0.85	35	65
Cu	4.1	1.0	2.7	0.35	27	73
La	1.3	0.48	0.76	0.08	39	61
Li	3.8	1.6	2.0	0.24	44	56
Mo	0.64	0.17	0.48	0	26	74
Ni	4.5	1.2	2.4	1.0	33	67
Pb	3.7	0.54	1.3	1.32	29	71
Sc	0.91	0.14	0.05	0.72	73	27
Sr	11	2.6	6.3	2.04	29	71
V	5.2	1.9	3.9	0	32	68
Y	1.8	2.2	0.1	0	96	4
Zn	3.1	3.0	1.7	0	63	37
Zr	9.1	12.3	0.19	0	98	2