

**TRACE ELEMENTS IN COAL FROM COLLINSVILLE, BOWEN  
BASIN, AUSTRALIA – IN-GROUND MODE OF OCCURRENCE  
AND BEHAVIOUR DURING UTILISATION.**

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**Abstract.**

Analysis of samples gathered during delineation of a coal resource is becoming increasingly sophisticated as various organisations attempt to predict and understand the technological behaviour of the mined product. Analysis to determine the concentration of trace elements in coal is becoming more prevalent, and not just merely for academic curiosity. Increased environmental awareness has impelled the need to consider potential negative impacts on the ecosystem caused by liberation of trace elements from coal during utilisation.

The aims of this thesis are to: 1) Determine the concentration of trace elements in coal seams mined to supply the Collinsville pulverised fuel combustion plant at the Collinsville open cut, Northern Bowen Basin, Australia; 2) Determine the mineralogy and, using graphical relationships, the likely mode of occurrence of trace elements in the sampled pits; 3) Determine the mode of occurrence of trace elements in the pulverised fuel of the Collinsville power plant using the USGS sequential leaching method, and contrast the results with the same analysis for an unrelated fuel from another coal fired power utility (Mitsui Mining's Omutu City plant, Kyushu, Japan); 4) Examine the partitioning behaviour of trace elements in the Collinsville power utility, and contrast the results with the partitioning behaviour of trace elements in the Mitsui combustion utility to assess the influence of trace element mode of occurrence on partitioning behaviour; 5) Examine the mobility of trace elements from solid ash waste from the Collinsville power utility, and compare with the mobility of trace elements from the Mitsui power utility solid waste to assess the influence of mode of occurrence on the leachability of trace elements and; 6) Determine the partitioning behaviour of trace elements in carbonisation of Bowen seam coal at the Bowen coke works and compare with the partitioning behaviour of the same elements in combustion.

Lithotype logging of coal exposed in the highwalls of the Blake Central, Blake West and Bowen No.2 pits was undertaken. Of particular note was the presence of dull heat affected coal toward the roof of the Blake Central pit seam, toward the floor of the

Bowen No.2 pit seam, and the presence of bed-parallel intrusions within the seam in the Blake West pit. In the Blake West pit seam, the intrusion caused thermal alteration of the coal to coke over a 60cm zone immediately adjacent to the intrusion with a further 1.10-1.25m zone of dull heat altered coal beyond the coked zone. In the Blake Central, 4.5m of dull heat-affected coal occurred near the roof of the seam. In the Bowen No.2 pit, 1.2m of heat-affected coal occurred near the floor of the seam. Beyond the heat affected zone, lithotype logging of the Blake seams noted a number of rock partings, but no convincing dulling upward cycles due to progressive drying of the mire, noted in other studies of Permian coal, were found. No partings were found in the Bowen seam and only one convincing dulling upward cycles was logged. In part the absence of dulling upward cycles is due to heat alteration of the coal, but the numerous influxes of sediment laden water into the Blake seam mire also acted to terminate any significant dulling upward cycles by raising both nutrient levels and the water table.

Following lithotype logging, channel sampling of the pits resulted in a total of 76 samples, 25 from the Blake Central pit, 36 from the Blake West pit and 15 from the Bowen No.2 pit. The channel sampling intervals were determined approximately by coal lithotype interval, with some amalgamations to restrict sample numbers. The channel samples were analysed for proximate analysis, coal petrography and vitrinite reflectance (selected samples) and for major and trace elements using XRF and INAA.

The lithotype logs, proximate analysis data and coal petrography were integrated to infer the depositional environment of the Blake and Bowen seams. The generally high ash yield, common stone bands, low sulphur content of the coal and rare pyrite in the Blake seam suggests the depositional environment was a Class 3 topotelmitic peat with a variable water table. The moderate ash yield, the absence of common stone bands, sulphur contents of ~2% and the moderate pyrite content of the coal in the Bowen seam suggests the depositional environment was a Class 2 topotelmitic peat with a high water table.

The igneous intrusions have caused extensive alteration of vitrinite to semi-coke, a general decrease in the volatile matter content and an increase in the vitrinite reflectance [Ro(max)] toward the intrusion.

Mineralogy was calculated from major and trace elements using normative analysis, calibrated by XRD analysis of low temperature ash from selected samples. The mineralogy of the Blake seam samples is dominated by kaolinite, with subordinate quartz, illite, feldspar, and siderite, and minor concentrations of pyrite, gorceixite, goyazite and anatase. The mineralogy of the Bowen seam samples is dominated by kaolinite, with subordinate quartz, illite and pyrite, and minor concentrations of siderite, gorceixite, goyazite and anatase/ rutile/ iron oxides.

The concentration of trace elements in the channel samples was determined by INAA and XRF. The INAA and XRF concentrations of iron and uranium show a reasonable statistical relationship suggesting the two analysis methods are consistent with each other. The concentration of trace elements in the Blake and Bowen seams is generally low compared to world average ranges for coal and to crustal averages. Only gold, copper, hafnium, thorium and ytterbium were found to be above the world coal average range in the Blake seam. Only gold and copper were found to be above world coal average range in the Bowen seam coal.

Trace element mode of occurrence was inferred using graphical relationships between normative mineral and trace element concentrations. In the Blake seam, arsenic, possibly chromium, copper, mercury, nickel and lead were inferred to be associated with pyrite. Bromine, cobalt, selenium, and zinc appeared to be organically bound. Cerium, caesium, europium, lanthanum, rubidium, and scandium showed a graphical relationship with illite. However, cerium, europium, lanthanum and scandium, along with hafnium, lutetium, neodymium, samarium, terbium, thorium, uranium and vanadium also showed a graphical relationship with gorceixite or gorceixite plus goyazite. It was inferred the latter group of elements are associated with monazite or zircon. In addition to the REE phosphate mode of occurrence, some rare earth elements also showed an affinity for

kaolinite. Thorium and uranium were also inferred to be associated with feldspars. Antimony, tantalum and ytterbium were found to be dominantly associated with kaolinite.

In the Bowen seam, arsenic, cobalt, possibly chromium, copper, mercury, molybdenum, nickel, lead, antimony, selenium and zinc showed a graphical relationship with pyrite. The elements cerium, hafnium, neodymium, rubidium, samarium, tantalum, thorium, uranium and tungsten all showed significant graphical relationships with the anatase/ rutile/ FeO grouping of minerals. It is inferred that the relationship is due to the presence of monazite, zircon, xenotime, REE phosphates, tungstates or other trace minerals, the distribution of which mirrors the distribution of the anatase/ rutile/ FeO grouping. Uranium and thorium were inferred to be associated with REE phosphates and zircon respectively, plus illite. The elements bromine, europium, lanthanum, terbium and vanadium were inferred to be associated with illite. A mixed illite/ heavy mineral suite mode of occurrence is inferred for samarium, tantalum, thorium and uranium. The elements caesium, lutetium, scandium, and ytterbium were inferred to be associated with kaolinite.

The effect of igneous intrusions on the concentration of a number of minerals and trace elements was also examined. The presence of semi-coke or an inferred distance of heat alteration was used to distinguish heat affected and unaffected samples. Depletion or enrichment of minerals and elements was inferred using ply thickness weighted average concentration figures for altered and unaltered samples and trends of concentration change toward the intrusion. Some consistent changes in the concentration of trace elements and minerals were found across all three pits sampled. The minerals siderite and pyrite are depleted in the heat affected zone, but goyazite is enriched, particularly toward the margins of the heat affected zone. The elements bromine and strontium (the latter mirroring the goyazite trend) are concentrated in the heat affected zone. The elements cobalt, mercury, manganese (mirroring the pyrite trend), nickel and possibly arsenic and zinc are depleted in heat affected samples from all three pits sampled. The inconsistent behaviour of some other trace elements (molybdenum, chromium and

possibly selenium) in response to the igneous intrusion appears to be the result of different modes of occurrence of trace elements between pits.

Samples of pulverised fuel were collected from the Collinsville and Japanese (Mitsui) pulverised fuel utilities. The concentration of major and trace elements was determined by INAA, XRF and (for the Collinsville sample) ICP-MS & ICP-AES. INAA analysis suggests gold, cerium, cobalt, europium, hafnium, lanthanum, lutetium, molybdenum, neodymium, scandium, selenium, samarium, strontium, tantalum, thorium, tungsten and ytterbium are at the upper end or above the world average concentration range in the Collinsville pulverized fuel. Only gold, hafnium and thorium are at the upper end or above the world coal concentration range in the Japanese pulverized fuel.

Sequential leaching of the pulverised fuels was undertaken according to the USGS protocol. The sequential leach data was interpreted to infer trace element mode of occurrence in the pulverised fuel. A number of significant differences in the mode of occurrence of antimony, arsenic, chromium, cobalt, nickel, selenium, uranium and zinc were found between the two combustion plants studied. The element vanadium had almost identical modes of occurrence in fuel from both plants studied.

A comparison of trace element mode of occurrence determined for the Collinsville power utility pulverised fuel by sequential leaching with mode of occurrence determined for the in-ground feed coals using graphical methods showed a reasonable level of agreement. It is concluded that the use of two methods of determining mode of occurrence provides better definition of mineral type in some cases. For example a siderite mode of occurrence could be determined using graphical relationship whereas the sequential leach data gave only a carbonate mode of occurrence. Further, the sequential leach data solved the problem of parallel graphical relationships. For example, galena was determined to be the mode of occurrence of lead from the sequential leach data, whereas graphical relationships indicated a pyrite mode of occurrence because of the relationship with sulphur.

Combustion of coal occurs in three phases, namely devolatilisation, combustion of the volatile matter, and combustion of the residual char. Mineral matter may be excluded from the residual char particles due to desegregation and separation in the milling process, or included within the char particle. During combustion, trace elements partition between the bottom ash, the fly ash, and flue gas (lost up the stack). The concentration of trace elements in ash samples from the Collinsville and Mitsui power utilities was determined by INAA and XRF. The partitioning behaviour of the trace elements is examined by calculating relative enrichment values for the trace elements. Generally the partitioning behaviour and classification of trace elements in this study matched those found in previous published studies for a given element.

The relative enrichment trends of elements exhibiting significant differences in mode of occurrence between the two combustion plants sampled (ie antimony, arsenic, chromium, cobalt, nickel, selenium, uranium and zinc plus vanadium) were examined to determine the control of mode of occurrence on the partitioning behaviour. It is hypothesised that the relative volatility of a particular element in combustion reflects the temperature at which the host mineral or the organic matter thermally decomposes. Thus organically bound elements should be more volatile than pyrite associated elements, which should be more volatile than carbonate associated elements, which should be substantially more volatile than silicate associated elements. Other factors that may influence partitioning behaviour such as the major element chemistry of the ash, plant design and operating conditions, and temperature variations within the combustion chamber were discounted as significantly influencing relative enrichment differences for the two combustion plants studied. It is concluded that element mode of occurrence has a strong influence on the relative volatility of a given element, and that comparison of sequential leach results from two pulverised fuel utilities has the potential allow prediction of the relative volatility of trace elements in combustion. Some complications may arise due to exclusion of some mineral grains and localised variations in the oxidation state within the combustion zone.

Solid combustion wastes (fly ash and bottom ash) are commonly disposed of in landfill and impoundment facilities. Unless the landfill is impermeable to water, disposal of solid

wastes in such fashion allows interaction with the hydrogeological system and could lead to detrimental environmental impacts. Leaching of indicative “total waste” composites made up by blending fly ash and bottom ash samples from each power utility in an 80/20 proportion was undertaken using the TCLP protocol. The concentration of trace elements in the leachates was compared to recreational water and drinkwater guideline values. The concentration of barium, manganese, and selenium in the Collinsville leachate exceeds both the recreational and drinkwater guideline concentrations. The concentration of nickel in the Collinsville leachate was found to exceed the recommended drinkwater concentration, but is below recreational water guideline value. The concentration of boron and selenium in the Mitsui leachate was found to exceed both the recreational and drinkwater guideline values. The concentration of barium in the Mitsui leachate was found to exceed the drinkwater standard. The concentration of an element in the ash sample was found to be a poor indicator of the mobility of the element.

Elements that showed substantial differences in mode of occurrence in the pulverised fuel (ie antimony, arsenic, chromium, cobalt, nickel, selenium, uranium and zinc plus vanadium) were examined to assess the influence of mode of occurrence on the leachability of the element from solid combustion waste. It is concluded that, where the difference in element mobility between the two composite ash samples is significant, mode of occurrence does exert some control on the proportion of a trace element in the ash that can be mobilised by the TCLP protocol. In particular, trace elements present in coal associated with silicates appear substantially unavailable for mobilisation by the TCLP protocol.

The concentration of trace elements in samples of feed coal, coke and breeze from the Bowen coke works was determined by INAA and XRF. A new index (the CRE index) was developed to characterise the enrichment or depletion of trace elements in the coke and breeze. Coke is classified as enriched (Class 1), neither enriched nor depleted (Class 2), depleted (Class 3) or highly depleted (Class 4). Breeze was classified as enriched (denoted “e”), neither enriched nor depleted (denoted “a”) and depleted (denoted “d”).

Comparison of the partitioning behaviour of trace elements in combustion and carbonisation was undertaken by comparing the RE and CRE data. It is concluded that all but the most volatile elements (sulphur, selenium, arsenic and tungsten) are substantially retained in the coke. The substantial retention of trace elements in coke is likely due to the lower temperature at which carbonisation occurs compared to pulverised fuel combustion temperatures. The behaviour of trace elements in the breeze is similar to their behaviour in combustion, being controlled by mode of occurrence and element volatility. Trace elements associated with pyrite are generally enriched in the breeze, excepting highly volatile elements such as sulphur, selenium and arsenic, which appear to substantially volatilise. Silicate associated elements and those elements associated with heavy minerals are also generally non-volatile excepting tungsten that is depleted in the coke and breeze.

The concentration of trace elements in the pit channel samples and in the pulverised fuel sample suggest the elements barium, selenium, mercury, thorium, copper, manganese, nickel and vanadium warrant further investigation in Collinsville pit and combustion wastes. The data suggests the elements thorium, boron, selenium and barium warrant further investigation in the Japanese combustion plant. Further work to verify that relative differences in mode of occurrence inferred from USGS sequential leaching are useful as indicators of trace element volatility and leachability is recommended.

The environmentally significant trace elements cobalt, molybdenum, antimony, strontium, zinc and possibly arsenic and chromium are enriched in the breeze samples from the Bowen coke works. Leaching studies to determine the proportion and concentration of trace elements in the leachate upon disposal of the waste is worth consideration. Further studies to characterise trace element partitioning during carbonisation in a slot oven are recommended.

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