

## Minerals and Inorganics Associated with South Australian Lignites

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### INTRODUCTION

South Australia is endowed with considerable reserves of low rank Permian to Jurassic sub-bituminous coal and Tertiary lignite. A number of these occurrences have been evaluated since the mid 1970's to assess their suitability for power generation. Of the lignites, the Bowmans (1,600 Mt) and Lochiel (580 Mt) deposits from the Northern St. Vincent Basin have been the subject of extensive research. Both these lignites contain in excess of 50% moisture and very high Na, Cl, and S contents, all of which create problems for any subsequent utilization. Combustion trials on both Bowmans and Lochiel lignites have been conducted as well as pilot scale gasification and circulating fluidized bed combustion tests. As a consequence of this work it has been realised that the non-carbonaceous component of the lignite presents major technical and economic problems.

In the light of this, an extensive research program has been conducted at the S.A. Institute of Technology to determine both the minerals and inorganics present and their distribution in South Australian lignites. A major part of this project was the development of techniques to enable the analysis of minerals using Scanning Electron Microscopy (SEM) with Back Scattered Electron (BSE) imaging, Energy Dispersive X-Ray Spectrography (EDS), X-Ray Diffraction (XRD) and mechanical dewatering to extract water for subsequent analysis.

### LITERATURE REVIEW

The occurrence of non-carbonaceous material in coals has been the subject of much research, especially in relation to its effect on utilization and ash formation ((1)-(7)). In contrast to high rank coals where the coal mineral matter represents the total non-carbonaceous fraction, the low rank coals have two categories of non-carbonaceous material : minerals (discrete particles e.g. quartz, marcasite, clays, etc) and inorganics (water soluble salts and exchangeable ions e.g. NaCl, Na<sub>2</sub>SO<sub>4</sub>, Al<sup>3+</sup>, etc.) ((8), (9)).

Much of the literature published on minerals is based on high rank coals, but can be related to low rank coals ((10)). In general, the silicate minerals represent the major component of the minerals contained in coal. The most common analytical methods for mineral characterisation and analysis are listed in Harvey and Ruch (11) and covered in detail in the "Analytical Methods for Coal and Coal Products" series (12).

The majority of the early studies on inorganics was based on the determination of the chloride content, its mode of occurrence, and why it was present (13). It is only in more recent years with the increase in low rank coal utilization where the inorganics have a considerable economic impact that detailed research on inorganics has been undertaken ((9), ((14)-(17))). This work indicates that the inorganics in low rank coals exist in two forms: as free ions present in the water associated with the coal and as cations exchanged on to the surface functional groups of the coal. Analysis of the inorganics is most commonly done using leaching to extract the inorganics, followed by Atomic Absorption techniques for cations and standard chemical analysis for anions.

## Samples

Typical analyses of the four South Australian lignites are given in Table 1. They are ranked as Lignite B on the ASTM system.

Table 1 South Australian Lignites\*

	Bowmans	Lochiel	Sedan	Kingston
Moisture	56	61	59	53
Higher Heat Value (wet basis)(MJ/kg)	10.6	9.1	9.1	10.6
% Ash (db)	14	16	20	15
% Vol. Matter (db)	46.7	49.9	43.9	46.9
% Sulphur (db)	5.0	2.8	5.5	2.9
% Sodium (db)	1.55	0.95	0.60	0.85
% Chlorine (db)	1.5	0.5	0.25	0.15
<u>Ultimate Analysis</u>				
% C	59.7	57.8	54.7	59.2
% H	3.9	4.7	4.1	4.1
% N	0.4	0.6	0.5	0.6
% O	17.0	18.2	15.0	18.3

\* Data from the Electricity Trust of South Australia

## TECHNIQUES USED IN THIS STUDY

### SEM-BSE /SEM-EDS

A Cambridge Stereoscan 100 Scanning Electron Microscope with a KEVEX Energy Dispersive Spectrography unit was used in all the experimental work. In order to ensure optimum conditions for the analysis, it was necessary for the lignite samples to be in the form of a polished section. Lignite samples were crushed to all passing 2mm and allowed to air equilibrate at 20°C for 2 days. These partially dried samples were then impregnated with epoxy resin. After the resin had set, each sample was polished using diamond paste and kerosene as a lubricant. Prior to viewing under the SEM, each polished section was coated with a fine layer of amorphous carbon using a vacuum arc coater to ensure adequate electrical conductivity to prevent charging.

To enable detection of fine mineral particles, (<20µm) back-scattered electron imaging was used. Once the minerals were detected, the EDS was used for analysis. Selected lignite particles were scanned to determine the distribution of minerals. Mineral types were then differentiated by variation in back scatter intensity and identified using the EDS. The relative proportions (major, minor) and size distributions of the minerals were recorded. The overall surface of the polished section was viewed and "massive" minerals were analyzed and their distribution and size recorded.

Inorganic analysis was conducted in conjunction with the mineral analysis. Particles analyzed previously for mineral content were analyzed for their inorganic content, and an overall analysis conducted. The resultant EDS spectra output was fed into a spreadsheet software package which was adapted by the authors to allow the calculation of a quantitative elemental analysis.

### X-Ray Diffraction

Lignite samples were predried at 105°C for 2 hours to remove the water which is a major impurity component, hence its removal in effect concentrates the mineral species. After drying, the samples were crushed using a mortar and pestle until all passing 75µm. The dried lignite powder was then mounted in a standard aluminium mounting plate and placed in a Philips X-ray Diffractometer with a Rigaku power source. A Co X-ray tube was used to suppress fluorescence of any elemental species. The resultant diffraction pattern was resolved using the JCPDS Fink and Hanawalt Indexes.

### Leaching

Standard procedures using leaching for determining inorganic species in low rank coals are well established. The procedures adopted for this study are given below. All lignite samples were crushed finer than 1mm and dried at 105°C for 2 hours. Samples weighing 2g were mixed with 100ml of distilled water and agitated for 1 hour. The resultant slurry was filtered and analyzed. The amounts of water soluble inorganics were calculated on a dry coal basis. For the acid extraction, 100ml distilled water and 15ml concentrated A.R. nitric acid were added, and the slurry boiled and simmered for 1 hour on a hot plate. The resultant slurry was filtered and analyzed to allow total inorganics present in the sample to be calculated.

### Mechanical Dewatering

The analysis of water soluble inorganics present in the lignites can be calculated from the analysis of water contacted with the lignite as described above. It is uncertain whether water leaching induces any chemical changes (e.g. dissociation of ions from the surfaces of lignite or minerals, etc.). It was therefore considered that a more appropriate means of determining the analysis of water soluble inorganics would be to remove the water from the lignite by mechanical means. Design of equipment capable of mechanically dewatering lignites was obtained from the Grank Forks Energy Technology Centre and CSIRO. Using these designs as a basis, a mechanical press was constructed. The basic criterion for design was that it would dewater a sufficiently large sample of lignite to obtain a suitable volume of water for subsequent analysis.

All the lignite samples were initially crushed to pass 1mm and contact with the atmosphere was kept to a minimum. A lignite sample was placed in the die. The punch (which transfers the pressure from the Avery machine to the lignite) was then placed in the die. The lignite was then pressed against a series of water permeable screens and drainage plates. Under the applied pressure, water was expressed from the lignite sample and exited the dewatering device via the screens and drainage plates, whilst the dewatered lignite was retained on the screens. The expressed water was analyzed by conventional means.

## RESULTS

The inorganics content of the lignite samples is given in Table 2 with the minerals and their distribution given in Table 3.

Table 2 Extractable Inorganics

SAMPLE	EXTn	COMPOSITION (%db)								
		Na	Ca	K	Mg	Fe	Al	Cl	S	SiO <sub>2</sub>
Bowmans	Acid	1.86	0.62	0.05	0.83	1.06	0.28	2.23	3.34	0.53
	Water	1.52	0.10	0.02	0.26	-	0.01	1.98	0.73	0.01
	Press	0.93	0.08	0.01	0.26	-	-	1.90	0.40	-
Lochiel 1	Acid	1.52	0.95	0.05	0.80	0.35	0.28	0.16	2.18	0.41
	Water	1.33	0.02	0.02	0.04	-	-	0.92	0.56	0.01
	Press	0.82	0.07	0.01	0.21	-	-	1.15	0.43	-
Sedan	Acid	0.39	1.59	0.05	0.52	2.16	0.42	0.01	4.32	0.68
	Water	0.39	1.30	1.12	1.19	0.02	0.17	0.12	3.87	0.04
	Press	0.23	0.05	-	0.55	0.08	0.15	0.11	1.38	0.03
Kingston 1	Acid	1.11	1.30	0.12	1.19	0.02	0.27	0.01	1.23	0.42
	Water	0.28	-	0.01	-	-	-	0.24	0.07	0.01

Acid - acid extractable inorganics

Water - water extractable inorganics

Press - inorganics removed by mechanical dewatering.

Table 3 Minerals and Distribution in Lignite Samples

SAMPLE	DISTn	DENSITY	DISTn	MINERAL SPECIES			
				Major	Size Range ( $\mu$ m)	Minor	Size Range ( $\mu$ m)
BOWMANS	-2+0.21mm	medium	even	Si	-500	CaS	-200
				Al, Si	-500	Fe, S	-200
-0.21mm	medium	uneven	Al, Si	-150	CaS	-100	
			Si	-150	NaCl	- 5	
			FeS	-150			
LOCHIEL 1	-2+0.21mm	low	uneven	Si	-500	Fe, S	-200
						Ca, S	-200
-0.21mm	low	uneven	Si	-200	Fe, S	-100	
			Al, Si	-200			
LOCHIEL 2	-2+0.21mm	medium	even	Al, Si	-200	Fe, S	-200
				Si	-500	Ca, S	- 5
KINGSTON 1	-2+0.21mm	medium	even	Si (acic)	- 20	Ca, S	- 20
				Al, Si	-200	Na, Al, Si	-150
-0.21mm	low	uneven	Si (acic)	- 20	Al, Si	- 20	
					Na, Al, Si	- 50	

KINGSTON 2			Si (acic)	- 20	Na,Al,Si	-200
-2+0.21mm	medium	uneven	Al,Si	-500	Fe, S	-200
					Ca, S	- 20
SEDAN			Si	-500	Fe, S	-500
-2+0.21mm	low	even	Ca, S	-500		
			Al, Si	- 50		
-0.21mm	medium	uneven	Ca, S	-200	Fe, S	-200
					Si	-150
					Al, Si	-150

#### Key to Table 3

Elements detected	Species	Elemental Analysis
Si	quartz	SiO <sub>2</sub> *
Si(acic)	acicular quartz	SiO <sub>2</sub>
Fe, S	marcasite	FeS <sub>2</sub> *
Ca, S	gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O*
NaCl	halite	NaCl
Al, Si	kaolinite	Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub> .2H <sub>2</sub> O*
Na, Al, Si	plagioclase	Na <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .6SiO <sub>2</sub>

\* elements detected using XRD

## DISCUSSION

### Analytical Techniques

The procedures developed for the analysis of the minerals and inorganics were the result of an extensive series of scouting tests to determine the optimum conditions for these specific sample types. This was then combined with general procedures for the analytical equipment (i.e. SEM-EDS and XRD units).

### SEM-EDS

The equipment and procedure used had several inherent problems including:

1. Poor sensitivity of the EDS for elements of low atomic number (especially Na and Mg) and an inability to detect elements with atomic numbers less than 10. The software can derive quantitative analysis from a spectrum taking into account the inherent insensitivity of the EDS to those elements whose atomic numbers approach the detection limit.
2. The detection difficulties were then accentuated by the characteristic background x-ray spectrum which was superimposed on the x-ray spectrum of interest. This was overcome by the modelling and subtraction of the background from the acquired x-ray spectrum.
3. Preliminary tests indicated that the distribution of inorganics within a particle could be a function of the rate at which the lignite sample was dried. Rapid drying rates resulted in a concentration of inorganics in the central zone of a particle, whereas slow drying rates resulted in a concentration at the outer perimeter of the particle.
4. To enable quantitative analysis of the inorganics it is necessary to have a known standard. Chemical analysis of the sample to determine the concentration of one species i.e. Cl or S etc. will give a suitable standard.

5. The analysis does not distinguish between minerals and inorganics in the lignite. Despite these drawbacks, it was possible to detect trends occurring in the inorganics associated with the lignite

The technique of BSE images on the SEM screen was ideal for the detection of minerals in low rank coals. The difference in atomic number between the major components of the coal matrix (i.e. C, H, N and O) and the elements present in the mineral species (i.e. Si, Al, Fe, Ca) means that the minerals fluoresce against the dark coal background. Variations in the BSE intensity between minerals was such that the different minerals present were also detectable. Using this technique, however, does in some cases make it difficult to differentiate between quartz and clay (kaolinite) just from a BSE image.

This problem can be overcome to an extent by differentiating between the actual crystal structure which is apparent between quartz, clay and other minerals.

A secondary problem occurs as the low density of the coal matrix allows for a beam penetration to a depth of approximately 10µm. This means that the BSE image represents a surface volume rather than just a plane. Minerals which are subsurface are therefore visible, however their intensity is diminished (e.g. subsurface marcasite can have a similar BSE intensity to clay on the surface).

Analysis of the minerals detected using SEM-EDS was effective with simple minerals, however, determination of clay types was difficult and it was not possible to determine whether a mineral species was anhydrous or hydrated.

### XRD

The limitation of an SEM-EDS analysis of minerals is that it cannot characterise the crystal structure of the minerals present. As a result it is difficult to determine some mineral types i.e.

1. differentiating clay types
2. whether the presence of Fe and S is indicative of pyrite, marcasite or FeSO<sub>4</sub>.
3. minerals which have anhydrous and hydrated forms.

XRD allows the determination of the actual mineral species present. The bulk coal samples resulted in an x-ray pattern with a high background due to the coal matrix. The major mineral species were easily determined however, the minor species could not be detected. As with the SEM-BSE analysis, interpretation of results in a quantitative manner (in relation to the coal) is difficult. The major mineral species detected were quartz, kaolinite, gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) and marcasite (FeS<sub>2</sub>).

Minor mineral species were not detected as their concentration in the samples was below the detection limits for XRD.

### Leaching

The limitation of water leaching is that some species which are not soluble within the coal sample may dissociate on leaching. For the acid leaching, a major problem arises from the dissolution of mineral species. This means that both cations exchanged onto the surface are removed as well as ions from the minerals and it is not possible to determine the amount of ions related to the two different environments.

### Mechanical Dewatering

The design of the mechanical dewatering press is such that there is a limit to the pressure under which the lignite is subjected. The dewatering pressure is one of the major factors determining the extraction of water, and a suitable sample of mechanically removed water

could not be obtained from the Kingston sample. Overall the technique was successful and several good water samples were obtained from the Bowmans, Lochiel and Sedan samples.

#### Data Obtained on South Australian Lignites

##### Inorganics

The inorganics analysis given in Table 2 show that all of the South Australian lignites have high Na, Cl and S contents. The Bowmans lignite has the highest Na and Cl levels of 1.86% and 1.98% respectively.

In general the water soluble inorganics consist of predominantly Na, Cl and S (as  $\text{SO}_4^{2-}$ ) with lesser amounts of Ca and Mg. The Bowmans and Lochiel lignites, both from the St. Vincents Basin, have very high Na, Cl and S as a consequence of the saline environment in this region. The Sedan lignite in contrast has very high Ca and Mg concentrations (1.3 and 1.19% respectively). The Kingston lignite exhibits a relatively low concentration of water soluble inorganics.

Acid leaching results give an indication of the total inorganics present in the coals, including:

- water soluble ions;
- cations exchanged onto the surface functional groups associated with the coal;
- cations exchanged onto the clay minerals
- ions emanating from the dissolution of hydrolysis of minerals.

The water soluble component is easily differentiated, however the other three are not. For the Bowmans, Lochiel and Sedan lignites the acid soluble components (i.e. total inorganics - water soluble inorganics) are predominantly cations (Na, Mg, Ca, Al and Fe) which are exchanged onto the lignite surface. In contrast, for Kingston lignite which has the highest acid soluble component, inorganics are (compared with the water soluble component) associated with ions associated with or exchanged in the clay minerals.

Analysis of the mechanically removed water showed some significant variations especially with respect to Na. It can be seen that for Bowmans, Lochiel and Sedan lignites, the Na content detected by mechanical removal of water is noticeably less than that for the water soluble Na. This aspect of the occurrence and distribution of Na (and Cl) within these samples was discussed in detail in a paper presented by the authors recently (17). The distribution of Na was found to be a function of the high negative surface charge of the coal surface resulting in adsorption of Na at this surface.

##### Minerals

All of the samples analysed showed, as expected, that the major mineral species were quartz and kaolinite (syngenetic), marcasite and gypsum (epigenetic). In general the quartz was present in two distinct size ranges: 500 $\mu\text{m}$  and 50 $\mu\text{m}$ .

One major variation was noted in the two Kingston samples where the majority of the quartz was acicular in form and -20 $\mu\text{m}$  in size. The size distribution of the kaolinite was quite variable and again the Kingston sample differed in that most of the kaolinite had Na associated with it. Marcasite was commonly present as an intimately associated impurity within the coal and in many cases it had replaced the original coal structure (pseudomorphing). The gypsum was present mainly in the -20 $\mu\text{m}$  size range. Overall the mineral matter content of the lignites was in the order of 5-10% (i.e. a medium distribution density).

## SUMMARY AND CONCLUSIONS

Minerals and inorganics from the South Australian lignite deposits have been determined using both standard and specifically developed analytical techniques. Techniques used include SEM-BSE/SEM-EDS, XRD, leaching and mechanical dewatering. The inorganics within the lignite samples showed variations between deposits and within the same deposit. Quartz and kaolinite were the predominant mineral species and these also exhibited major variations within and between deposits.

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