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# Analytical and Characterization Studies of Organic and Inorganic Species in Brown Coal

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Detailed studies have been carried out on the distribution of organic functional groups and inorganic species in as-received (ar) and acid-washed (aw) brown coals using elemental analysis, energy dispersive X-ray analysis (SEM-EDX), X-ray photoelectron spectroscopy (XPS), and Time-of-flight–secondary ion mass spectrometry (TOF–SIMS). Surface concentrations of the various carbon groups, organic oxygen, and inorganic hydroxide were obtained using XPS, but oxygen from clay and quartz, if present, interfered with organic oxygen determinations for the coals. A comparison of ar and aw coals using XPS and SEM-EDX is provided in terms of inorganic and organic sulfur groups. Chloride in these coals is present mainly as acid extractable forms, but small amounts of chloride in the organic matrix were indicated by the elemental analysis of ultra low-ash coals. TOF–SIMS fragments from brown coals were indicative of polymers consisting mainly of single aromatic groups linked by hydrocarbons with carboxyl and phenol functional groups. Sulfur fragments were from inorganic sulfur, thiols, organo-sulfates, and S–N–organic species. Numerous fragments containing organically bound chloride were observed. Fragments of the inorganic species Na, Mg, Al, Si, K, Ca, Ti, Cr, Fe, Mn, Ni, Cu, and Ga were also observed. Environmentally undesirable species, particularly from organo-sulfur and organo-chloride groups in brown coal, are likely to emerge from processes that heat coal–water mixture.

## Introduction

Brown coal is a heterogeneous organic substance containing oxygen, sulfur, nitrogen, chloride, and inorganic species at concentrations ranging from a percentage of the coal weight down to parts per million. Increasingly, more information is needed on the major and minor constituents that are characteristic of brown coal to ensure its efficient and clean utilization.<sup>1–6</sup> For example, the combined effects of volatile inorganic species, including chloride and sulfur, may cause corrosion, fouling, and emissions of pollutants, while trace elements are likely to have an adverse environmental impact. The constituents in brown coal also impact on environmental aspects of coal process technologies; for example, treatment processes that heat coal and water mixtures to high temperatures, such as the hydro-thermal process, release a variety of water-soluble organic

species into wastewater, and these are derived from organo-oxy, organo-sulfur, and organo-chloride groups in the coal.<sup>7</sup> Additionally, processes using acidic coal and water mixtures, such as that of Clean Coal Technology Pty Ltd., release significant amounts of inorganic species and some organic species (depending on the temperature employed) into wastewater streams.<sup>8</sup> It is important, therefore, to be able to characterize organic and inorganic species in these coals to obtain an assessment of likely environmental impacts. It is equally important to develop methodologies and suitable techniques to identify such constituents over a large concentration range.

Although a great deal has been reported on the composition of high rank coals, less is known of the composition of brown coal, particularly about the forms of chloride and sulfur. Chloride exists mainly as inorganic chloride but has also been thought to be associated with the coal matrix. Sulfur has been classified as inorganic sulfide, sulfate, and a variety of organic forms (thiols, sulfides, thiophenes, and sulfones) with little information on the type and extent of the various sulfur functional groups.<sup>9–20</sup> A useful methodology is that of conventional

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(1) Vassilev, S. V.; Tascón, J. M. D. *Energy Fuels* **2003**, *17*, 271–281.

(2) Benson, S. A.; Hurley, J. P.; Zygarrlicke, C. J.; Steadman, E. N.; Erickson, T. A. *Energy Fuels* **1993**, *7*, 746–754.

(3) Srinivasachar, S.; Helble, J. J.; Ham, D. O.; Domazetis, G. *Prog. Energy Combust. Sci.* **1990**, *16*, 303–309.

(4) Pavageau, M.-P.; Peácheyranc, C.; Krupp, E. M.; Morin, A.; Donard, O. F. X. *Environ. Sci. Technol.* **2002**, *36*, 1561–1573.

(5) Danihelka, P.; Volna, Z.; Jones, J. M.; Williams, A. *Int. J. Energy Res.* **2003**, *27*, 1181–1203.

(6) Ting B. T. G.; Manahan, S. E. *Environ. Sci. Technol.* **1979**, *13*, 1537–1540.

(7) Favas, G.; Jackson, W. R. *Fuel* **2003**, *82*, 59–69.

(8) (a) Domazetis, G. *Chem. Aust.* **2004**, *17*, 11–13. (b) Domazetis, G. *Treatment of Wastewater from Coal Cleaning*; Clean Coal Technology Pty Ltd.: 2001; Report RN02.

(9) Barman, B. N.; Cebolla, V. L.; Mehrotra, A. K.; Mansfield, C. T. *Anal. Chem.* **2001**, *73*, 2791–2804.

elemental chemical analysis and non-intrusive examinations of as-received (ar) samples, supplemented by a similar study of the same coal samples after acid treatment (aw). Suitable acid treatment may remove inorganic species, leaving the unaffected coal matrix. Information on the functional groups in coal may be obtained using XPS and TOF-SIMS. XPS detects major elements and their chemical states on the surface of the coal particles and may be used to differentiate between organic and inorganic species, while high-resolution TOF-SIMS may detect inorganic and organic fragments and also fragments from trace constituents.<sup>21–24</sup>

This paper presents studies of a number of ar and aw brown coal samples using conventional elemental analysis, XPS, SEM-EDX, and TOF-SIMS. These techniques are shown to be suitable for detecting and characterizing carbon, oxygen, sulfur, and chloride groups (including organic chloride and organic S–N functional groups) in brown coals.

### Experimental Section

**Coal.** The Australian coal samples used in this study were obtained from the Loy Yang and Yallourn open cut mines at the La Trobe Valley in Victoria, the Lochiel and Bowmans coal fields in South Australia, and the Esperance coal field in Western Australia. German brown coals were supplied by Rheinbraun GBT.

Each coal sample was crushed with an IKA-Werke MF10 impact analytical mill, then passed through a Mesh 10 sieve (1.68 mm opening), thoroughly mixed, and stored in an airtight polyethylene container.

Coal was acid-washed by mixing 100 g of raw coal with 400 mL of a 1:1 solution of deionized water and concentrated HCl, heated, and then stirred at 90–100 °C for >5 h, similar to that previously described.<sup>25</sup> The mixture was then filtered, and the coal was again washed with deionized water and filtered through a Büchner funnel until the pH of the filtrate remained unchanged. Samples of coal were also acid-washed using H<sub>2</sub>SO<sub>4</sub> (for chloride determinations) and also with HCl (for sulfur determinations). All chemicals were AR grade. The aw coal was stored in an airtight polyethylene container.

Selected samples of Loy Yang and German coals with ultra low ash were provided by Clean Coal Technology Pty Ltd. (Australia). Additional samples were prepared for XPS studies to assist in the assignment of oxygen, sulfur, and chloride. These included (a) humic acids extracted from Esperance coal, (b) dried coals mixed

with inorganic sulfates and chloride, (c) poly(acrylic acid) (PAA) and a mixture of known amounts of PAA and tartaric acid, (d) a precipitate obtained by mixing PAA and a solution of iron chloride, (e) a mixture of acid-washed coal with added NaCl and MgSO<sub>4</sub>, (f) chars obtained by heating acid-washed coal with known amounts of iron hydroxide species in a stream of nitrogen at 300 °C, and (g) ash samples.

**Analysis.** Coal samples were analyzed for C, H, O, N, Cl, S, ash, and moisture by the Campbell Microanalytical Laboratory in the University of Otago, New Zealand. The analytical method used is based on the complete and instantaneous oxidation of the sample by “flash combustion”, which converts all organic and inorganic substances into combustion products under conditions sufficient to completely oxidize the coal sample. The sample is held in a tin capsule (containing the catalyst tungstic oxide and copper) and dropped into a vertical quartz tube maintained at a temperature of 1020 °C. The helium carrier gas is temporarily enriched with pure oxygen as the sample is dropped into the tube. Quantitative combustion is achieved by passing the mixture of gases over a catalyst layer and then through copper to remove excess oxygen and reduce nitrogen oxides to nitrogen. The resulting mixture passes into a chromatographic column where carbon dioxide, water, sulfur dioxide, and nitrogen are separated, and quantitative analysis is performed using a thermal conductivity detector. Oxygen is determined using the same methodology, but without added oxygen, in a helium carrier gas and is reported as total oxygen for the sample. Duplicate results were obtained for each element in the coal sample. Error for all analyses is ±0.3 wt %, with duplicates within 0.3 wt %. Ultimate analysis of selected coals was also carried out by the Australian Coal Industry Research Laboratory Ltd. using standard methods.<sup>26</sup>

Total ash for coals with high amounts of sodium was determined by heating a known weight of dry coal to 300 °C to remove volatiles, followed by heating the char to 900 °C to a constant weight. For coals with low amounts of sodium, the char was ashed at 1050 °C to a constant weight. Ash was analyzed using XRF and, for samples with small amounts of ash, using ICP-OES.<sup>27,28</sup>

Coal samples were dried, and moisture was determined by heating the sample in an oven at 105–110 °C for 24 h and then allowing it to cool in a desiccator over P<sub>2</sub>O<sub>5</sub>. This was repeated to a constant sample weight.

Analysis of inorganics, sulfur, and chloride for coal samples supplied by Clean Coal Technology Pty Ltd. was performed at the CSIRO Lucas Heights Science and Technology Centre by dissolving a known weight of coal sample in a fusion flux and performing elemental analysis of the solution using ICP-OES.

**XPS, SEM-EDX, and AAS.** XPS experiments were performed using a Kratos Axis Ultra XPS spectrometer with monochromatized Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV) operating at 150 W. The spectrometer energy scale was calibrated using the Au 4f<sub>7/2</sub> photoelectron peak at binding energy (BE) = 83.98 eV. Spectra were charge corrected with reference to C–C species at BE = 285.0 eV. Such surface charge neutralization was used to effect a slight improvement in peak resolution. Survey and region spectra were collected at 100 and 40 eV pass energies, respectively. The analysis area was 700  $\mu\text{m} \times 300 \mu\text{m}$ .

Spectra were quantified using Kratos XPS elementary sensitivity factor data after background subtraction and the fitting of Gaussian (70%)/Lorentzian (30%) component peaks. The full width at half-maximum (fwhm) of the peaks was maintained constant or within a chosen range for all components in a particular spectrum. Uncertainties for all fitted spectra were estimated to be ±10% of the measured atomic concentrations. The practical detection limit for elements is  $\leq 0.5$  at. %

- (10) Huggins, F. E. *Int. J. Coal Geol.* **2002**, *50*, 169–214.
- (11) Hodges, N. I.; Ladner, W. R.; Martin, L. G. *J. Inst. Energy* **1983**, *56*, 158–169.
- (12) Ward, C. R. *Int. J. Coal Geol.* **2002**, *51*, 135–168.
- (13) Huggins, F. E.; Huffman, G. P. *Fuel* **1995**, *74*, 556–569.
- (14) Huggins, F. E.; Huffman, G. P. *Coal Sci. Technol.* **1991**, *17*, 43–61.
- (15) Martínez-Tarazona, M. R.; Palacios, J. M.; Cardin, J. M. *Fuel* **1988**, *67*, 1624–1628.
- (16) Jiménez, A.; Martínez-Tarazona, M. R.; Suárez-Ruiz, I. *Fuel* **1999**, *78*, 1559–1565.
- (17) Vassilev, S. V.; Eskenazy, G. M.; Vassileva, C. G. *Fuel* **2000**, *79*, 923–938.
- (18) Huffman, G. P.; Shah, N.; Huggins, F. E.; Stock, L. M.; Chatterjee, K.; Kilbane, J. J., II; Chou, M.-I. M.; Buchanan, D. H. *Fuel* **1995**, *74*, 549–555.
- (19) Huggins, F. E.; Srikantapura, S.; Parekh, B. K.; Blanchard, L.; Robertson, J. D. *Energy Fuels* **1997**, *11*, 691–701.
- (20) Gorbaty, M. L.; Kelemen, S. R. *Prepr. Symp. Am. Chem. Soc.; Div. Fuel Chem.* **2000**, *45*, 177–180.
- (21) Buckley, A. N.; Lamb, R. N. *Int. J. Coal Geol.* **1996**, *32*, 87–106.
- (22) McIntyre, N. S.; Martin, R. R.; Chauvina, W. J.; Winder, C. G.; Brown J. R.; MacPhee, J. *Fuel* **1985**, *64*, 1705–1712.
- (23) Sun, X. *Int. J. Coal Geol.* **2001**, *47*, 1–8.
- (24) Dai, S.; Hou, X.; Ren, D.; Tang, Y. *Int. J. Coal Geol.* **2003**, *55*, 139–150.
- (25) Domazetis, G.; Liesegang, J.; James, B. D. *Fuel Process Technol.* **2005**, *86*, 463–486.

(26) Brockway, D. J.; Higgins, R. S. In *The Science of Brown Coal*; Durie, R. A., Ed.; Butterworth Heinmann: Oxford, 1991; Chapter 5.

(27) Metz, J. G. H.; Domazetis, G. *ACHEMA 2000*; DECHEMA: Frankfurt, 2000.

(28) Domazetis, G.; Raoarun, M.; James, B. D.; Liesegang, J. *Energy Fuels* **2005**, *19*, 1047–1055.

**Table 1. Composition of Coal Samples (dry,  $\pm 0.3\%$ )**

sample	% C	% H	% N	% O	% S	% Cl	% ash
Esperance	43.30	3.26	0.37	19.97	3.95	8.82	20.32
Esperance <sup>a</sup>	40.53	3.72	0.28	21.15	4.57	nd	29.75
Esperance <sup>b</sup>	60.82	4.97	0.74	27.63	3.71	0.63	1.49
German	59.49	4.37	0.59	30.42	<0.3	<0.3	4.54
German <sup>b</sup>	63.77	4.27	0.93	30.82	0.3	0.22	0.40
Bowman	48.61	3.65	0.43	28.24	4.87	1.01	13.19
Bowman <sup>b</sup>	59.71	4.83	0.68	28.79	4.26	0.33	1.40
Lochiel	53.42	4.28	0.20	25.16	3.11	0.89	12.95
Lochiel <sup>b</sup>	56.59	4.58	0.59	30.49	3.04	0.26	4.45
Loy Yang <sup>a</sup> -A	63.34	5.19	0.65	28.20	0.37	nd	2.14
Loy Yang-B	62.56	4.88	0.28	26.94	0.90	0.30	4.14
Loy Yang <sup>b</sup>	65.22	5.01	0.51	28.64	0.41	0.10	0.10
Loy Yang <sup>c</sup>	65.45	5.03	0.52	28.78	0.42	<0.1	0.04
humic acid <sup>d</sup>	53.95	4.51	1.07	30.06	6.30	0.62	3.49

<sup>a</sup> O determined by difference, Cl undetermined. <sup>b</sup> aw coal. <sup>c</sup> Demineralized coal. <sup>d</sup> Extracted from Esperance coal.

**Table 2. Elemental Analysis of Coal Samples (daf)**

sample	% C	% H	% N	% O	% S	% Cl
Esperance	54.35	4.09	0.46	25.07	4.96	11.08
Esperance <sup>a</sup>	57.70	5.30	0.40	30.10	6.50	ND
Esperance <sup>b</sup>	63.15	4.86	0.72	27.02	3.63	0.62
German	62.33	4.58	0.62	31.87	<0.3	<0.3
German <sup>b</sup>	63.77	4.27	0.92	30.82	0.3	<0.3
Bowman	55.99	4.21	0.50	32.54	5.61	1.16
Bowman <sup>b</sup>	63.63	4.33	0.73	26.42	4.54	0.35
Lochiel	61.36	4.91	0.23	28.91	3.57	1.02
Lochiel <sup>b</sup>	65.38	4.02	0.68	26.10	3.51	0.31
Loy Yang <sup>a</sup> -A	64.73	5.31	0.67	28.82	0.38	0.10
Loy Yang-B	65.27	5.09	0.30	28.10	0.93	0.31
Loy Yang <sup>a</sup>	65.29	5.01	0.51	28.67	0.41	0.10
Loy Yang <sup>c</sup>	65.45	5.03	0.52	28.78	0.42	<0.1
humic acid <sup>d</sup>	55.89	4.67	1.11	31.15	6.53	0.64

<sup>a</sup> O determined by difference, Cl undetermined. <sup>b</sup> aw coal. <sup>c</sup> Demineralized coal. <sup>d</sup> Extracted from Esperance coal.

The coal samples were all examined using SEM-EDX using a JEOL 840A scanning electron microscope operated at an accelerating voltage of 20kV with a Link Analytical Pentafet thin window X-ray detector with an energy resolution of 144 eV, as described previously.<sup>28</sup> Dried coal samples with relatively large amounts of added iron were also finely ground under hexane and pressed into pellets to study surface iron and oxygen concentration with a decrease in the particle size distribution of the coal sample. Inorganic species in the coal samples were acid extracted for analysis by AAS performed with a GBC 933 Plus atomic absorption spectrometer, as described previously.<sup>28</sup>

**TOF-SIMS.** TOF-SIMS spectra from coal powders and pellets were obtained using a TOF-SIMS IV (Ion-Tof GmbH, Germany) instrument with a reflectron analyzer, a Ga<sup>+</sup> ion source (25 keV), and a pulsed electron flood source for charge neutralization, as previously described.<sup>28</sup> The identification of the relevant peaks in the spectra was performed following appropriate calibration of the mass scale, using an ion fragment library incorporated in the Ion-Tof spectral analysis package.

## Results and Discussion

### Elemental Composition and SEM-EDX of Coal Samples.

The samples used were low-, medium-, and high-ash brown coals containing varying amounts of sulfur and chloride. Elemental analyses data on a dry basis (dry) shown in Table 1 were obtained using the microanalysis method. Analysis data for Esperance and Loy Yang coals were also obtained by conventional coal analysis for comparison. Loy Yang coal samples included two with different amounts of ash (labeled A and B), an aw coal, and a demineralized coal. Table 2 presents the elemental analyses on a dry ash free basis (daf). The heterogeneous nature of brown coal inevitably leads to variations

in analytical results, and although these variations may be minimized by thoroughly mixing the samples, they cannot be removed. Oxygen and chloride have been obtained by direct measurement; the oxygen content includes both inorganic and organic oxygen. Analyses data for ash from the coal samples are shown in Table 3; chloride and sulfur in these ash samples has been retained as salts (NaCl, Na<sub>2</sub>SO<sub>4</sub>, and CaSO<sub>4</sub>). The determination of oxygen by difference for Esperance coal overestimates the value, while for Loy Yang with low ash and chloride, the variation in the values is within that expected for these heterogeneous samples. Methods for directly measuring oxygen have been discussed, including combustion of coal and FTIR analysis of the combustion products<sup>29</sup> and chemical analysis of oxygen functional groups in brown coals.<sup>30</sup> The oxygen measured for samples with high-ash content includes significant amounts of inorganic oxygen present in clays (e.g., Al<sub>2</sub>SiO<sub>5</sub>). The organic oxygen may be estimated by using an approximate correction for inorganic oxygen from clays. This approach may be illustrated for Lochiel coal, which is estimated to contain ~5% clay. The oxygen value in Table 2 for the untreated coal is due to organic oxygen groups, oxygen from small amounts of CaSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> and from clay oxygen; the oxygen for aw coal is the sum of organic oxygen and clay. After correction, the organic oxygen in each of the aw coal samples is estimated at 25.7%.

SEM-EDX provided additional information on the heterogeneous nature of the coal samples, with individual mineral particles including quartz identified in the coal samples. Previous SEM-EDX of coal samples with added iron hydroxyl species has shown that higher concentrations of the iron complex are present on the outer portions of large particles, with smaller amounts in the interior, while the amounts of iron are relatively uniform in the smaller coal particles.<sup>28</sup>

The direct (microanalysis) determination method uses a smaller amount of sample, and as a result, very thorough mixing of the bulk sample was required to ensure the small sample used was representative of the bulk. The errors of the method are given at  $\pm 0.3$  wt %; the duplicate results for each sample have shown maximum differences of  $\pm 0.5$  wt % for C,  $\pm 0.2$  wt % for H,  $\pm 0.2$  wt % for Cl,  $\pm 0.3$  wt % for O, and  $\pm 0.2$  wt % for N and S. The limits for determining the analysis results were within the range typical for brown coal.<sup>26</sup> Acid treatment of the coals removed inorganic sulfur and chloride, Na, K, Mg, and Ca from the coal matrix and also from extraneous mineral particles.

To ensure that coal samples used for studies of S and Cl were not "contaminated" by any acid used in the acid treatment, duplicate results were obtained by providing two samples of the aw coal, one sample treated with HCl and the other with H<sub>2</sub>SO<sub>4</sub>. These coals were then washed with copious amounts of distilled water, and the elemental analysis and SEM-EDX results indicated the acid treatment did not alter either Cl or S in the coal sample.

Figure 1 shows SEM-EDX results for Esperance coal before and after acid treatment. SEM-EDX detects all elements with  $Z \geq 6$  and also provides qualitative information on any extraneous particles allowing differentiation between the inorganics Na, Ca, Mg, Fe, Cl, and S in the coal matrix and any present in discrete mineral particles. The SEM-EDX results of

(29) Solomon, P. R.; Serio, M. A.; Carangelo, R. M.; Bassilakis, R.; Gravel, D.; Baillargeon, M.; Baudais, F.; Vail, G. *Energy Fuels* **1990**, *4*, 319–333.

(30) Murata, S.; Hosokawa, M.; Kidena, K.; Nomura, M. *Fuel Process. Technol.* **2000**, *67*, 231–243.



Table 3. Ash Components in Coal, as a Percentage of the Dry Weight of Coal

sample	% SiO <sub>2</sub>	% TiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% Fe	% Mg	% Ca	% Na	% K	% Cl	% S
Esperance	1.51	0.03	1.54	0.04	1.07	0.35	8.61	0.12	10.44	+ <sup>a</sup>
Esperance <sup>b</sup>	2.65	0.04	1.85	0.19	0.01	0.01	+	+	0.01	+
German	0.02	+	0.02	1.27	0.24	0.66	+	0.01	+	+
German <sup>b</sup>	0.02	0.01	0.01	0.01	+	+	+	+	+	+
Bowman	4.78	0.02	0.63	0.54	1.27	2.42	1.05	0.10	0.60	1.34
Bowman <sup>b</sup>	2.24	0.01	0.14	0.19	0.06	0.04	0.04	0.03	0.00	0.10
Lochiel	8.03	0.06	2.24	0.24	0.80	0.67	1.23	0.12	0.17	0.94
Lochiel <sup>b</sup>	4.72	0.11	1.03	0.44	0.81	1.36	0.42	0.09	0.27	0.43
Loy Yang-A	0.09	0.01	0.11	0.49	0.06	0.03	0.04	0.01	+	+
Loy Yang-B	3.77	0.04	1.51	0.18	0.04	0.00	0.10	0.00	+	+
Loy Yang <sup>b</sup>	0.07	0.01	0.01	+	+	+	+	+	+	+

<sup>a</sup> +, below analytical detection limits. <sup>b</sup> aw coal.

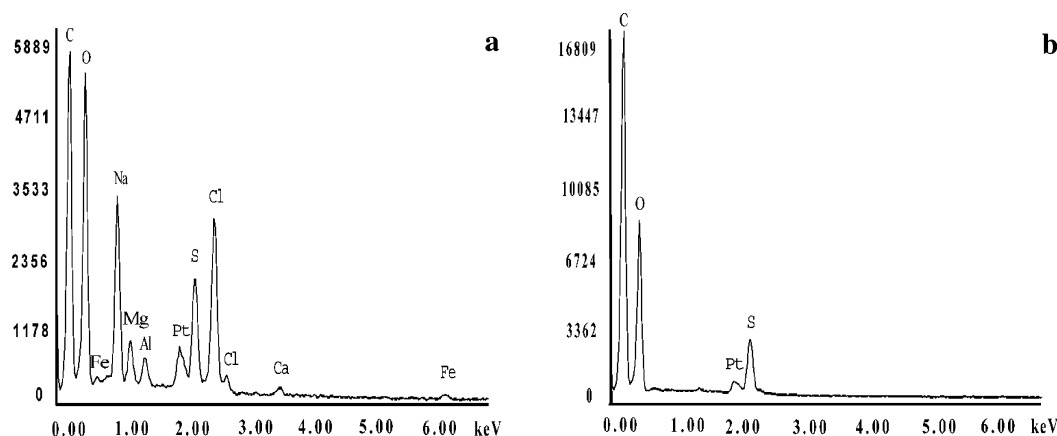


Figure 1. SEM-EDX of Pt-coated (a) ar Esperance coal and (b) aw Esperance coal.

Table 4. Inorganics in Ultra Low-Ash Coal Samples (ppm of the dry sample)

sample	V	Na	Mg	Al	Si	K	Ca	Fe	Ti	Cl	S
Loy Yang	<2	20	<2	20	20	<10	9	9	8	610	2890
German	<1	5	7	19	94	<5	23	42	35	770	4200

acid-treated coals confirmed that inorganics and chloride had been removed to below detection limits and also identified any aluminum- and silicon-containing mineral particles.

The results of the analyses of Loy Yang and German coals with ultra low-ash content, for inorganic constituents, are shown in Table 4. The amount of chloride that remained after treatment with acid (600–800 ppm) represents a small portion of the total chloride in the original coal sample, consistent with the bulk of chloride being acid extractable. A significant amount of sulfur remains after the treatment, consistent with a relatively high portion of organic sulfur in these coal samples.

**XPS.** This technique identifies elements in a sample from binding energies of core electron orbital (BE) and may also provide their chemical state by curve fitting of region scans after subtraction of background. The C 1s BE energies and at. % values from the region scans for a number of ar and aw coals are listed in Table 5. These values are similar to those obtained from black coal, asphaltene, lignite, and peat.<sup>30–34</sup> The variation in the relative surface concentration of the carbon groups is consistent with the heterogeneous nature of brown coals. Average at. % values for carbon groups from aw coals are (standard deviation from the mean given in parentheses): [C/CH] = 52.2 (2.4); [C–O] = 17.2 (1.6); [C=O] = 4.3 (0.8);

[OC=O] = 5.3 (1.6); [ $\pi$ – $\pi$ ] = 1.6 (0.3). Organic oxygen O 1s BE values shown in Table 6 are similar to those from PAA (O 1s C=O 531.7 eV, O 1s C–O 533.3 eV) and a mixture of PAA and tartaric acid (O 1s C=O 532.2 eV and O 1s C–O 533.4 eV). A mixture of PAA and tartaric acid with SiO<sub>2</sub> provides similar O1s values, with an increase in the relative intensity of the 532.2 eV, showing oxygen in SiO<sub>2</sub> contributes to this peak. XPS data for inorganic oxides added to coal are discussed below. The XPS data (after correcting the wt % for hydrogen, assumed at 5 wt %) have been compared with the elemental analysis of the same coal samples (oxygen directly measured), and the ratios of C:O from elemental analysis and XPS analysis are shown in Table 7. In view of the heterogeneous nature of the samples, the data in Table 7 show that XPS C:O ratios may be comparable to those from elemental analysis data, as in the case for Lochiel and Bowman coals; however, the variation in XPS C:O ratios may be significant, as in the case for German, Loy Yang, and Esperance coals, which have shown higher C:O ratios.

Variations in C:O ratios for other coals have been previously discussed and thought to be due to the adsorption of matter on the surface of the samples.<sup>21</sup> For brown coals, the variability is likely to also be due to the inherent heterogeneity of these coals. XPS obtains chemical information on the outermost atomic layers of a material, the analysis depth usually being within the range 0.5–5 nm. C:O ratios have been examined for a number of materials (PAA, tartaric acid, and poly(ethylene terephthalate)) and compared with the values for the coals. SiO<sub>2</sub> and clays that may be present have been shown to interfere, but the variation observed for the brown coals appears to be due mainly to the heterogeneous nature of brown coals and their large surface area. Changes in surface concentrations of Fe and OH from iron hydroxyl species added to brown coal have been

(31) Dehkissia, L. S.; Adnot, A.; Chornet, E. *Energy Fuels* **2004**, *18*, 1744–1756.

(32) Kelemen, S. R.; Kwiatek, P. J. *Energy Fuels* **1996**, *9*, 841–848.

(33) Kelemen, S. R.; Afeworki, M.; Gorbaty, M. L.; Cohen, A. D. *Energy Fuels* **2002**, *16*, 1450–1462.

(34) Grzybnek, T.; Kreiner, K. *Langmuir* **1997**, *13*, 909–912.

Table 5. C 1s BE and At. % from XPS Region Scans of Brown Coals

sample	H-C-C (eV)	at. %	C-O (eV)	at. %	C=O (eV)	at. %	O-C=O (eV)	at. %	shake up (eV)	at. %
ar										
German	285.0	52.6	286.4	16.7	287.5	4.7	289.0	4.0		
Lochiel	285.0	51.0	286.3	18.5	287.6	3.8	289.1	5.8		
Bowman	285.0	43.8	286.5	17.6	287.9	5.8	289.1	5.2		
Loy Yang	285.0	55.8	286.5	16.2	287.6	4.6	289.1	4.2		
Esperance	285.0	53.9	286.4	12.4	287.5	4.9	288.8	3.9		
aw										
German	285.0	50.4	286.6	19.5	288.2	4.3	289.5	4.4	291.5	1.2
Lochiel	285.0	47.1	286.4	19.2	287.8	3.9	289.3	4.7	291.2	1.3
Bowman	285.0	52.2	286.5	15.6	287.6	4.6	289.3	4.7		
Loy Yang	285.0	53.3	286.6	16.5	288.1	3.3	289.3	5.0	291.0	1.9
Esperance	285.0	54.5	286.5	15.6	287.8	3.6	289.3	5.0	291.7	1.7

Table 6. BE and At. % Assignments for Oxygen Groups in aw Brown Coals

sample	C-O (eV)	at. %	C=O (eV)	at. %
German	533.5	12.3	532.1	6.1
Lochiel	533.6	10.1	532.4	11.3
Bowman	533.5	11.4	532.2	8.9
Loy Yang	533.6	12.3	532.2	7.1
Esperance	533.6	10.7	532.1	7.5

Table 7. Carbon and Oxygen from Elemental Analysis and XPS, aw Coals (wt %)

samples	analysis		XPS		C:O ratios	
	C	O	C	O	analysis	XPS
German	65.2	28.8	70.0	24.7	2.26	2.83
Loy Yang	65.3	27.7	69.2	24.2	2.28	2.86
Lochiel	65.4	26.1	64.0	26.3	2.51	2.43
Bowman	63.6	26.4	65.3	25.8	2.41	2.53
Esperance	63.2	27.0	68.4	22.9	2.34	2.99

shown to be attributed to particle sizes and the “woody” nature of portions of the coal samples (see below).

The number of oxygen atoms per 100 carbon atoms obtained from the elemental analysis of the aw coal samples ranged from 30 to 33, while that obtained from the XPS was 24 to 31. Values of oxygen atoms per 100 carbons have been reported as 20.3 for North Dakota-B lignite; 18 for Montana lignite; 18.8 for Beulah Zap lignite; 23.3 for Texas lignite; and 23.5 for Alaska lignite.<sup>32,33</sup>

Conventional chemical analyses of functional groups in brown coals have been reported to identify 54–64 wt % of the total oxygen, leaving 34–46 wt % unaccounted for.<sup>30</sup> As a result, techniques such as <sup>13</sup>C NMR, IR, and XPS have been used in an attempt to provide the complete distribution of oxygen in brown coals. The present XPS data (Table 5) provide the following at. % distribution of carbon–oxygen (average values, with their average deviation in parentheses): [C–O] = 17.2 (1.6); [C=O] = 4.3 (0.8); [OC=O] = 5.3 (1.6). The at. % distribution of oxygen groups (Table 6) is [C–O] = 11.1 (0.7); [C=O] = 7.7 (1.4); ~41% of the oxygen in these coals is identified as carboxyl and carbonyl, and 59% as hydroxyl, phenol and ether. From the distribution of C 1s as [C=O] and [O–C=O], the organic oxygen in brown coals can be distributed as 23% carboxyl, 18% carbonyl, and the remainder 59% distributed among phenol, hydroxyl, ether, and methoxyl groups. Oxygen present as hydroxide in Fe and Ni complexes has also been identified (see below) and differentiated from oxygen in coal carboxyl and phenoxyl groups involved in the formation of iron complexes.<sup>35</sup>

**Inorganics.** Survey and region XPS scans detected inorganic species in brown coal (usually Na, Fe, Ca, Mg Al, Si, Mn, K, and Ti). The XPS spectra of iron compounds consisted of

multiple Fe 2p<sub>3/2</sub> envelopes for Fe<sup>3+</sup> and Fe<sup>2+</sup>, with satellite peak structures often ascribed to shake-up or charge-transfer processes. Fe 2p<sub>3/2</sub> BE values for Fe<sub>2</sub>O<sub>3</sub> were reported at 710.8–711.0 eV and for FeOOH at 711.4 eV; (O<sup>2-</sup> 1s at 530.0–529.9 eV and [OH]<sup>-</sup> at 531.1 eV). O 1s BE values for iron oxides at 531.3 and 530.1 eV have been assigned to Fe–OH and Fe–O, respectively, and for CaO, TiO<sub>2</sub>, and ZrO<sub>2</sub> at 531–532 eV.<sup>25,28,36–39</sup> The region XPS scan of brown coal samples with added Fe and Ni, provided an additional peak at 530 eV assigned to inorganic oxygen,<sup>25</sup> and for PAA/[Fe(III)–OH] (O 1s 530.1 eV).

Organic and inorganic oxygen was identified by XPS for coal and also char samples. Complicated Fe<sup>III</sup> 2p features were observed for coal samples with significant amounts of monomeric and polymeric iron hydroxy species (illustrated in Figure 2b). The concentration of Fe on the surface of these coal samples was considerably larger than that obtained from elemental analysis (the XPS values were as high as 50 wt % of the coal sample, compared with 12–14 wt % obtained from bulk elemental analysis). SEM-EDX of larger particles revealed that most of the iron-hydroxy species were located on the outer layers of the coal particles, particularly ‘woody’ particles.<sup>28</sup> A reduction of their particle size distribution reduced the surface concentrations of Fe<sup>3+</sup> to be between 19 wt % and 35 wt %. Figure 2, panels a–c illustrate the features of XPS region scans for the following: (a) German aw coal, (b) the same coal with 12.4% Fe: (O 1s 530.7 eV, 532.0 eV, and 534.0 eV; Fe<sup>III</sup> 2p<sub>3/2</sub> 710.5 eV), and (c) char prepared from (b) under nitrogen at 500 °C (O 1s, 530.7 532.0, and 534.0 eV; Fe<sup>III</sup> 2p<sub>3/2</sub>, 710.5 eV). The XPS spectra also illustrates the change in the C 1s of C–CH, C–OH, and the O–C=O carbon for samples with high iron concentrations (Figure 2b). The at. % ratios of 285 eV (C–CH) to 286 eV (C–OH) for aw coals and coals with low amounts of iron were 2.7 to 3.4 and increased to 3.8–4.0 for coal samples with large amounts of iron (10–12 at. % Fe). The relative changes are likely to be due to the bonds formed with carboxyl groups, and coordinate bonds formed with phenol groups, with the iron.<sup>35</sup> The XPS of char (Figure 2c) shows that most of the carboxyl groups have disappeared, consistent with loss of these groups during pyrolysis to form CO<sub>2</sub>; the inorganic oxygen (as iron oxides) also increase as the coal mass decreases.

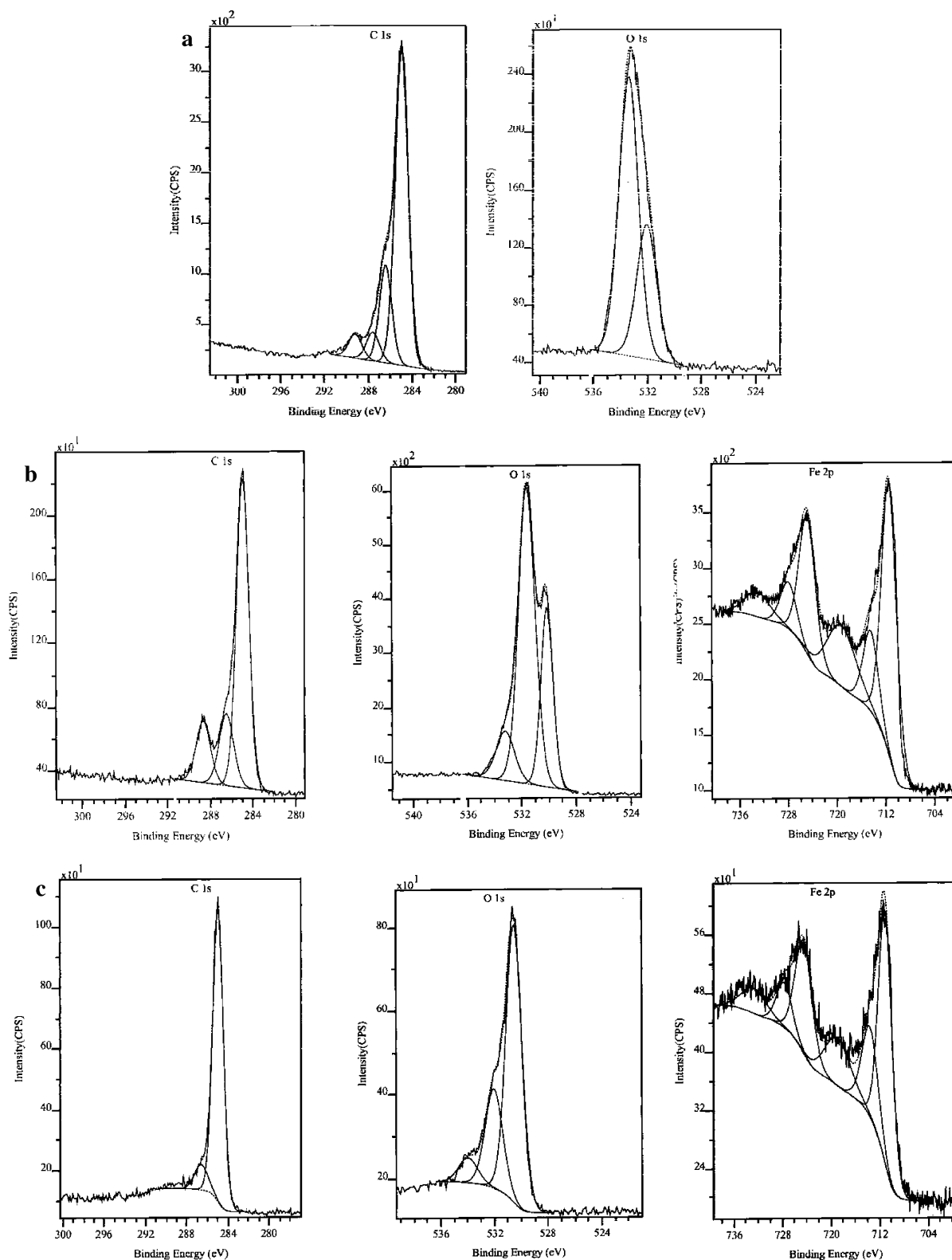
(36) McCafferty, E.; Wightman, J. P. *Surf. Interface Anal.* **1998**, *26*, 549–564.

(37) (a) Grosvenor, P.; Kobe, B. A.; Biesinger, M. C.; McIntyre, N. S. *Surf. Interface Anal.* **2004**, *36*, 1564–1574. (b) Aronniemi, M.; Sainio, J.; Lahtinen, J. *Surf. Sci.* **2005**, *578*, 108–123. (c) Hawn, D. D.; DeKoven, B. B. *Surf. Interface Anal.* **1987**, *10*, 63–74.

(38) Suzuki, S.; Yanagihara, K.; Hirokawa, K. *Surf. Interface Anal.* **2000**, *30*, 372–376.

(39) Dupin, J.-C.; Gonbeau, D.; Vinatier, P.; Levasseur, A. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1319–1324.

(35) Domazetis, G.; James, B. D. *Org. Geochem.* **2006**, *37*, 244–259.



**Figure 2.** Region XPS scans of German brown coal: (a) aw, (b) with 12.4 wt % Fe, (c) char with Fe.

**Sulfur and Chloride.** Organic sulfur is present in coal as alkyl and aryl thiols, thiophenic, and oxidized sulfur, such as sulfones (TOF-SIMS data, discussed below, shows organic S–N groups are also present). Inorganic sulfur is present as sulfate salts and pyrites. The XPS region scans of brown coal (ar and aw) generally provided two doublets for S  $2p_{3/2}$  at 164 and 169.0 eV, which were attributed to thiol sulfur and oxidized sulfur, respectively. Reported BE values are as follows: thiols

S  $2p_{3/2}$  162.0–163.3 eV; thiophenes 164.1 eV; sulfoxides 167.9 eV; sulfones 168.1–168.4; and sulfonic 169.5–170.4 eV; S  $2p_{3/2}$  at 163.3 eV assigned to sulfidic and the S  $2p_{3/2}$  at 164.1 eV to thiophenic.<sup>40–45</sup> The S  $2p_{3/2}$  XPS peak for sulfate salts, such as

(40) Kelemen, S. R.; George, G. N.; Gorbaty, M. L. *Fuel Process. Technol.* **1990**, 24, 425–429.

(41) Zhua, Z.; Gu, Y.; George, S. C.; Wilson, M. A.; Huggins, F. E.; Huffman, G. P. *Coal Sci. Technol.* **1995**, 24, 1681–1684.

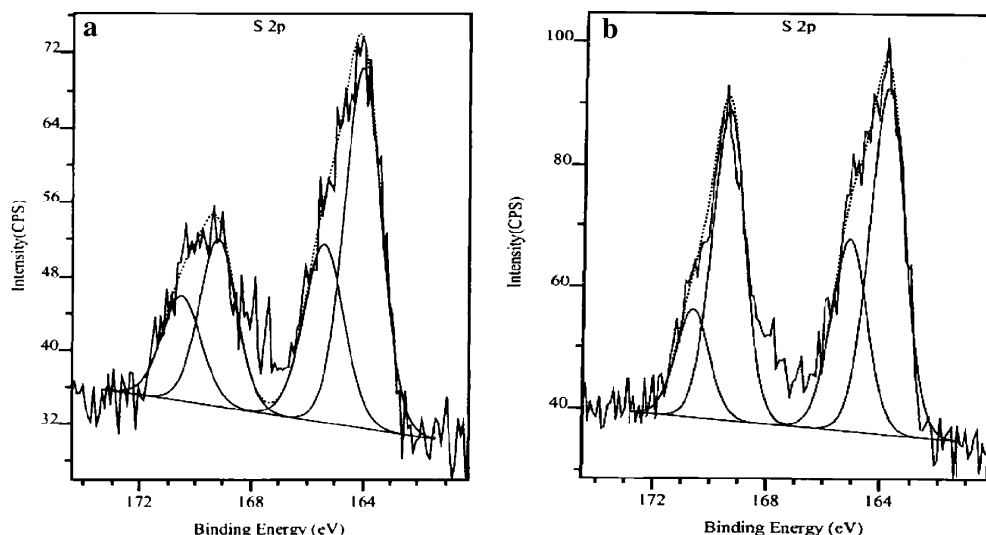


Figure 3. XPS region scan for sulfur (a) Lochiel coal and (b) aw Lochiel coal.

in  $\text{Na}_2\text{SO}_4$  and  $\text{CaSO}_4$ , was at 169–170 eV, and for metals sulfides is in the range 160.0–161.2 eV. XPS (and TOF–SIMS) studies of carbon treated with  $\text{SO}_2$  identified  $\text{HS}^-$  and  $\text{HSO}_4^-$  groups.<sup>46,47</sup>

The relative intensities of the S peaks for aw coals were lower, consistent with the lower sulfur content for these samples observed in the Elemental analysis; the S  $2p_{3/2}$  peak at 164 eV was assigned to thiol sulfur, and the S  $2p_{3/2}$  peak at 169 eV was assigned to oxidized sulfur. Figure 3 illustrates the region scan for Lochiel coal (ar and aw). The region scan of the humic acids extracted from Esperance coal provided almost equal amounts of sulfide and oxidized sulfur. These may be compared with the XPS and XANES values reported for humic acids from leonardite in which 27% of sulfur was assigned to organosulfides and 73% to oxidized organic sulfur.<sup>45</sup> The region scan for acid-washed Esperance coal was similar to that of the extracted humic acid, except the at. % of reduced sulfur (S  $2p_{3/2}$  163.8 eV) was about eight times greater than that of the oxidized sulfur (S  $2p_{3/2}$  169.2 eV). Acid treatment removed inorganic sulfates and pyrites from Esperance coal, the greatest reduction being in the inorganic sulfide (S  $2p_{3/2}$  at 164.1 eV), with a smaller reduction in the sulfate (S  $2p_{3/2}$  169.2 eV). The XPS survey scan of the aw coal did not detect any iron, sodium, magnesium, and calcium that were previously observed in the ar coal.

The XPS region scan for aw Lochiel coal provided peaks due to reduced and oxidized sulfur, similar to those observed for aw Esperance coal. The relative at. % concentrations of un-oxidized to oxidized sulfur was 1.4:1 in the treated coal, compared to the ratio of 3.5:1 for the untreated coal, indicating that inorganic sulfide (pyrites) and sulfates had been removed by the acid treatment. The region scan for untreated Bowman coal contains the features of un-oxidized and oxidized sulfur, with a relative at. % ratio of 0.7:1. The region scan for the aw

coal indicated a reduced amount of oxidized sulfur (S  $2p_{3/2}$  168.0 eV) and provided an organosulfide (S  $2p_{3/2}$  164.0 eV) to organosulfoxide ratio of 4.4:1. The XPS region scan for ar, aw, and demineralized Loy Yang and German coals occasionally detected peaks above the noise assigned to organic sulfide and/or thiophene sulfur, at S  $2p_{3/2}$  164.1 eV; but in most cases the amount of sulfur in these coals was at or below the detection limits of XPS. Region scans of char prepared at 400 °C from German aw coal (in which sulfur has been concentrated due to overall mass loss) revealed reduced sulfur at S  $2p_{3/2}$  164.3 eV and S  $2p_{1/2}$  165.5 eV.

Inorganic chloride was detected for (a) samples of PAA treated with iron chloride; (b) a dry sample made from paste of coal, NaCl, and  $\text{CaCl}_2$ ; (c) ash samples containing chloride; and (d) char samples prepared from coal samples with added chloride salts. These XPS region scans provided BE values that were Cl  $2p_{3/2}$  197.6 to 198.6 eV, ( $2p_{1/2}$  199.3 to 200.2 eV) and for char samples were Cl  $2p_{3/2}$  198.9 eV, ( $2p_{1/2}$  200.5 eV). Inorganic chloride was detected in Esperance, Lochiel, and Bowman coals (Cl  $2p_{3/2}$  at 198.5 eV and Cl  $2p_{1/2}$  at 200.5 eV). The Cl 2p BE values for organic chloride are at 199–201 eV; e.g.,  $\text{C}_6\text{H}_5\text{Cl}$ , Cl 2p at 200–201 eV, and  $\text{CH}_2=\text{CHCl}$  at 199.6–200.3 eV. The inorganic and organic Cl 2p peaks overlap, and the amount of organic chloride is considered low; as a result, detection of organic chloride by XPS, with an acceptable signal-to-noise ratio, may require further work (organic chloride has been detected using TOF–SIMS, discussed below).

The major purpose of this work has been to obtain information characteristic of a range of brown coal samples and to develop techniques for the detection of potentially polluting species, such as organic sulfur and chloride functional groups. This capability is important for developing environmentally friendly coal processing technology. Although a discussion on the nature of waste products from brown coal processing is outside the scope of this paper, an example is illustrative. A mixture of inorganic and organic components were identified in an XPS spectrum of a wastewater sample (after water had been evaporated) with ~30 wt % organic. The region scan for C 1s consisted mainly of C/CH and C–O, and a small amount of O=C=O, indicating mainly organic hydroxyl and a small amount from carboxylic acids. The region scan for oxygen consisted of a broad peak at BE 532–533 eV that could not be resolved. Considerable amounts of chloride (Cl  $2p_{3/2}$  197.6 eV), oxidized sulfur (S  $2p_{3/2}$

(42) Huffman, G. P.; Shah, N.; Huggins, F. E.; Stock, L. M.; Chatterjee, K.; Kilbane, J. J., II; Chou, M.-I. M.; Buchanan, D. H. *Fuel* **1995**, *74*, 549–555.

(43) Grzybek, T.; Pietrzak, R.; Wachowska, H. *Fuel Process. Technol.* **2002**, *77–78*, 1–7.

(44) Marinov, S. P.; Tyuliev, G.; Stefanova, M.; Carleer, R.; Yperman, J. *Fuel Process. Technol.* **2004**, *85*, 267–277.

(45) Olivella, M. A.; del Río, J. C.; Palacios, J.; Vairavarnurthy, M. A.; de las Heras, F. X. C. *J. Anal. Appl. Pyrolysis* **2002**, *63*, 59–68.

(46) Smart, R. S. C.; Skinner, W. M.; Gerson, A. R. *Surf. Interface Anal.* **1999**, *28*, 101–105.

(47) Poleunis, C.; Eynde, X. V.; Grivei, E.; Smet, H.; Probst, N.; Bertrand, P. *Surf. Interface Anal.* **2000**, *30*, 420–424.



Table 8. Negative Chloride Fragments from aw Brown Coals

fragment	<i>m/z</i>	rel int	fragment	<i>m/z</i>	rel int
Cl <sup>-</sup>	34.970	1	C <sub>2</sub> H <sub>3</sub> Cl <sup>-</sup>	61.992	0.007
CCl <sup>-</sup>	46.972	0.002	COCl <sup>-</sup>	62.968	0.011
ClO <sup>-</sup>	50.966	0.004	C <sub>3</sub> H <sub>7</sub> Cl <sup>-</sup>	78.021	0.004

169.4 eV), and Na, Fe, Ca, Mg, Si, Al inorganic species were also present.

**TOF-SIMS.** TOF-SIMS is a surface analysis technique that allows differentiation of molecular fragments sputtered from the surface of the material being analyzed. TOF-SIMS is a very sensitive technique for the detection of a wide range of inorganic and organic species in heterogeneous samples such as coal. Quantification of spectra is difficult and generally only possible by reference to appropriate standards. This is due to the complexity of the ionization process and the impact of the matrix, primary ion properties, and post-ionization behavior on the detected fragments and their yields. Thus the fragments detected provide qualitative data on the functional groups and species on the surface of the coal samples.<sup>21,24</sup> The high mass resolution of the technique enables different species to be distinguished, allows good peak assignments to be made, and thus identifies the various fragments obtained directly from the constituents of the surface of the substance.

Positive and negative mass spectra were obtained for untreated and acid-treated coal samples. The observed hydrocarbon fragments are consistent with a macromolecular matrix consisting predominantly of single phenyl groups connected by aliphatic units, with an abundance of oxygen functionalities, and smaller amounts of organic S, N, and Cl groups. TOF-SIMS data reported for well-characterized polymers containing similar functional groups have been compared with that from the brown coal samples to enable an assessment of functional groups, including oxygen-containing functional groups and organic chloride.

**Negative Fragments Spectra.** The major negative mass fragments for the coal samples studied (relative intensities with O<sup>-</sup> = 100) are typically O<sup>-</sup>(100), OH<sup>-</sup>(59), CH<sup>-</sup>(47), C<sup>-</sup>(20), and C<sub>2</sub>H<sup>-</sup>(19). Fragments of lower intensity were observed for: S<sup>-</sup>(6), CN<sup>-</sup>(3), and Cl<sup>-</sup>(2). All of the brown coals provided similar major negative fragments, but their relative intensities differ; for example, the intensities of the major fragments for German brown coal were O<sup>-</sup> > CH<sup>-</sup> > OH<sup>-</sup> and > C<sub>2</sub>H<sup>-</sup>, but for Lochiel coal, it was O<sup>-</sup> > OH<sup>-</sup> > CH<sup>-</sup> > C<sup>-</sup> and > C<sub>2</sub>H<sup>-</sup>.

The negative sulfur fragments for acid-washed coals were S<sup>-</sup>, HS<sup>-</sup>, SOH<sup>-</sup>, SO<sub>3</sub>H<sup>-</sup>, SO<sub>4</sub><sup>-</sup>, and SO<sub>4</sub>H<sup>-</sup> (S the most intense). The only organic fragment was C<sub>2</sub>H<sub>4</sub>S<sup>-</sup>. Each of the brown coals provided differing intensities of these fragments. Generally coal samples with larger amounts of sulfur provided peaks of greater intensity.

The negative chloride fragments observed for all of the acid-washed brown coals are shown in Table 8, with intensities listed relative to Cl<sup>-</sup> (Cl<sup>-</sup> was the highest intensity fragment, HCl<sup>-</sup> was not detected, and the organic fragments C<sub>2</sub>H<sub>3</sub>Cl<sup>-</sup> and C<sub>3</sub>H<sub>7</sub>Cl<sup>-</sup> were observed). While studies of the mass spectra of coals with extractable chloride have reported HCl, the mass spectra of chlorinated bituminous coals (containing large amounts of organically bound chloride), provided organic fragments such as C<sub>6</sub>H<sub>5</sub>Cl, CHCl<sub>2</sub>, CCl<sub>3</sub>, and C<sub>7</sub>H<sub>5</sub>Cl<sub>3</sub>.<sup>48</sup> Although the bulk of chloride in the brown coal samples is water soluble, a small amount appears to be associated with the organic matrix. Positive fragments, discussed below, are consistent with

organic chloride in brown coal. The detection of organo-chloride is significant because water-soluble organo-chloride compounds (and also organo-sulfur compounds, discussed below) may form and pass into wastewater during coal treatment processes mentioned in the Introduction.

**Positive Fragment Spectra.** The positive fragments from the brown coals have been compared with those observed in TOF-SIMS data from high rank coals.<sup>21,23</sup> Fragments such as C<sub>*n*</sub>H<sub>(*n*+1)}<sup>+</sup>, C<sub>*n*</sub>H<sub>(2*n*-1)}<sup>+</sup>, and C<sub>*n*</sub>H<sub>(2*n*+1)}<sup>+</sup> predominate, with the most intense being C<sub>2</sub>H<sub>3</sub><sup>+</sup>, followed by (decreasing intensities) C<sub>3</sub>H<sub>5</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, C<sub>3</sub>H<sub>7</sub><sup>+</sup>, C<sub>4</sub>H<sub>7</sub><sup>+</sup>, CH<sub>3</sub><sup>+</sup>, C<sub>4</sub>H<sub>9</sub><sup>+</sup>, C<sub>2</sub>H<sub>2</sub><sup>+</sup>, C<sub>4</sub>H<sub>5</sub><sup>+</sup>, and CH<sub>2</sub><sup>+</sup>. Hydrogen-depleted fragments C<sub>*n*</sub>H<sub>(*n*-1)}<sup>+</sup> are not abundant. Fragments indicative of aromatic groups and their intensities relative to C<sub>2</sub>H<sub>3</sub><sup>+</sup> = 100, include [C<sub>5</sub>H<sub>5</sub>]<sup>+</sup> (7.8), [C<sub>6</sub>H<sub>5</sub>-C<sub>2</sub>H<sub>3</sub>]<sup>+</sup> (3.9), and [C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>]<sup>+</sup> (1.8). Resolution of oxygen-containing fragments from hydrocarbon fragments with similar *m/z* values was readily achieved, such as for example, C<sub>4</sub>H<sub>7</sub><sup>+</sup>/C<sub>3</sub>H<sub>3</sub>O<sup>+</sup> (*m/z* 55), C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>+</sup>/C<sub>3</sub>H<sub>7</sub>O<sup>+</sup> (*m/z* 59), and C<sub>4</sub>H<sub>5</sub>O/C<sub>5</sub>H<sub>9</sub> (*m/z* 69). The intensity ratios of these fragments 11/1, 9.6/1, and 8.2/1 are comparable to those observed from the oxygen-containing aliphatic polymer poly(methyl methacrylate).<sup>49</sup> Oxygen fragments obtained from phenol-containing polymers, such as poly(4-vinyl phenol), and from oxidized polyethylene are similar to the fragments from brown coal (e.g., CHO<sup>+</sup>, C<sub>2</sub>H<sub>2</sub>O<sup>+</sup>, C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>, C<sub>2</sub>H<sub>5</sub>O<sup>+</sup>, C<sub>3</sub>HO<sup>+</sup>, C<sub>3</sub>H<sub>3</sub>O<sup>+</sup>, C<sub>2</sub>HO<sup>+</sup>, C<sub>7</sub>H<sub>5</sub>O<sup>+</sup>, C<sub>7</sub>H<sub>7</sub>O<sup>+</sup>, CHO<sub>2</sub><sup>+</sup>, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>+</sup>, and C<sub>4</sub>H<sub>7</sub>O<sup>+</sup>).<sup>50</sup> Thermo-gravimetry-photoionization mass spectrometry studies of coals of various rank provided C<sub>*n*</sub>H<sub>2*n*</sub>O fragments indicative of the fragmentation of alkenols and aldehydes.<sup>51,52</sup> Such a series has been observed only for *n* = 1–4 in our studies (i.e., up to C<sub>4</sub>H<sub>8</sub>O<sup>+</sup>). The TOF-SIMS data for the brown coal are thus indicative of a polymeric substance containing phenolic and carboxyl groups linked by hydrocarbons. Fragments indicating condensed phenyl groups were not observed in these studies.</sub></sub></sub></sub>

Positive inorganic fragments were observed from Na, Mg, Al, Si, K, Ca, Ti, Cr, Fe, Mn, Ni, Cu, and Ga species in the coal samples. Typically, positive fragments obtained from a German brown coal were Al<sup>+</sup>, Ca<sup>+</sup>, CaH<sup>+</sup>, CaO<sup>+</sup>, CaOH<sup>+</sup>, Cr<sup>+</sup>, CrO<sup>+</sup>, Fe<sup>+</sup>, FeH<sup>+</sup>, FeO<sup>+</sup>, FeOH<sup>+</sup>, FeS<sup>+</sup>, K<sup>+</sup>, Mg<sup>+</sup>, MgH<sup>+</sup>, MgOH<sup>+</sup>, Mn<sup>+</sup>, Na<sup>+</sup>, NaHS<sup>+</sup>, Na<sub>2</sub><sup>+</sup>, Si<sup>+</sup>, SiH<sup>+</sup>, SiOH<sup>+</sup>, SiH<sub>2</sub>O<sup>+</sup>, and SiH<sub>3</sub>O<sup>+</sup>. The fragments from the acid-washed coal were similar, but the relative intensities were significantly lower: Al<sup>+</sup>, Ca<sup>+</sup>, Fe<sup>+</sup>, Cr<sup>+</sup>, Si<sup>+</sup>, Ga<sup>+</sup>, SiHO<sub>3</sub><sup>+</sup>, Mg<sup>+</sup>, SiH<sup>+</sup>, SiHO<sup>+</sup>, FeH<sup>+</sup>, Na<sup>+</sup>, CrH<sup>+</sup>, FeO<sup>+</sup>, FeOH<sup>+</sup>, K<sup>+</sup>, CrO<sup>+</sup>, and Ti<sup>+</sup>. For example, the intensity of Ca<sup>+</sup> from the untreated coal (relative to the major positive hydrocarbon fragment C<sub>2</sub>H<sub>3</sub><sup>+</sup>) was 62.7, while for the acid-washed coal this was 2.1. This trend was observed for Na, Mg, Ca, and Fe. The intensities of Al and Si, however, were similar for both samples because clays in the coal were not removed by the acid treatment. Low intensity positive fragments were observed from minor inorganic species, including Cr, Ni, Cu, Ga, and Mn for ar and aw coal samples. It is likely that the nature of the inorganic fragments observed in these studies is influenced by the interaction of the inorganic with the brown coal organic matrix.<sup>53</sup>

The sulfur-containing positive fragments have been observed for untreated and acid-washed coal samples and were of

(49) Briggs, D.; Fletcher I. W.; Gonçalves, N. M. *Surf. Interface Anal.* **2000**, 29, 303–309.

(50) Liu, S.; Weng, L.-T.; Chan, C.-M.; Li, L.; Ho, N. K.; Jiang, M. *Surf. Interface Anal.* **2001**, 31, 745–753.

(51) Zoller, D. L.; Johnston, M. V. *Energy Fuels* **1999**, 13, 1097–1104.

(52) Briggs, D.; Brewis, D. M.; Dahm R. H.; Fletcher, I. W. *Surf. Interface Anal.* **2003**, 35, 156–167.

(53) Briggs, D.; Fletcher I. W. *Surf. Interface Anal.* **1997**, 25, 167–176.

(48) Fynes, G.; Herod, A. A.; Hodges, N. J.; Stokes, B. J.; Ladner, W. R. *Fuel* **1988**, 67, 822–830.

**Table 9. Positive Sulfur Fragments from the Samples of Brown Coals**

fragment	<i>m/z</i>	fragment	<i>m/z</i>	fragment	<i>m/z</i>
S <sup>+</sup>	31.971	C <sub>6</sub> H <sub>7</sub> S <sup>+</sup>	111.028	C <sub>4</sub> H <sub>13</sub> SN <sub>3</sub> <sup>+</sup>	135.084
HS <sup>+</sup>	32.979	C <sub>5</sub> H <sub>10</sub> SN <sup>+</sup>	116.054	C <sub>3</sub> H <sub>13</sub> SN <sub>4</sub> <sup>+</sup>	137.086
H <sub>3</sub> S <sup>+</sup>	34.997	C <sub>5</sub> H <sub>11</sub> SN <sup>+</sup>	117.063	C <sub>3</sub> H <sub>12</sub> SN <sub>3</sub> O <sup>+</sup>	138.072
CH <sub>2</sub> S <sup>+</sup>	45.989	C <sub>5</sub> H <sub>12</sub> SN <sup>+</sup>	118.069	C <sub>7</sub> H <sub>11</sub> SN <sup>+</sup>	141.062
CH <sub>3</sub> S <sup>+</sup>	46.996	SiCH <sub>9</sub> SN <sub>3</sub> <sup>+</sup>	123.029	CH <sub>13</sub> SN <sub>5</sub> O <sup>+</sup>	143.083
C <sub>2</sub> H <sub>3</sub> S <sup>+</sup>	58.996	SiH <sub>9</sub> SN <sub>4</sub> <sup>+</sup>	125.032	C <sub>6</sub> H <sub>13</sub> SNO <sup>+</sup>	147.074
C <sub>2</sub> H <sub>5</sub> S <sup>+</sup>	61.014	C <sub>2</sub> H <sub>11</sub> SN <sub>3</sub> O <sup>+</sup>	125.062	C <sub>5</sub> H <sub>11</sub> S <sub>2</sub> N <sup>+</sup>	149.033
S <sub>2</sub> <sup>+</sup>	63.944	SiH <sub>10</sub> SN <sub>4</sub> <sup>+</sup>	126.039	C <sub>4</sub> H <sub>12</sub> O <sub>4</sub> S <sup>+</sup>	152.055
CHSO <sub>2</sub> <sup>+</sup>	76.971	CH <sub>7</sub> SN <sub>2</sub> O <sub>3</sub> <sup>+</sup>	127.018	C <sub>6</sub> H <sub>14</sub> O <sub>4</sub> S <sup>+</sup>	162.070
C <sub>4</sub> H <sub>7</sub> S <sup>+</sup>	87.028	SiH <sub>11</sub> SN <sub>4</sub> <sup>+</sup>	127.048	C <sub>5</sub> H <sub>11</sub> O <sub>4</sub> S <sup>+</sup>	163.044
CH <sub>4</sub> SNO <sub>2</sub> <sup>+</sup>	93.997	C <sub>6</sub> H <sub>10</sub> SN <sup>+</sup>	128.054	C <sub>5</sub> H <sub>14</sub> O <sub>4</sub> S <sup>+</sup>	166.066
C <sub>3</sub> H <sub>3</sub> SN <sup>+</sup>	98.979	C <sub>6</sub> H <sub>11</sub> SN <sup>+</sup>	129.063	C <sub>7</sub> H <sub>6</sub> SO <sub>3</sub> <sup>+</sup>	169.993
C <sub>3</sub> H <sub>7</sub> S <sup>+</sup>	99.028	C <sub>4</sub> H <sub>6</sub> SN <sub>2</sub> O <sup>+</sup>	130.020	C <sub>6</sub> H <sub>16</sub> O <sub>4</sub> S <sup>+</sup>	180.081
C <sub>4</sub> H <sub>9</sub> SN <sup>+</sup>	103.047	C <sub>6</sub> H <sub>12</sub> SN <sup>+</sup>	130.069	C <sub>9</sub> H <sub>13</sub> O <sub>2</sub> S <sup>+</sup>	181.072
C <sub>2</sub> H <sub>3</sub> SO <sub>3</sub> <sup>+</sup>	106.975	SiCH <sub>4</sub> SN <sub>4</sub> <sup>+</sup>	131.993	C <sub>7</sub> H <sub>13</sub> O <sub>4</sub> S <sup>+</sup>	189.062

**Table 10. Positive Chloride Fragments from All Brown Coals**

fragment	<i>m/z</i>	fragment	<i>m/z</i>
CCl <sub>1</sub> <sup>+</sup>	46.970	C <sub>11</sub> H <sub>18</sub> Cl <sup>+</sup>	185.104
CH <sub>2</sub> Cl <sup>+</sup>	48.988	C <sub>12</sub> H <sub>8</sub> Cl <sup>+</sup>	187.035
C <sub>3</sub> H <sub>5</sub> Cl <sub>2</sub> <sup>+</sup>	110.977	C <sub>14</sub> H <sub>17</sub> Cl <sup>+</sup>	220.098
CCl <sub>3</sub> <sup>+</sup>	116.904	C <sub>13</sub> H <sub>11</sub> Cl <sup>+</sup>	226.060
C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> Cl <sup>+</sup>	134.013	C <sub>15</sub> H <sub>12</sub> Cl <sup>+</sup>	227.066
C <sub>10</sub> H <sub>9</sub> Cl <sup>+</sup>	164.043	C <sub>15</sub> H <sub>14</sub> Cl <sup>+</sup>	229.077
C <sub>10</sub> H <sub>16</sub> Cl <sup>+</sup>	171.090	C <sub>16</sub> H <sub>11</sub> Cl <sup>+</sup>	238.075
C <sub>10</sub> H <sub>17</sub> Cl <sup>+</sup>	172.099	C <sub>18</sub> H <sub>14</sub> Cl <sup>+</sup>	265.070
C <sub>11</sub> H <sub>8</sub> Cl <sup>+</sup>	175.026		

relatively low intensity. Overall, the sulfur fragments originated from thiol and sulfone groups in the coal samples, consistent with the XPS data. While the fragments listed in Table 9 are representative of the brown coal samples, individual coals also exhibit different sulfur-containing fragments. A number of S- and N-containing fragments were observed (e.g., the fragment C<sub>5</sub>H<sub>10</sub>SN<sup>+</sup> may be due to a sulfur-substituted piperidine group). The C:H ratios for fragments C<sub>4</sub>H<sub>9</sub>SN<sup>+</sup>, C<sub>5</sub>H<sub>11</sub>SN<sup>+</sup>, and C<sub>6</sub>H<sub>12</sub>SN<sup>+</sup> indicate aliphatic species, such as for example, [H<sub>2</sub>NCH<sub>2</sub>—CH<sub>2</sub>—CH=CH—SH]<sup>+</sup>. The sulfur fragments S<sup>+</sup>, HS<sup>+</sup>, H<sub>3</sub>S<sup>+</sup>, and S<sub>2</sub><sup>+</sup> were of low intensity, while C<sub>2</sub>H<sub>3</sub>S<sup>+</sup> and C<sub>2</sub>H<sub>5</sub>S<sup>+</sup> were observed only for Lochiel coal. Loy Yang and German coals instead provided the low *m/z* fragments CH<sub>2</sub>S<sup>+</sup> and CH<sub>3</sub>S<sup>+</sup>. The fragments C<sub>4</sub>H<sub>12</sub>O<sub>4</sub>S<sup>+</sup> and C<sub>4</sub>H<sub>7</sub>S<sup>+</sup> are indicative of organic sulfates and thiol groups. Lochiel coal gave oxidized sulfur fragments of higher *m/z* values (C<sub>7</sub>H<sub>6</sub>SO<sub>3</sub><sup>+</sup>, C<sub>6</sub>H<sub>16</sub>O<sub>4</sub>S<sup>+</sup>, C<sub>7</sub>H<sub>13</sub>O<sub>4</sub>S<sup>+</sup>, C<sub>8</sub>H<sub>14</sub>O<sub>4</sub>S<sup>+</sup>, and C<sub>9</sub>H<sub>13</sub>O<sub>2</sub>S<sup>+</sup>), which may originate from aromatics and substituted phenols; e.g., C<sub>6</sub>H<sub>7</sub>S<sup>+</sup>, C<sub>7</sub>H<sub>6</sub>—SO<sub>3</sub><sup>+</sup>, CH<sub>3</sub>—(O)C<sub>6</sub>H<sub>3</sub>—SO<sub>2</sub><sup>+</sup>, CH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)SO<sub>3</sub><sup>+</sup>, and C<sub>6</sub>H<sub>5</sub>—CHSO<sub>3</sub><sup>+</sup>. The nature of these sulfur groups, oxidized sulfur groups, and S—N-containing fragments also indicates that a number of polluting organo-sulfur species may be released into wastewater when coal—water mixtures are heated to elevated temperatures, and further study of the surface of evaporated residues from wastewater is required.

The positive chloride-containing fragments listed in Table 10 show that organic chloride is present in all of the brown coals. All of the fragments were of low intensities as compared to the hydrocarbon peaks. The major positive fragment for Lochiel and Loy Yang coals was C<sub>11</sub>H<sub>18</sub>Cl<sup>+</sup>, but for the German coal it was C<sub>15</sub>H<sub>12</sub>Cl<sup>+</sup>. Lochiel also contained the positive fragment CCl<sub>3</sub><sup>+</sup>. The fragment C<sub>11</sub>H<sub>18</sub>Cl<sup>+</sup> indicates that chloride may be part of either aliphatic or aromatic groups. The fragments C<sub>11</sub>H<sub>18</sub>Cl<sup>+</sup> and C<sub>15</sub>H<sub>12</sub>Cl<sup>+</sup> observed in the spectra of German coals may also be derived from phenyl-alkyl and aliphatic groups. Fragments include those considered diagnostic of

chloride-containing polymers such as poly(vinyl chloride) (e.g., CH<sub>2</sub>Cl<sup>+</sup>, C<sub>3</sub>H<sub>5</sub>Cl<sub>2</sub><sup>+</sup>).<sup>49,54</sup>

**Functional Groups and Inorganics in Brown Coals.** Negative fragments include S<sup>−</sup>, Cl<sup>−</sup>, and Br<sup>−</sup>; Br<sup>−</sup> is a minor constituent. Fragments were observed from Na, K, Mg, Al, Si, Ca, Ti, Fe, Cr, Ni, Cu, and Ga in brown coal.

The sulfur observed using TOF—SIMS is from un-oxidized and oxidized sulfur, consistent with the XPS spectra previously discussed. The data also shows (S,N)-organo groups are present in brown coals, although full identification of such groups will require additional studies.

The detection of organo-chloride fragments indicates that a small amount of chloride is covalently bonded to carbon in brown coal. Although most of the chloride is extractable and thus noncovalently bonded, consistent with previous reports,<sup>11</sup> this study has provided the first direct evidence of organically bound chloride in brown coal. It has been suggested that “bound” chloride may be present as part of a quaternary nitrogen chloride groups within the coal matrix. Mass spectral data from a quaternary chloride salt, however, did not provide organo-chloride fragments, while that from samples of chlorinated coal has shown that covalently bonded chloride in coal gives rise to a number of organic fragments, such as CHCl<sub>2</sub>, CCl<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>Cl, C<sub>7</sub>H<sub>5</sub>Cl<sub>3</sub>,<sup>33</sup> similar to the positive fragments observed from the brown coal samples in this paper.

## Conclusion

Studies of ar and aw brown coal samples, using a combination of elemental analysis, SEM-EDX, XPS, and TOF—SIMS have provided information on the major and minor constituents in these coals.

The organic and inorganic oxygen in brown coals may be differentiated using XPS, but oxygen from aluminosilicate clays can interfere. Forms of organic sulfur can be identified using XPS data for aw coal samples.

TOF—SIMS fragments from brown coal samples indicate aromatic groups with aliphatic linkages, containing carboxyl and phenyl groups. Sulfur-containing fragments from aw coals consisted of thiols, oxidized sulfur, and groups containing sulfur and nitrogen. Although chloride in brown coal is predominantly inorganic, organically bound chloride has been detected using TOF—SIMS.

A number of the sulfur and chloride organic groups identified may provide polluting species, especially if brown coal and water mixtures were heated at elevated temperatures; potentially polluting species would include organic hydroxyl, organic sulfur (reduced sulfur, oxidized sulfur, and S—N compounds), and organo-chlorides.

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(54) Aubriet, F.; Poleunis, C.; Bertrand, P. *J. Mass Spectrom.* **2001**, *36*, 641–665.