# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1. Coal studied

The Tshikondeni coal studied was submitted to Coal and Mineral Technologies (Pty) Ltd for proximate and ultimate analysis, major ash analysis and the determination of major petrographic characteristics. Table 4.1 lists the results for the proximate analysis on an air-dry basis and the ultimate analysis. Table 4.2 lists the major ash percentages. The major petrographic characteristics of Tshikondeni coal are shown in Table 4.3. The coal is classified as meta-bituminous (medium rank B), similar to the coal used by Stiller et al. [107 - 109], and has a vitrinite content of 93%.

**Table 4.1: Proximate (air-dry-basis) and ultimate analysis of Tshikondeni coal**

| **PROXIMATE ANALYSIS** | | **ULTIMATE ANALYSIS (DRY ASH FREE)** | |
|---|---|---|---|
| Moisture | 0.9% | Carbon | 90.86% |
| Ash | 9.4% | Hydrogen | 4.88% |
| Volatile matter | 23.3% | Nitrogen | 2.07% |
| Fixed carbon | 66.4% | Oxygen (by difference) | 2.19% |
| Total sulphur | 0.81% | | |

### Table 4.2: Ash analysis of Tshikondeni coal

| | |
|---|---|
| $SiO_2$ | 51.4% |
| $Al_2O_2$ | 25.5% |
| $Fe_2O_3$ | 6.00% |
| $P_2O_5$ | 0.82% |
| $TiO_2$ | 2.24% |
| CaO | 5.05% |
| MgO | 2.52% |
| $K_2O$ | 1.46% |
| $Na_2O$ | 0.36% |
| $SO_3$ | 4.45% |
| **TOTAL** | **99.79** |

### Table 4.3: Major petrographic characteristics

| | |
|---|---|
| Rank (ECE-UN In SEAM Classification) | Meta-bituminous (Medium Rank B) |
| Mean random reflectance | 1.33 |
| Vitrinite-class distribution | V 10 to V 16 |
| Standard deviations | 0.177 |
| Abnormalities | Extended vitrinte-class distribution |
| **Petrographic composition**<br>Maceral analysis: | |
| Vitrinite content % | 93 |
| Liptinite content % | <1 |
| Total reactive maceral % | 94 |
| Total inertinite % | 6 |
| More highly reflecting material % | 1 |
| Cracks and fissures | Occasionally observed |
| Signs of advanced weathering/thermal effects | Very occasionally seen |

## 4.2 Dissolution of coal and Refcoal recovery

Figure 4.1 is a plot of absorbance (section 3.3 above) versus time, showing the progress of the different extraction runs with sodium hydroxide and dimethylformamide only. The data for the different extraction runs are given in Appendix 2, Table A2.1. The extraction process shows S-shape progression nature of the CSIR-developed Refcoal process, as reported [4,112,120]. All the curves show an induction period of about 15 minutes, which is representative of the S-shape progression. The maximum absorbance was about 1.00; this is consistent with the literature report [112,120] which implies that the solution obtained was an 8% solution. The Refcoal is recovered from the solution either by evaporating the solvent or by precipitation in water. Recovery of Refcoal by precipitation is preferred because, as reported in the literature, this lowers the amount of ash in the Refcoal, furthermore, Refcoal recovered by precipitation forms better coke. Therefore, for the purpose of this study, the Refcoal was recovered by precipitation in water.

As reported, $H_2S$ together with propane-triol aids in the demetalation of porphyrins. It was reasoned that a promising approach would be to introduce $Na_2S$ into the extraction vessel during extraction to aid in complexing the metal ions released and thus precipitate them with the rest of the residue separated from the Refcoal solution. Not all the elements are likely to be associated with the porphyrin-type complexes, with nitrogen bonding to the central metal atom. Oxygen-loving elements such as boron, titanium, zirconium and tungsten are more likely to be associated with the polyhydroxy, or hydroxy-acid types of compound.

It was noticed that, on coking, the Refcoal derived from extraction with both sodium hydroxide and sodium sulphide hydrate swells better than the Refcoal derived from extraction with sodium hydroxide only.The better swelling implies that the Refcoal extracted with both sodium hydroxide and sodium sulphide goes through a more liquid phase, which suggests a better mesophase.

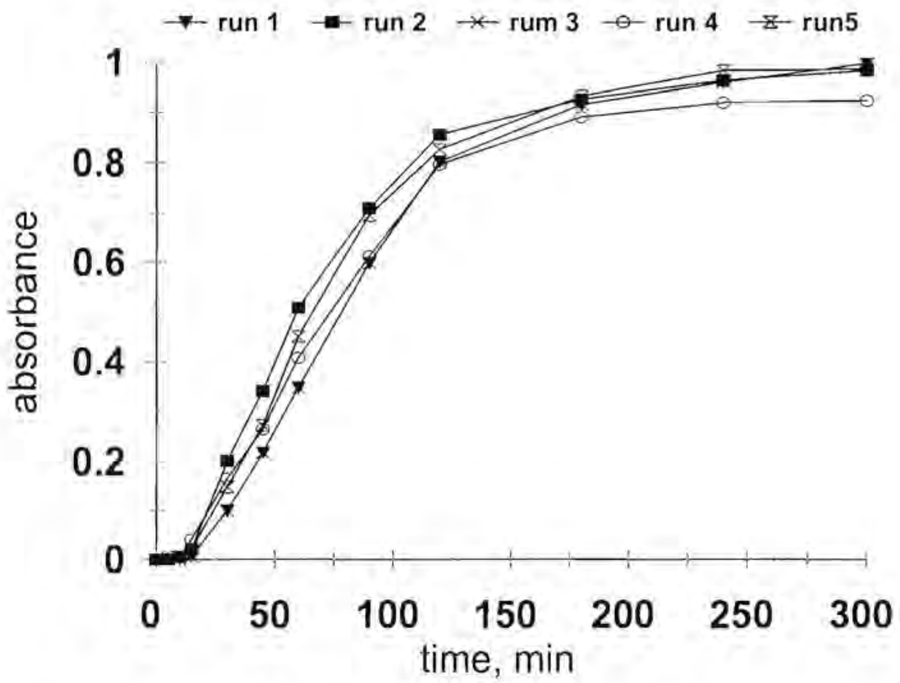

**Figure 4.1:** **Progress of extraction with NaOH only showing reproducibility of the method. Mass ratio used is 100:10:1, DMF:Coal:NaOH**

The swelling was determined at Coal and Mineral Technologies (Pty) Ltd by measuring the change in volume as the sample is taken from low temperature to about 500 °C in an inert atmosphere. Table 4.4 lists the swelling numbers for the Refcoal extracted with sodium hydroxide only and that extracted with both sodium hydroxide and sodium sulphide. Refcoal extracted with sodium hydroxide only gave a swelling number of 4.5, while Refcoal extracted with both sodium hydroxide and sodium sulphide gave swelling numbers of 9.0 and 9.5.

**Table 4.4: Ash contents and swelling numbers of Refcoal**

| Mole ratio ($NaOH:Na_2S$) | Ash (%) | Total sulphur (%) | Swell (#) |
|---|---|---|---|
| 1 : 0 | 1.7 | 0.72 | 4.5 |
| 2 : 1 | 1.2 | 0.78 | 9 |
| 4 : 1 | 7.4 | 1.03 | 9.5 |
| 8 : 1 | 5.6 | 1.78 | 9 |
| 1 : 1 | 3.3 | 1.12 | 9.5 |

**Table 4.5: Percentage solids in Refcoal derived from the extraction with sodium sulphide**

| mass of $Na_2S$ | with sodium hydroxide | without sodium hydroxide |
|---|---|---|
| 6.3g | 9% | 6% |
| 12.6g | 6% | 2% |
| 25.2g | 3% | 2% |

The better foaming during coking of Refcoal extracted using both sodium hydroxide and sodium sulphide prompted us to do optimisation experiments with different $NaOH:Na_2S$ mole ratios. Figure 4.2 is a plot of absorbance versus time, showing the progress of extraction with the different doses of sodium sulphide used together with a fixed amount of sodium hydroxide. The amount of sodium sulphide used in these experiments was determined as a mole ratio to the amount of sodium hydroxide. The different data are given in Appendix 2, Table A2.2. The amount of sulphur increased, which could be the result of the added sulphide or could be due to insufficient washing during the Refcoal recovery. The ash content of the Refcoal extracted using both sodium hydroxide and sodium sulphide is higher than that obtained by extraction using sodium hydroxide only. This could be due to insufficient washing during the Refcoal recovery. In an industrial process where counter-current is employed to wash the Refcoal during the recovery process, both the ash and the sulphur content could be significantly lowered. Table 4.5 lists the percentage solids in Refcoal solution obtained from the extraction with varying amounts of sodium sulphide, calculated according to the following equation:

$$\% Solids = \frac{mass\ of\ dry\ solids}{mass\ of\ coal\ solution} \times 100$$

The dry coal solids were obtained by precipitating a known amount of coal solution in water. The results show a decrease in the percentage solids from 9% to 3% in the Refcoal solution derived from extraction using both sodium hydroxide and sodium sulphide. As indicated in Figure 4.3, the smaller the amount of sodium sulphide used, the better the extraction. Extraction with smaller amounts of sodium sulphide, i.e. the 10:1, 8:1 and 4:1 NaOH:$Na_2S$ mole ratios, gave better extraction of the coal. Extraction using larger amounts of sodium sulphide, i.e. a 1:1 NaOH:$Na_2S$ mole ratio, gave poor extraction results. Figure 4.3 is a plot of absorbance versus time of the different runs for the 1:1 NaOH:$Na_2S$ mole ratio. The detailed data are given in Appendix 2, Table A2.2. The curve showing the progress of this extraction goes through a maximum and then drops to an absorbance of about 0.200.

The drop in the absorbance may be due to moisture released by the sodium sulphide reagent, which inhibits the extraction of coal, as reported by Morgan [112,120], or may be due to some chemical reaction or back-precipitation of the dissolved coal. By comparison with the extraction using sodium hydroxide only (0:1 ratio, Figure 4.2), the extraction using both sodium hydroxide and sodium sulphide is faster at the beginning and gradually slows down. The increased rate of extraction could be a result of the dissolved sulphide at the beginning of the extraction process acting as a phase-transfer catalyst. The slowing down of the extraction rate may be due to a side-reaction releasing some inhibitors such as water and/or oxygen, which slow down the extraction, as reported in the literature [112,120].

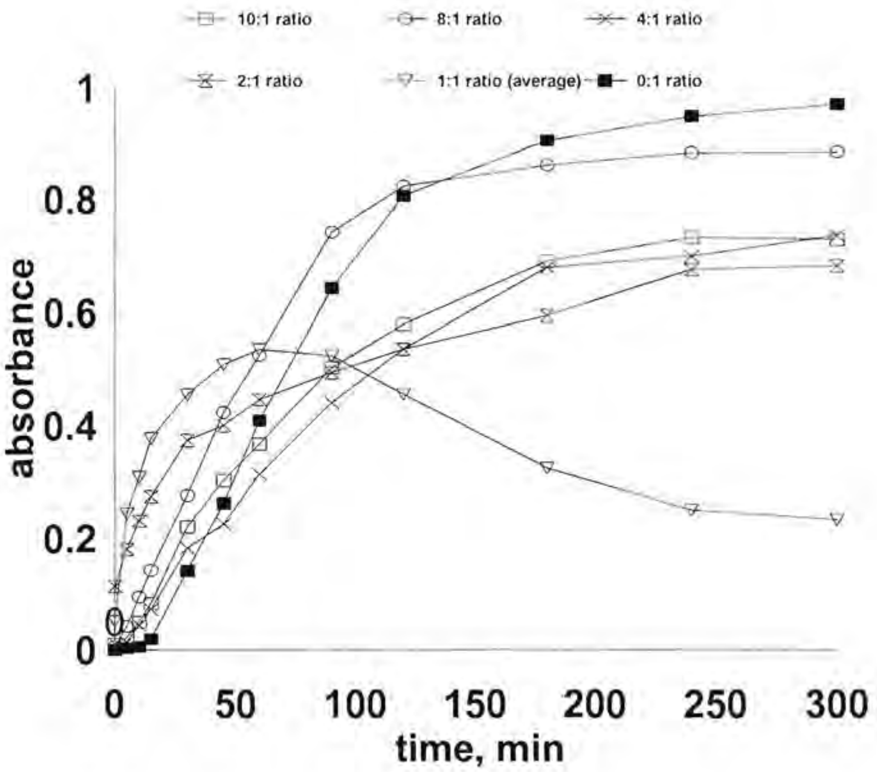

**Figure 4.2: Progress of extraction with NaOH, showing different doses of $Na_2S$. Mass of DMF used: 800 g, mass of coal: 80 g, mass of NaOH: 8 g**

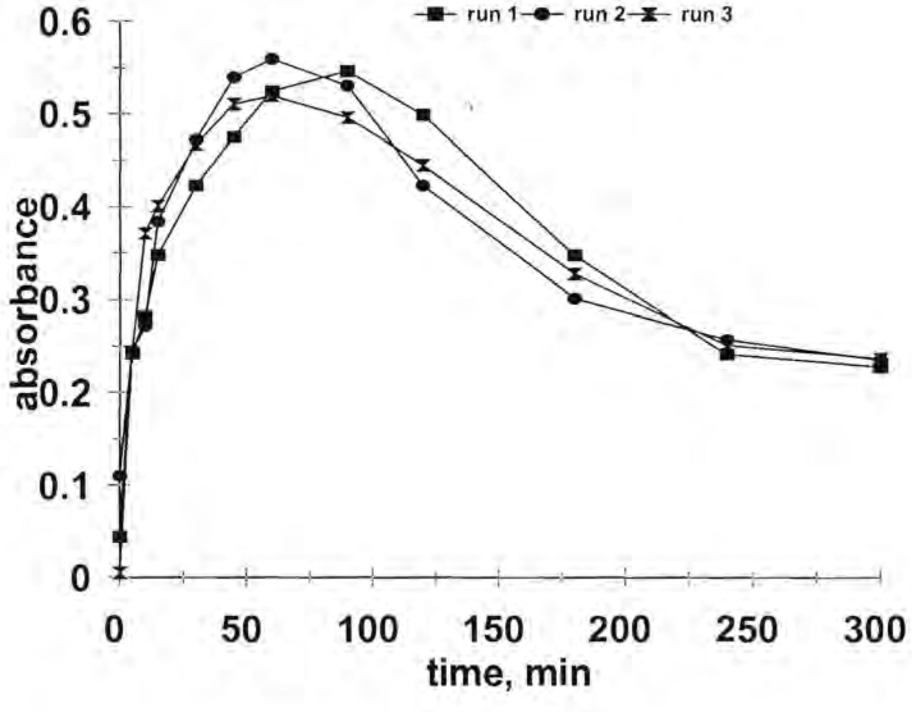

**Figure 4.3: Progress of extraction showing bleaching effect of high doses of $Na_2S$. Mass of DMF:800 g, mass of coal: 80 g, mass of NaOH: 8 g and mass of $Na_2S$: 25.2 g**

In order to minimise the impurities introduced into the Refcoal, we attempted the extraction of coal using dimethylformamide and sodium sulphide only. The same amounts of sodium sulphide used for the extraction using both sodium hydroxide and sodium sulphide were used for these experiments. Figure 4.3 is a plot of absorbance versus time, showing the progress of extraction without sodium hydroxide for the different doses of sodium sulphide ( 6.34 g, 12.61 g and 25.17 g). The detailed data are given in Appendix 2, Table A2.3. The results show a decrease in the percentage solids from 6% to 2% (Table 4.5) in the Refcoal solution derived from extraction using sodium sulphide only. Therefore, the resulting Refcoal solution was less than 8%. As indicated in Figure 4.5, the absorbance with the different amounts of sodium sulphide is less than 0.500, which is less than the absorbance of 1.00 for an 8% solution. This suggests that sodium sulphide alone is not suitable for extracting a reasonable amount of carbon from coal because the sulphide is a weaker nucleophile than the hydroxide. A strong nucleophile is required to extract a reasonable amount of carbon from coal. The extractions using large amounts of sodium sulphide (25.17 g), both those with sodium hydroxide and sodium sulphide and those with sodium sulphide only, gave the same results. For both the experiments, the curves (Figures 4.3 and 4.5) showing the progress of the extraction using a large amount of sodium sulphide go through a maximum and then drop to an absorbance of about 0.200. This shows that the behaviour was also reproducible for the extraction with sodium sulphide only (Figure 4.5). As mentioned before, this may be due to moisture released by the sodium sulphide, which inhibits the extraction of coal, as reported by Morgan [112,120], or may be due to some chemical reaction or back-precipitation of the dissolved coal.

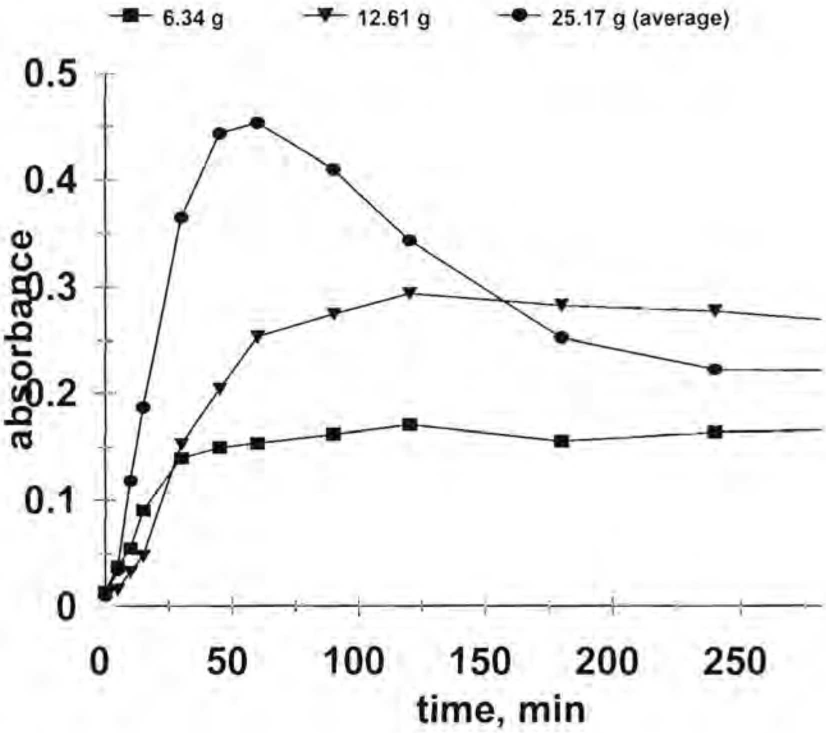

**Figure 4.4: Progress of extraction without NaOH, showing different doses of $Na_2S$. Mass of DMF used: 800g, mass of coal: 80g**

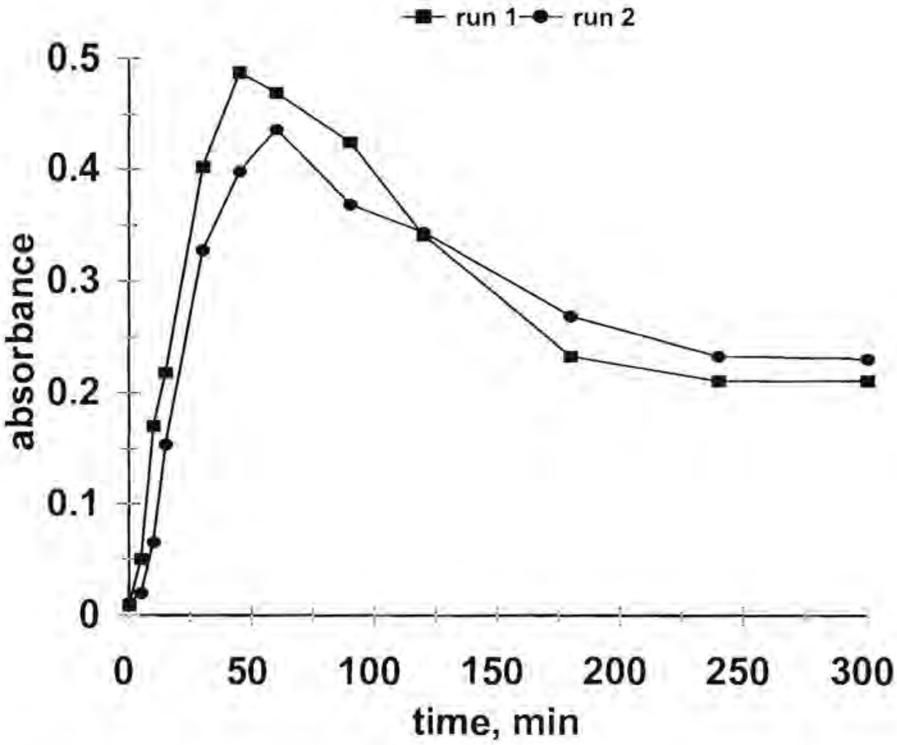

**Figure 4.5:** **Progress of extraction without NaOH, showing bleaching effect of $Na_2S$. Mass of DMF: 800 g, mass of coal: 80 g and mass of $Na_2S$: 25.2 g**

## 4.3 Trace element analysis

Trace element analysis of the original coal, unpurified Refcoal, acid-treated Refcoal and resin-treated Refcoal was done by means of ICP-AES and INAA. The dried samples of the original coal, unpurified Refcoal and purified Refcoal were submitted to Dr R. Hart of the Schonland Research Centre at the University of the Witwatersrand for analysis by INAA. Samples were also submitted to the National Energy Corporation of South Africa (NECSA) for analysis by ICP-AES. INAA and ICP-AES are very much standard techniques which were at our disposal. Table 4.6 lists the concentrations of trace elements as determined by ICP-AES. The concentrations are averages of two determinations. As indicated, the concentrations of most of the elements determined were less than the detection limits, but the cobalt concentrations were shown to be consistently higher. The high cobalt concentrations could probably be due to method error. ICP-AES is not suitable for determining the concentrations of trace elements in the unpurified Refcoal, acid-treated Refcoal and resin-treated Refcoal since these elements are present in concentrations lower than the detection limits for this method. The analysis of the trace elements for most of this work was therefore done by means of INAA. INAA is a good choice for this work because, with the exception of boron, trace elements which are easily activated by neutrons can be determined satisfactorily. A major disadvantage of this method, however, is the time it takes to analyse a set of samples. It took eight to twelve weeks before we could obtain the results of the samples submitted for analysis. Consequently, not many repetitive samples could be analysed for this work. The results of the analyses are shown in Appendix 2, Tables A2.1 to A2.4, as sample RC for the original coal, RCW for the unpurified Refcoal, RCA for the acid-treated Refcoal and RCR for the resin-treated Refcoal. Samples analysed for both unpurified and purified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, were only those with the 8:1 NaOH:$Na_2S$ mole ratios.

**Table 4.6:** **Concentrations of trace elements in Refcoal as determined by ICP-AES (ppm)**

| Element | DL | RCW | RCA1 | RCA2 | RCA3 | RCR1 | RCR2 |
|---|---|---|---|---|---|---|---|
| B | 19 | < 19 | < 19 | < 19 | < 19 | < 19 | < 19 |
| Ca | 3 | 20 | < 3 | < 3 | < 3 | < 3 | < 3 |
| Cd | 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 |
| Co | 10 | 59 | 53 | 57 | 52 | 64 | 53 |
| Cr | 5 | 10 | < 5 | < 5 | < 5 | < 5 | < 5 |
| Cu | 3 | 21 | < 3 | 13 | < 3 | < 3 | 4 |
| Dy | 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 |
| Eu | 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 |
| Fe | 3 | 299 | 92 | 4 | < 3 | 223 | 237 |
| Gd | 13 | < 13 | < 13 | < 13 | < 13 | < 13 | < 13 |
| Mg | 1 | 43 | < 1 | < 1 | < 1 | 11 | 26 |
| Mn | 4 | < 4 | < 4 | < 4 | < 4 | < 4 | < 4 |
| Mo | 4 | < 4 | < 4 | < 4 | < 4 | < 4 | < 4 |
| Ni | 21 | < 21 | < 21 | < 21 | < 21 | < 21 | < 21 |
| Sm | 40 | < 40 | < 40 | < 40 | < 40 | < 40 | < 40 |
| Sn | 118 | 436 | 391 | 422 | 390 | 452 | 320 |
| Ti | 24 | 1161 | 1062 | 816 | 629 | 1162 | 1189 |
| V | 6 | 35 | 32 | 23 | 15 | 36 | 36 |
| Zn | 12 | 41 | < 12 | < 12 | 16 | < 12 | 18 |

Note: DL = Detection limit; RCW = unpurified Refcoal; RCA = acid-treated Refcoal; RCR = chelating (TP260) resin-treated Refcoal

### 4.3.1 Trace element analysis of unpurified Refcoal

Table 4.7 and Table 4.8 list the concentrations of the elements Ba, Br, Co, Cr, Cs, Fe, Hf, La, Sc, Sm, Ta, Tb, Th and U, monitored for the original coal and unpurified Refcoal. The concentrations given are an average of at least two determinations as given in Appendix 3. Table 4.9 lists the extent of purification, calculated as a ratio of concentration in the original coal to concentration in the Refcoal, for each of the elements monitored. The extent of purification is discussed below:

*Barium*: The barium concentration was lowered from 3 190 ppm in the original coal to 202 in unpurified Refcoal derived from the extraction with sodium hydroxide only. The barium concentration was lowered from 3 190 ppm in the original coal to 448 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. In both cases the leaching of barium is high, which suggests that barium is predominately in inorganic association in the original coal. Using barium as an indicator element for alkaline earth metals, we can conclude that these elements are predominantly in inorganic association in coal, and therefore can be easily separated from the organic component of the coal. This observation is consistent with those made in the literature [17,20 - 25]. Barium has a boron equivalent of $1 \times 10^{-4}$, which means that a concentration of 202 ppm is not a cause for concern with regard to nuclear graphite, since further purification of the Refcoal should be able to bring down the concentration to below 10 ppm.

*Bromine*: The bromine concentration was lowered from 4.1 ppm in the original to 0.7 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only. The bromine concentration was lowered from 4.1 ppm in the original to 0.9 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The high purification values for bromine in both cases suggests that bromine is predominately in inorganic association in the original coal, which is not consistent with literature report [26]. With respect to nuclear graphite, the amount of bromine in the coal is unimportant since this will easily come off the coal matrix during carbonisation.

*Cesium:* The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.3 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 1.1 ppm in the original coal to 0.11 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The purification value of 10 suggests that cesium occurs predominantly in inorganic association in the coal. Cesium has been reported to occur predominantly in inorganic association in coal [26], which is consistent with the observations made here. If we use cesium as the indicator element, we can conclude that alkali metals are predominantly in inorganic association in the coal matrix, and therefore can be easily separated from the organic component of the coal. A purification value of 3.7, obtained from the unpurified Refcoal derived from the extraction with sodium hydroxide only, indicates a high recovery of cesium, which suggests contamination and/or analytical variations. Cesium has a boron equivalent of $3 \times 10^{-3}$. With respect to nuclear carbon, this does not pose a serious problem since at a concentration of less than 1 ppm, the boron equivalent will be less than $3 \times 10^{-3}$.

*Cobalt*: The concentration of cobalt was lowered from 8.7 ppm in the original coal to 6.9 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only. The concentration of cobalt was lowered from 8.7 ppm in the original coal to 4.8 ppm in untreated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. High recoveries of cobalt were observed; this suggests the presence of organometallic species, which are soluble in organic solvents. This is consistent with the observations reported [26]. In some experiments, the cobalt concentrations were higher in the unpurified Refcoal than in the original parent coal. The high cobalt concentration could be due to contamination or analytical variations. Since the concentration of cobalt drops with subsequent purification of the Refcoal, this observation suggests that the contamination occurred during extraction to prepare the unpurified Refcoal. The high recoveries of cobalt could have arisen from the stainless steel reactor vessel and its components, or the reagents used. Samples taken from the reactor lid, the stirrer blade, the stirrer, reactor blades, and reactor wall were sent to the Department of Metallurgy of the University of Pretoria for cobalt analysis by the transmission electron microscopy (TEM). As indicated in Figures A3.1 – A3.7 in Appendix 3, these samples did not show any presence of cobalt. Contamination from the reagents, dimethylformamide and sodium hydroxide, was also investigated. A concentration of 0.09 ppm was found for sodium hydroxide and 0.03 ppm for dimethylformamide. This suggests that the contamination from the reagents was not too serious. Cobalt has a boron equivalent of $9 \times 10^{-3}$, which means that a concentration of less than 0.05 ppm is required, since cobalt forms stable carbides during carbonisation and therefore does not evaporate. Upon activation by neutrons, cobalt forms cobalt-60 which is more radioactive and has a longer half-life. For the coal to be employed in the manufacture of nuclear graphite, a purification method for cobalt will have to be developed.

*Chromium*: The concentration of chromium was lowered from 11.0 ppm in the original coal to 7.2 ppm in untreated Refcoal derived from the extraction with sodium hydroxide only. The concentration of chromium was lowered from 11.0 ppm in the original coal to 7.1 ppm in untreated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. High recoveries of chromium were observed; this suggests the presence of organometallic species, which are soluble in organic solvents. This is consistent with the observations reported [26]. In some experiments, chromium concentrations were higher in the unpurified Refcoal than in the original parent coal. The increase in concentration could be due to contamination. Chromium has a boron equivalent of $8 \times 10^{-4}$ so a concentration of 7.2 ppm in the unpurified Refcoal is not a cause for concern with respect to nuclear graphite.

*Europium:* The concentration of europium was lowered from 0.6 ppm in the original coal to 0.08 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 0.6 ppm in the original coal to 0.1 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The purification values of 7.5 and 10 indicate a low recovery of europium, which suggests that europium occurs predominantly in inorganic association in the coal matrix. Europium has been reported to occur predominantly in organic association in the coal matrix [28], which is inconsistent with the observations made here. At this stage of purification, europium is a potential problem with respect to nuclear, since it has a very high boron equivalent ($4 \times 10^{-1}$), therefore further purification is necessary to bring its concentration to below 0.005 ppm.

*Hafnium:* The concentration of hafnium was lowered from 2.8 ppm in the original coal to 1.7 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 2.8 ppm in the original coal to 1.9 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values indicate a high recovery of hafnium, which suggests that hafnium occurs predominantly in organic association in the coal matrix. Hafnium has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. The low purification values may also suggest a contamination problem. Hafnium has a high boron equivalent (8 x $10^{-3}$), and therefore its concentration needs to be lowered to below 0.1 ppm for the coal to be used for the production of nuclear carbon. Further purification will, therefore, be necessary.

*Iron:* The concentration of iron was lowered from 3400 ppm in the original coal to 433 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only. The concentration of iron increased from 3400 ppm in the original coal to 4100 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which suggests contamination or analytical variations. The increase in iron concentration in relation to Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide is probably due to the precipitation of iron ions as pyrite. The low purification value indicates a high recovery of iron, which suggests that iron occurs predominantly in organic association in the coal matrix. Iron has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. Since iron has a low boron equivalent (7 x $10^{-4}$), it poses no serious problem with respect to nuclear carbon as with further purification its concentration can be brought to below 50 ppm.

*Lanthanum:* The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 1.6 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 15.8 ppm in the original coal to 4.8 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The purification value of 10 indicates a low recovery of lanthanum, which suggests that lanthanum occurs predominantly in inorganic association in the coal matrix. However, the purification value of 3.3 indicates a high recovery of lanthanum, which suggests either that lanthanum occurs predominantly in organic association in the coal matrix or that there was a contamination problem when sodium sulphide was used. Lanthanum has been reported to occur predominantly in organic association in the coal matrix [27, 28]. Since lanthanum has a low boron equivalent (9 x $10^{-4}$), it poses no serious problem with respect to nuclear carbon as with further purification its concentration can be brought to below 0.05 ppm.

*Scandium:* The concentration of scandium was lowered from 5.7 ppm in the original coal to 2.7 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 5.7 ppm in the original coal to 2.2 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The purification values of 2.1 and 2.6 indicate a high recovery of scandium, which suggests that scandium occurs predominantly in organic association in the coal. The low purification values of may also suggest a contamination problem.. Scandium has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. Since scandium has a high boron equivalent (9 x $10^{-3}$), further purification will be necessary to bring the concentration down below 0.05 ppm in order for the coal to be suitable for use in the manufacture of nuclear carbon.

*Samarium:* The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.6 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 2.7 ppm in the original coal to 2.3 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values of 4.5 and 1.2 indicate a high recovery of samarium, which suggests that samarium occurs predominantly in organic association in the coal matrix. Samarium has been reported to occur predominantly in organic association in the coal matrix [27, 28], which is consistent with the observations made here. The low purification values may also suggest a contamination problem. Samarium has a very high boron equivalent (5 x $10^{-1}$), and therefore its concentration needs to be lowered to below 0.005 ppm for the coal to be used for the production of nuclear carbon. Further purification will, therefore, be necessary.

*Tantalum:* The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 0.6 ppm in the original coal to 0.3 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values of 1.2 and 2 indicate a high recovery of tantalum, which suggests that tantalum occurs predominantly in organic association in the coal matrix. Tantalum has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. The low purification values may also suggest a contamination problem. Tantalum has a low boron equivalent (2 x $10^{-3}$), and therefore it poses no serious problem with respect to nuclear carbon since its concentration is less than 1 ppm..

*Terbium:* The concentration of terbium was lowered from 0.6 ppm in the original coal to 0.2 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only. The concentration of terbium increased from 0.6 ppm in the original coal to 0.7 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which suggests contamination or analytical variations. The low purification value of 3 indicates a high recovery of terbium, which suggests that terbium occurs predominantly in organic association in the coal matrix. Terbium has been reported to occur predominantly in inorganic association in the coal matrix [28], which is inconsistent with the observations made here. Terbium has a low boron equivalent (2 x $10^{-3}$), and therefore it poses no serious problem with respect to nuclear carbon since with further purification its concentration can be brought to below 0.05 ppm..

*Thorium:* The concentration of thorium was lowered from 4.9 ppm in the original coal to 2.6 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 4.9 ppm in the original coal to 1.7 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values of 1.9 and 2.9 indicate a high recovery of thorium, which suggests that thorium occurs predominantly in organic association in the coal matrix. Thorium has been reported to occur predominantly in inorganic association in the coal matrix [26, 28], which is inconsistent with the observations made here. The low purification values may also suggest a contamination problem. Thorium has a low boron equivalent ($4 \times 10^{-4}$), and therefore it poses no serious problem with respect to nuclear carbon.

*Uranium:* The concentration of uranium was lowered from 2.0 ppm in the original coal to 0.4 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 2.0 ppm in the original coal to 1.3 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values of 5 and 1.5 indicate a high recovery of uranium, which suggests that uranium occurs predominantly in organic association in the coal matrix. Uranium has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. The low purification values also suggest a contamination problem. Uranium has a very low boron equivalent ($2 \times 10^{-4}$), and therefore it poses no serious problem with respect to nuclear carbon since with further purification its concentration can be brought to below 0.05 ppm.

**Table 4.7: Average concentrations of elements in Tshikondeni coal and Refcoal derived from NaOH extraction, showing different stages of treatment (ppm)**

| Element | Coal | Unpurified Refcoal | HCl-treated | HF-treated | TP260-treated | TP208-treated | TP214-treated |
|---|---|---|---|---|---|---|---|
| Ba | 3190 | 202 | 436 | 381 | 23.5 | nd | 13.5 |
| Br | 4.1 | 0.7 | 2.6 | 3.2 | 1.0 | 2.2 | 1.3 |
| Co | 8.7 | 6.9 | 5.5 | 5.9 | 4.8 | 4.3 | 4.5 |
| Cr | 11 | 7.2 | 5.0 | 6.3 | 4.7 | 4.2 | 3.7 |
| Cs | 1.1 | 0.3 | 0.03 | nd | 0.02 | 0.04 | 0.04 |
| Eu | 0.6 | 0.08 | nd | nd | nd | nd | 0.008 |
| Fe | 3400 | 1000 | 150 | 70 | 10 | 50 | 50 |
| Hf | 2.8 | 1.7 | 0.8 | 0.9 | 0.1 | 0.1 | 0.08 |
| La | 15.8 | 1.6 | 0.6 | 0.6 | 0.3 | 0.6 | 1.8 |
| Sc | 5.7 | 2.7 | 0.4 | 0.1 | 0.09 | 0.08 | 0.07 |
| Sm | 2.7 | 0.6 | 0.13 | 0.2 | 0.05 | 0.4 | 0.4 |
| Ta | 0.6 | 0.5 | 0.5 | 0.5 | 0.5 | 0.6 | 0.4 |
| Tb | 0.6 | 0.2 | nd | nd | nd | nd | nd |
| Th | 4.9 | 2.6 | 1.3 | 2 | 0.6 | 0.7 | 1.2 |
| U | 2.0 | 0.4 | 1.5 | 1.4 | nd | 0.3 | 0.2 |

Note: nd = undetected

**Table 4.8: Average concentrations of elements in Tshikondeni coal and Refcoal derived from the NaOH-$Na_2S$ extraction, showing different stages of treatment (ppm)**

| Element | Coal | Unpurified Refcoal | HCl-treated | HF-treated | TP260-treated | TP208-treated | TP214-treated |
|---|---|---|---|---|---|---|---|
| Ba | 3190 | 448 | 327 | 324 | 491 | 159 | 217 |
| Br | 4.1 | 0.9 | 2.2 | 2.1 | 4.3 | 2.9 | 3.6 |
| Co | 8.7 | 4.8 | 2.4 | 5.1 | 3.4 | 2.4 | 3.9 |
| Cr | 11 | 7.1 | 4.0 | 5.4 | 3.5 | 4.4 | 4.0 |
| Cs | 1.1 | 0.1 | 0.03 | 0.08 | 0.03 | 0.03 | 0.03 |
| Eu | 0.6 | 0.06 | 0.01 | 0.05 | 0.005 | nd | nd |
| Fe | 3400 | 4100 | 100 | nd | 200 | nd | 100 |
| Hf | 2.8 | 1.9 | 0.6 | 1.3 | 0.06 | 0.2 | 0.05 |
| La | 15.8 | 4.8 | 0.7 | 0.5 | 0.03 | 0.7 | 0.04 |
| Sc | 5.7 | 2.2 | 0.5 | 0.5 | 0.05 | 0.2 | 0.05 |
| Sm | 2.7 | 2.3 | 0.06 | 0.1 | 0.03 | 0.03 | 0.05 |
| Ta | 0.6 | 0.3 | 0.5 | 0.6 | 0.5 | 0.6 | 0.3 |
| Tb | 0.6 | 0.7 | nd | 0.9 | nd | nd | nd |
| Th | 4.9 | 1.7 | 0.09 | 0.4 | 0.07 | 0.07 | 0.1 |
| U | 2.0 | 1.3 | 0.2 | 0.6 | 0.1 | 0.7 | 0.4 |

Note: nd = undetected

**Table 4.9: Extent of purification of trace elements in Tshikondeni Refcoal**

| **Element** | **NaOH-extracted** | | | | | **NaOH and $Na_2S$-extracted** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | RCW | HCl | TP 260 | TP 208 | TP 214 | RCW | HCl | TP 260 | TP 208 | TP 214 |
| Ba | 16 | 7.3 | 136 | >300 | 228 | 7.1 | 10 | 6 | 20 | 15 |
| Br | 5.9 | 1.6 | 2.7 | 2 | 3.2 | 4.6 | 2.6 | <1 | 1.4 | 1.1 |
| Co | 1.3 | 1.6 | 1.6 | 2 | 1.9 | 1.2 | 3.6 | 2.6 | 3.6 | 2.2 |
| Cr | 1.5 | 2.2 | 2.1 | 2.6 | 3 | 1.5 | 2.8 | 3.1 | 2.5 | 2.8 |
| Cs | 3.7 | 37 | 18 | 28 | 28 | 11 | 16 | 37 | 37 | 37 |
| Eu | 7.5 | >120 | >120 | >120 | 75 | 10 | 60 | 120 | >12 | >120 |
| Fe | 7.9 | 23 | 300 | 60 | 60 | <1 | 34 | 15 | >300 | 30 |
| Hf | 1.7 | 3.5 | 28 | 28 | 35 | 1.5 | 4.7 | 47 | 15 | 56 |
| La | 10 | 26 | 53 | 26 | 8.8 | 3.3 | 23 | 527 | 23 | 395 |
| Sc | 2.1 | 14 | 63 | 81 | 81 | 2.6 | 11 | 114 | 29 | 114 |
| Sm | 4.5 | 27 | 54 | 6.8 | 9 | 1.2 | 45 | 90 | 90 | 54 |
| Ta | 1.2 | 1.2 | 1.2 | 1 | 1.5 | 2 | 1.2 | 1.2 | 1 | 2 |
| Tb | 3 | >56 | >56 | >56 | >56 | <1 | >56 | >56 | >56 | >56 |
| Th | 1.9 | 3.8 | 4.5 | 7 | 4.1 | 2.9 | 54 | 70 | 70 | 49 |
| U | 2.5 | 1.3 | >20 | 6.7 | 10 | 1.5 | 10 | 20 | 3.3 | 5 |

Note: RCW = water-precipitated unpurified Refcoal; HCl = HCl-treated Refcoal; TP 260 = Lewatit TP 260 chelating resin-treated Refcoal; TP 208 = Lewatit TP 208 chelating resin-treated Refcoal; TP 214 = Lewatit TP 214 chelating resin-treated Refcoal

### 4.3.1.1 Conclusions

As seen in Table 4.7 and Table 4.8, Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide appears to be lower in cobalt but high in almost all the other elements determined. Therefore, future work should be directed towards the extraction of carbon from coal with as small an amount of sodium sulphide as possible in order to improve the foaming of the Refcoal during carbonisation and, hopefully, improve the formation of mesophase. High amounts of sodium sulphide should be avoided. It will be necessary to develop a proper washing process for recovering the Refcoal from the Refcoal solution. The rare earth metals (La and Sm) are not consistent to each other, which could be attributed to contamination, analytical variations and/or that there was insufficient washing during the recovery of the Refcoal.

### 4.3.2 Extraction of trace elements from Refcoal gel with hydrochloric acid and hydrofluoric acid

It has been reported [147,148] that demetalation of porphyrins takes place when the metal complex is boiled in hydrochloric acid. Demetalation with hydrofluoric acid was also attempted by precipitating the Refcoal solution in concentrated hydrofluoric acid. Scanning electron microscopy (SEM) was used to determine qualitatively the extent of purification in the presence of acids. This is shown in Figure 4.6 for the unpurified Refcoal, in Figure 4.7 for the hydrofluoric acid-treated Refcoal, and in Figure 4.8 for the Refcoal treated with hydrochloric acid followed by hydrofluoric acid. The presence on the SEM micrograph of many bright spots against a dark carbon background (Figure 4.6), indicates more impurities. The analysis of the energy-dispersive spectrometer (EDS) showed that the unpurified Refcoal contains more titanium-rich impurities. For the Refcoal treated with hydrochloric acid only, the micrograph shows fewer bright spots than for the unpurified Refcoal. EDS analysis of the hydrofluoric acid-treated Refcoal, showed that these impurities contain compounds consisting mainly of Na, Al and F, which suggests the presence of insoluble compounds such as $NaAlF_4$. This is consistent with the observation made by Steel et al. [94,95]. The Refcoal treated with hydrochloric acid followed by treatment with hydrofluoric acid shows even fewer bright spots on the SEM micrograph, which demonstrates that the number of impurities has been reduced. EDS analysis showed that these impurities contain compounds consisting mainly of Ca and F, which suggests the presence of insoluble compounds such as $CaF_2$ The presence of compounds such as $NaAlF_4$ was not observed, which suggests that the treatment of Refcoal with hydrochloric acid removes most of the insoluble fluoride-forming ions from the coal matrix. Consequently, most of the samples prepared were first treated with hydrochloric acid, followed by hydrofluoric acid.

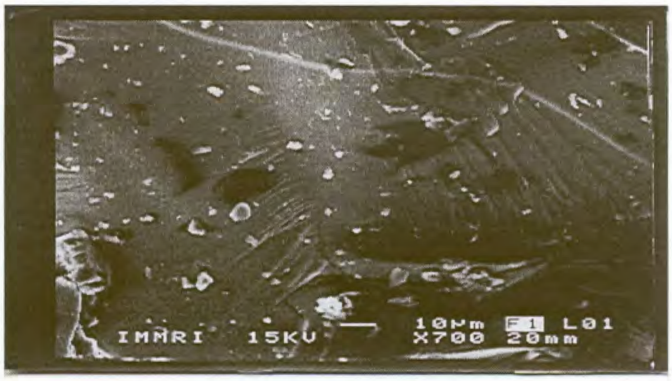

**Figure 4.6: SEM micrograph of showing unpurified Refcoal**

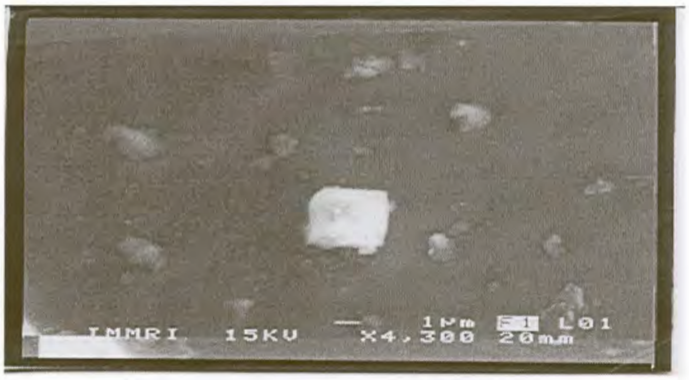

**Figure 4.7: SEM micrograph of Refcoal treated with HF**

**Figure 4.8: SEM micrograph of Refcoal treated with HCl followed by HF**

To minimise the formation of dimethylamine from dimethylformamide as a result of reaction with hydrochloric acid, the Refcoal solution was first precipitated from water to form a gel containing less DMF, followed by treatment with the acids. Table 4.7 and Table 4.8 respectively list the average concentrations of the elements monitored in the acid-treated Refcoal samples for the extractions using sodium hydroxide only and those for the extractions using both sodium hydroxide and sodium sulphide. The purification experiments conducted using hydrochloric and hydrofluoric acid were initial experiments and were not optimised. The concentrations given are an average of at least two determinations as given in Appendix 3. Table 4.9 lists the extent of purification, calculated as the ratio of concentration in the original coal to that in the Refcoal, for each of the elements monitored. Purification of the elements monitored is discussed below.

*Barium*: The concentration of barium was lowered from 3 190 ppm in the original coal to 436 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. This concentration was then lowered to 381 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of barium increased from 202 ppm in unpurified Refcoal to 436 ppm and 381 ppm respectively in the hydrochloric acid-treated Refcoal and hydrofluoric acid-treated Refcoal, which suggests contamination, or analytical variations. The increase in concentration with respect to the hydrofluoric acid-treated Refcoal is probably due to the precipitation of insoluble barium fluoride. The concentration of barium was lowered from 3 190 ppm in the original coal to 327 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 327 ppm in the hydrochloric acid-treated Refcoal was then lowered to 324 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. No significant purification was achieved in proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid treated Refcoal. With respect to the unpurified Refcoal no barium purification was achieved with acid treatment. This may be either because of the precipitation of barium fluorides, or an indication that the washing method used, although similar, was ineffective.

*Bromine*: The concentration of bromine was lowered from 4.1 ppm in the original coal to 2.6 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. This concentration was then increased to 3.2 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of bromine increased from 0.7 ppm in unpurified Refcoal to 3.2 ppm in both the hydrochloric acid-treated Refcoal and hydrofluoric acid-treated Refcoal, which suggests bromine contamination by the acids. The concentration of bromine was lowered from 4.1 ppm in the original coal to 1.6 ppm and 1.7 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with hydrochloric acid and hydrofluoric acid. The concentration of bromine increased from 0.9 ppm in unpurified Refcoal to 1.6 ppm and 1.7 ppm in the hydrochloric acid-treated Refcoal and hydrofluoric acid-treated Refcoal respectively, again suggesting bromine contamination by the acids. Therefore, using either hydrochloric acid or hydrofluoric acid introduces bromine into the sample. The extent of contamination appears to be lower with the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. Contamination by bromine is, however, not a problem with regard to the manufacture of nuclear carbon, since bromine will easily volatilise during carbonisation. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Cesium:* The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.03 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with hydrochloric acid. This concentration was then lowered to a concentration that is close to the detection limit after treatment with hydrofluoric acid. The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.03 and 0.08 ppm respectively in the Refcoal derived from the extractions with both sodium hydroxide and sodium sulphide, after treatment with both hydrochloric acid and hydrofluoric acid. From the high purification values of 37 and 16 it can be concluded that acid treatment is suitable for the leaching cesium out of the original coal and/or Refcoal. Cesium was used as an indicator element for alkali metals, which suggests that sodium, which is a catalyst for oxidation, and which is added during extraction could be removed. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which may be due to contamination, analytical variations and inefficient washing of the Refcoal.

*Cobalt*: The concentration of cobalt was lowered from 8.7 ppm in the original coal to 5.5 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of 4.8 ppm in the hydrochloric acid-treated Refcoal then increased to 5.9 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only, which suggests contamination or analytical variations. The concentration of cobalt was lowered from 8.7 ppm in the original coal to 2.4 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 2.4 ppm in the hydrochloric acid-treated Refcoal then increased to 5.1 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, again suggesting contamination. No significant cobalt purification is achieved when proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal for both the Refcoal derived from the extraction with sodium hydroxide only and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Chromium*: The concentration of chromium was lowered from 11.0 ppm in the original coal to 5.0 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of 5.0 ppm in the hydrochloric acid-treated Refcoal then increased to 6.3 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only, which suggests contamination. The concentration of chromium was lowered from 11.0 ppm in the original coal to 4.0 ppm and 5.4 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with hydrochloric acid and hydrofluoric acid. This observation suggests a strong organic association for chromium. In relation to the unpurified Refcoal, no significant chromium purification is achieved with acid treatment. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no chromium purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Europium:* The concentration of europium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with both hydrochloric acid and hydrofluoric acid. The europium concentration was lowered from 0.6 ppm in the original coal to 0.01 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 0.01 ppm in the hydrochloric acid-treated Refcoal then increased to 0.05 ppm in the hydrofluoric acid-treated Refcoal, which suggests contamination or analytical variations. However, acid treatment was found to be suitable for leaching europium out of the original coal and/or Refcoal. In proceeding from hydrochloric acid-treated to hydrofluoric acid-treated Refcoal, no purification was achieved for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which may be due to contamination, analytical variations and inefficient washing of the Refcoal.

*Hafnium:* The concentration of hafnium was lowered from 2.8 ppm in the original coal to 0.8 ppm and 0.9 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after hydrochloric acid and hydrofluoric acid treatment respectively. The concentration of hafnium was lowered from 2.8 ppm in the original coal to 0.6 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after hydrochloric acid. The concentration of 0.6 ppm then increased to 1.3 ppm in hydrofluoric acid- treated Refcoal, which suggests contamination when sulphide is used.

No significant hafnium purification is achieved when proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal for both the Refcoal derived from the extraction with sodium hydroxide only and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Iron:* The concentration of iron was lowered from 3400 ppm in the original coal to 150 ppm and 70 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with both hydrochloric acid and hydrofluoric acid respectively. In proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal, no significant iron purification was achieved. The concentration of iron was lowered from 3400 ppm in the original coal to 100 ppm after treatment with hydrochloric acid and to a concentration that is close to the detection limit in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. In proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal a purification value greater than 10 was observed, therefore a significant purification was achieved. Acid treatment was, therefore, found to be sufficient to leach out iron from the coal and/or Refcoal.

*Lanthanum:* The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 0.6 ppm after hydrochloric acid treatment, and then lowered to 0.2 ppm after hydrofluoric acid treatment in the Refcoal derived from the extraction with sodium hydroxide only. In proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal an increase in concentration to 0.2 ppm was observed, which suggests contamination. The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 0.7 and 0.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after hydrochloric acid and hydrofluoric acid treatment respectively. Again, in proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal an increase in concentration to 0.2 ppm was observed, which suggests contamination. The high purification values indicate that acid treatment is sufficient to leach out lanthanum from the coal and/or

Refcoal, therefore further purification is not necessary. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Scandium:* The concentration of scandium was lowered from 5.7 ppm in the original coal to 0.4 and 0.1 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with hydrochloric acid and hydrofluoric acid respectively. The concentration of scandium was lowered from 5.7 ppm in the original coal to 0.5 ppm for both the hydrochloric acid and hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. With regard to the Refcoal derived from the extraction with sodium hydroxide only, no further purification is necessary, although a further purification step is necessary for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Samarium:* The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.1 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. This concentration then increased to 0.2 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only, which suggests contamination. The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.06 ppm for the hydrochloric acid and 0.1 ppm for the hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The purification values below 20 indicate that acid treatment is not sufficient to leach out samarium from the coal and/or Refcoal. Therefore, further purification is necessary to bring the concentration of samarium down to about 0.005 ppm. In proceeding from hydrochloric acid-treated

Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Tantalum:* The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm for the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of 0.5 ppm in the hydrochloric acid-treated Refcoal then remained at 0.5 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with both hydrochloric acid and hydrofluoric acid. The concentration of tantalum increased from 0.3 ppm in unpurified Refcoal to 0.5 ppm in both hydrochloric acid and hydrofluoric acid-treated Refcoal, again suggesting contamination. The low purification values indicate a high recovery of tantalum, which suggests that acid treatment does not leach out tantalum from the coal and/or Refcoal. No significant tantalum purification is achieved when proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal for both the Refcoal derived from the extraction with sodium hydroxide only and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Terbium:* The concentration of terbium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit for both the hydrochloric acid and hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of terbium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit after hydrochloric acid treatment of the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. This concentration was then increased to 0.9 ppm in the hydrofluoric acid-treated Refcoal, which suggests contamination. The high purification values observed, indicate that acid treatment is sufficient to leach out terbium from the coal and/or Refcoal and therefore further purification is not necessary. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Thorium:* The concentration of thorium was lowered from 4.9 ppm in the original coal to 1.3 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of 1.3 ppm in the hydrochloric acid-treated Refcoal then increased to 2.0 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only, which suggests contamination. The concentration of thorium was lowered from 4.9 ppm in the original coal to 0.09 ppm in hydrochloric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 0.09 ppm in the hydrochloric acid-treated Refcoal then increased to 0.4 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values indicate a high recovery of thorium, which suggests that acid treatment is not sufficient to leach out thorium from the coal and/or Refcoal, but further purification is not necessary since thorium is the nuclear fission product. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Uranium:* The concentration of uranium was lowered from 2.0 ppm in the original coal to 1.5 ppm and 1.4 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with hydrochloric acid and hydrochloric acid respectively. The concentration of uranium was lowered from 2.0 ppm in the original coal to 0.4 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 0.2 ppm in the hydrochloric acid-treated Refcoal then increased to 0.6 ppm in the hydrofluoric acid-treated Refcoal, again suggesting contamination. The low purification values indicate a high recovery of uranium, which suggests that acid treatment is not sufficient to leach out uranium from the coal and/or Refcoal and therefore further purification is necessary. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

### 4.3.2.1 Conclusions

The observations made above lead to the following conclusions:

- The concentrations of the elements fluctuate for the different stages of purification, i.e. in moving from the original coal to the unpurified Refcoal, to the hydrochloric acid-treated Refcoal and to the hydrofluoric acid-treated Refcoal. Fluctuations in concentrations suggest a serious contamination problem, or inefficiency in the washing method that was used. Analytical errors cannot be ruled out. The fluctuations in concentrations, however, do not affect the major conclusions with regard to the acid-washing process as a Refcoal purification method.

- With regard to the original coal, the degrees of purification after acid treatment of the Refcoal derived from the extraction with sodium hydroxide only are as follows:

    - High purification, with purification values of 20 and above, is observed for Cs, Eu, Fe, La, Sm and Tb.
    - Values between 5 and 15 are observed for Ba and Sc.
    - Purification values below 5 are observed for Br, Co, Cr, Hf, Ta, Th and U.

- The degrees of purification after acid treatment of the Refcoal derived from the extraction with sodium hydroxide and sodium sulphide are as follows:
    - High purification, with purification values of 20 and above, is observed for Eu, Fe, La, Sm, Tb and Th.
    - Purification values of between 15 and 20 are observed for Cs.
    - Values between 5 and 15 are observed for Ba, Sc and U.
    - Purification values below 5 are observed for Br, Co, Cr, Hf and Ta.

- For the hydrochloric acid-treated Refcoal, the samples derived from the extraction with both sodium hydroxide and sodium sulphide appear to be lower in the rare earths than the samples derived from the extraction with sodium hydroxide only. The hydrofluoric acid-treated samples also show a similar trend, which suggests that sodium sulphide is necessary for the demetalation of the metal complex in the coal matrix. Both the hydrochloric acid and hydrofluoric acid-treated samples show an increase in the concentration of Br, which suggests contamination by the acids. Contamination with Br is not serious for the Refcoal to be used for the production of nuclear graphite because Br will easily be lost during carbonisation of the Refcoal. With the exception of iron, the hydrofluoric acid-treated samples appear to have a serious contamination problem, therefore no significant purification was achieved in proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid treated Refcoal. Acid treatment of the Refcoal gel was carried out under very harsh conditions only. Therefore future work must examine the optimum concentration of the acid required to obtain better purification. The contamination problem also needs to be addressed. Although purification values below 5 are demonstrated for Br, Co, Cr, Hf and Th at this stage of the purification, Br, Cr, Hf and Th are not a problem with respect to nuclear graphite, the only real problem is Co.

### 4.3.3 Extraction of trace elements from Refcoal solution with chelating resins

Table 4.10 lists the average concentrations of the trace elements monitored in the Refcoal samples derived from treating Refcoal solution with chelating resins. The purification experiments conducted were initial experiments and were not optimised. The concentrations given are an average of at least two determinations as given in Appendix 3. Table 4.11 lists the extent of purification, calculated as a ratio of concentration in the original coal to concentration in the Refcoal, for each of the elements monitored. The extent of purification is discussed below::

*Barium*: The concentration of barium was lowered from 3 190 ppm in the original coal to 87 ppm, 636 ppm and 82 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260 and Lewatit TP 214 chelating resins respectively. With regard to the unpurified Refcoal, an increase in concentration occurred from 202 ppm in the unpurified Refcoal to 636 ppm in the Refcoal from the extraction with sodium hydroxide only, treated with Lewatit TP 208 chelating resins, which suggests contamination. The concentration of barium was lowered from 3 190 ppm in the original coal to 686 ppm, 897 ppm and 516 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the unpurified Refcoal, an increase in concentration occurred from 486 ppm in the unpurified Refcoal to 686 ppm, 897 ppm and 516 ppm in Refcoal treated with Lewatit TP 260, TP 208 and Lewatit TP 214 chelating resins respectively, which suggests contamination. Purification appears to be better for the Refcoal derived from the extraction with sodium hydroxide only than for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Bromine*: The concentration of bromine was increased from 4.1 ppm in the original coal to 6.3 ppm and 6.9 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit

TP 260 and Lewatit TP 214 chelating resins respectively, which suggests contamination. The concentration of bromine was lowered from 4.1 ppm in the original coal to 0.4 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 208 chelating resins. The concentration of bromine was increased from 4.1 ppm in the original coal to 5.6 ppm and 7.4 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260 and Lewatit TP 214 chelating resins respectively, which suggests contamination.. The concentration of bromine was lowered from 4.1 ppm in the original coal to 3.2 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 208 chelating resins. For all the samples analysed, no significant bromine purification was demonstrated.

*Cesium:* The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.09 ppm, 0.07 ppm and 0.1 ppm respectively in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.2 ppm, 0.04 ppm and 0.1 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. It appears that the Lewatit TP 208 and Lewatit TP 214 chelating resins give better purification for cesium than the Lewatit TP 260 chelating resin. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

*Cobalt*: The concentration of cobalt was lowered from 8.7 ppm in the original coal to 4.9 ppm, 5.6 ppm and 5.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of cobalt was lowered from 8.7 ppm in the original coal to 7.4 ppm, 6.2 ppm and 6.2 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. For all the samples analysed, no significant cobalt purification was demonstrated.

*Chromium*: The concentration of chromium was lowered from 11.0 ppm in the original coal to 6.1 ppm, 6.8 ppm and 9.0 ppm respectively in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260 and Lewatit TP 208 and Lewatit TP 214 chelating resins. The concentration of chromium was lowered from 11.0 ppm in the original coal to 8.5 ppm, 8.8 ppm and 6.4 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. An increase in chromium concentration was observed from 7.1 ppm in the unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, to 8.5 ppm and 8.8 ppm after treatment with Lewatit TP 260 and Lewatit TP 208 chelating resins respectively, which suggests contamination. For all the samples analysed, no significant chromium purification was demonstrated.

*Europium:* The concentration of europium was lowered from 0.6 ppm in the original coal to 0.2 ppm, 0.04 ppm and 0.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of europium was lowered from 0.6 ppm in the original coal to 0.04 ppm, 0.2 ppm and 0.2 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 260 chelating resin gives better purification for europium than the Lewatit TP 208 and Lewatit TP 214 chelating resins. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Hafnium:* The concentration of hafnium was lowered from 2.8 ppm in the original coal to 1.5 ppm, 2.2

ppm and 1.5 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the unpurified Refcoal, an increase in concentration occurred from 1.7 ppm in the unpurified Refcoal to 2.2 ppm in Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 208 chelating resins, which suggests contamination. The concentration of hafnium was lowered from 2.8 ppm in the original coal to 1.7 ppm and 1.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260 and Lewatit TP 208 chelating resins respectively. The concentration of hafnium was increased from 2.8 ppm in the original coal to 4.1 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 214 chelating resins, which suggests contamination. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Iron:* The concentration of iron was lowered from 3400 ppm in the original coal to 200 ppm, 100 ppm and 150 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating respectively. The concentration of iron was lowered from 3400 ppm in the original coal to 200 ppm, 300 ppm and 100 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Lanthanum:* The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 2.4 ppm, 0.7 ppm and 1.6 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 2.5 ppm, 1.6 ppm and 2.7 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Scandium:* The concentration of scandium was lowered from 5.7 ppm in the original coal to 2.4 ppm, 1.7 ppm and 2.7 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of scandium was lowered from 5.7 ppm in the original coal to 2.5 ppm, 2.0 ppm and 1.4 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Samarium:* The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.8 ppm, 0.5 ppm and 1.3 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. An increase in samarium concentration was observed from 0.6 ppm in the unpurified Refcoal derived from the extraction with sodium hydroxide only, to 0.8 ppm and 1.3 ppm after treatment with Lewatit TP 260 and Lewatit TP 214 chelating resins respectively, which suggests contamination. The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.7 ppm, 0.5 ppm and 0.6 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Tantalum:* The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.4 ppm, 0.2 ppm and 0.5 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm, 0.4 ppm and 0.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 208 chelating resin gives better purification for tantalum than the Lewatit TP 260 and Lewatit TP 214 chelating resins. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Terbium:* The concentration of terbium was lowered from 0.6 ppm in the original coal to 0.1 ppm, 0.2 ppm and 0.1 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of terbium was lowered from 0.6 ppm in the original coal to 0.1 ppm in all the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Thorium:* The concentration of thorium was lowered from 4.9 ppm in the original coal to 2.3 ppm, 2.4 ppm and 2.4 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of thorium was lowered from 4.9 ppm in the original coal to 2.7 ppm, 2.2 ppm and 2.6 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Uranium:* The concentration of uranium was lowered from 2.0 ppm in the original coal to1.4 ppm, 1.1 ppm and 1.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the unpurified Refcoal derived from the extraction with sodium hydroxide only, an increase in uranium concentration was observed from 0.4 ppm in the, to 1.4 ppm, 1.1 ppm and 1.2 ppm after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively, which suggests contamination. The concentration of uranium was lowered from 2.0 ppm in the original coal to 1.2 ppm, 0.7 ppm and 1.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

**Table 4.10: Average concentration of elements in Tshikondeni Refcoal derived from treating Refcoal solution with chelating resins (ppm)**

| Element | Coal | NaOH-extracted | | | | NaOH and $Na_2S$-extracted | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | RCW | TP 260 | TP 208 | TP 214 | RCW | TP 260 | TP 208 | TP 214 |
| Ba | 3190 | 202 | 87 | 636 | 82 | 448 | 686 | 897 | 516 |
| Br | 4.1 | 0.7 | 6.3 | 0.4 | 6.9 | 0.9 | 5.6 | 3.2 | 7.4 |
| Co | 8.7 | 6.9 | 4.9 | 5.6 | 5.2 | 4.8 | 7.4 | 6.2 | 6.2 |
| Cr | 11 | 7.2 | 6.1 | 6.8 | 9.0 | 7.1 | 8.5 | 8.8 | 6.4 |
| Cs | 1.1 | 0.3 | 0.09 | 0.07 | 0.1 | 0.1 | 0.20 | 0.04 | 0.1 |
| Eu | 0.6 | 0.08 | 0.18 | 0.04 | 0.2 | 0.06 | 0.04 | 0.20 | 0.1 |
| Fe | 3400 | 1000 | 200 | 100 | 150 | 4100 | 200 | 300 | 100 |
| Hf | 2.8 | 1.7 | 1.5 | 2.2 | 1.5 | 1.9 | 1.7 | 1.5 | 4.1 |
| La | 15.8 | 1.6 | 2.4 | 0.7 | 1.7 | 4.8 | 2.5 | 1.6 | 2.7 |
| Sc | 5.7 | 2.7 | 2.4 | 1.7 | 2.7 | 2.2 | 2.5 | 2.0 | 1.4 |
| Sm | 2.7 | 0.6 | 0.8 | 0.5 | 1.3 | 2.3 | 0.7 | 0.5 | 0.6 |
| Ta | 0.6 | 0.5 | 0.4 | 0.2 | 0.5 | 0.3 | 0.5 | 0.4 | 0.5 |
| Tb | 0.6 | 0.2 | 0.1 | 0.2 | 0.1 | 0.7 | 0.1 | 0.1 | 0.1 |
| Th | 4.9 | 2.6 | 2.3 | 2.4 | 2.4 | 1.7 | 2.7 | 2.2 | 2.6 |
| U | 2.0 | 0.4 | 1.4 | 1.1 | 1.2 | 1.3 | 1.2 | 0.7 | 1.5 |

Note: nd = undetected; RCW = water-precipitated unpurified Refcoal; TP 260 = Lewatit TP 260 chelating resin-treated Refcoal; TP 208 = Lewatit TP 208 chelating resin-treated Refcoal; TP 214 = Lewatit TP 214 chelating resin-treated Refcoal

**Table 4.11: Extent of purification of trace elements in Tshikondeni Refcoal**

| **Element** | **NaOH-extracted** | | | | **NaOH and $Na_2S$-extracted** | | | |
|---|---|---|---|---|---|---|---|---|
| | RCW | TP 260 | TP 208 | TP 214 | RCW | TP 260 | TP 208 | TP 214 |
| Ba | 16 | 37 | 5 | 39 | 7.1 | 5 | 4 | 6 |
| Br | 5.9 | <1 | 10 | <1 | 4.6 | <1 | 1.3 | <1 |
| Co | 1.3 | 1.8 | 1.6 | 1.7 | 1.2 | 1.2 | 1.4 | 1.4 |
| Cr | 1.5 | 1.8 | 1.6 | 1.2 | 1.5 | 1.3 | 1.2 | 1.7 |
| Cs | 3.7 | 12 | 16 | 10 | 11 | 5.5 | 28 | 10 |
| Eu | 7.5 | 3.3 | 15 | 3 | 10 | 15 | 3 | 3 |
| Fe | 7.9 | 15 | 30 | 20 | <1 | 15 | 10 | 30 |
| Hf | 1.7 | 1.9 | 1.3 | 1.9 | 1.5 | 1.6 | 1.9 | <1 |
| La | 10 | 6.6 | 23 | 10 | 3.3 | 6.3 | 10 | 5.9 |
| Sc | 2.1 | 2.4 | 3.4 | 2.1 | 2.6 | 2.3 | 2.9 | 4.1 |
| Sm | 4.5 | 3.4 | 5.4 | 2.1 | 1.2 | 3.9 | 5.4 | 4.5 |
| Ta | 1.2 | 1.5 | 3 | 1.2 | 2 | 1.2 | 1.5 | 1.2 |
| Tb | 3 | 6 | 3 | 6 | <1 | 6 | 6 | 6 |
| Th | 1.9 | 2.1 | 2 | 2 | 2.9 | 1.8 | 2.2 | 1.9 |
| U | 2.5 | 1.4 | 1.8 | 1.7 | 1.5 | 1.7 | 2.9 | 1.3 |

Note: RCW = water-precipitated unpurified Refcoal; TP 260 = Lewatit TP 260 chelating resin-treated Refcoal; TP 208 = Lewatit TP 208 chelating resin-treated Refcoal; TP 214 = Lewatit TP 214 chelating resin-treated Refcoal

### 4.3.3.1 Conclusions

The above observations can be summarised as follows for Refcoal derived from the extraction with sodium hydroxide only and Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide treated with Lewattit TP 260 chelating resins:

- High purification, with purification values of 20 and above, is observed for Ba.

- Purification values of between 15 and 20 are observed for Fe.
- Values between 5 and 15 are observed for Cs, La and Tb.
- Purification values below 5 are observed for Br, Co, Cr, Eu, Hf, Sc, Sm, Ta, Th and U.

The above observations can be summarised as follows for Refcoal derived from the extraction with sodium hydroxide only and Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide treated with Lewattit TP 208 chelating resins:

- High purification, with purification values of 20 and above, is observed for Fe and La.
- Values between 5 and 15 are observed for Ba, Br, Cs, Eu and Sm.
- Purification values below 5 are observed for Co, Cr, Hf, Sc, Ta, Tb, Th and U.

The above observations can be summarised as follows for Refcoal derived from the extraction with sodium hydroxide only and Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide treated with Lewattit TP 214 chelating resins:

- High purification, with purification values of 20 and above, is observed for Ba and Fe.
- Values between 5 and 15 are observed for Cs and La.
- Purification values below 5 are observed for Br, Co, Cr, Eu, Hf, Sc, Sm, Ta, Tb, Th and U.

Treatment of Refcoal solution with chelating resins did not remove rare earth metals to any significant extent. Low purification of Sm, Th and U may be due to contamination or analytical variations. Alkali metals, represented by Cs, together with Fe appear to be the only elements removed completely when the Refcoal solution is treated with chelating resins. A serious contamination problem occurs when the Refcoal solution is treated with chelating resins, suggesting. No significant difference in purification between the Refcoal solution derived from the extraction with sodium hydroxide only and that derived from the extraction with both sodium hydroxide and sodium sulphide was observed, as shown in Table 4.10.

### 4.3.4 Extraction of trace elements from Refcoal gel with chelating resins

The average concentrations of the trace elements monitored in the Refcoal samples derived from treating Refcoal gel are listed in Table 4.7 for the extraction with sodium hydroxide only, and in Table 4.8 for the extraction with both sodium hydroxide and sodium sulphide. The purification experiments conducted were initial experiments and were not optimised. The concentrations given are an average of at least two determinations as given in Appendix 3. Table 4.9 lists the extent of purification, calculated as a ratio of concentration in the original coal to concentration in the Refcoal, for each of the elements monitored. The extent of purification is discussed below:

*Barium*: The concentration of barium was lowered from 3190 ppm in the original coal to 23.5 ppm and 13.5 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260 and Lewatit TP 214 chelating resins respectively. The concentration of barium was lowered from 3 190 ppm in the original coal to a concentration that is close to the detection limit in Lewatit TP 208 chelating resin-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of barium was lowered from 3 190 ppm in the original coal to 490 ppm, 158 ppm and 217 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to hydrofluoric acid-treated Refcoal, an increase in concentration occurred from 324 ppm in hydrofluoric acid-treated Refcoal to 490 ppm in the Lewatit TP 260 chelating resin-treated Refcoal, which suggests contamination. It appears that the Lewatit TP 208 chelating resin gives better purification for barium than the Lewatit TP 260 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with sodium hydroxide only than for that derived from the extraction with both sodium hydroxide and sodium sulphide.

*Bromine*: The concentration of bromine was lowered from 4.1 ppm in the original coal to 1.0 ppm, 2.2 ppm and 1.3 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of bromine increased from 4.1 ppm in the original coal to 4.3 ppm in Lewatit TP 260 chelating resin-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which suggests contamination. The concentration of bromine was lowered from 4.1 ppm in the original coal to 2.9 ppm and 3.6 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With respect to hydrofluoric acid-treated Refcoal, an increase in concentration occurred from 1.7 ppm in hydrofluoric acid-treated Refcoal to 4.2 ppm, 2.9 ppm and 3.6 ppm in the Refcoal treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively, which suggests contamination. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and the extent of purification in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Cesium:* The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.2 ppm, 0.04 ppm and 0.04 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.03 ppm in all the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 208 and Lewatit TP 214 chelating resins give better purification for cesium than the Lewatit TP 260 chelating resin. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for that derived from the extraction with sodium hydroxide only.

*Cobalt*: The concentration of cobalt was lowered from 8.7 ppm in the original coal to 4.8 ppm, 4.3 ppm and 4.5 in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of cobalt was lowered from 8.7 ppm in the original coal to 3.4 ppm, 2.4 ppm and 3.9 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed. For all the samples analysed, no significant cobalt purification was demonstrated.

*Chromium*: The concentration of chromium was lowered from 11.0 ppm in the original coal to 4.7 ppm, 4.2 ppm and 3.7 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of chromium was lowered from 11.0 ppm in the original coal to 3.5 ppm, 4.4 ppm and 4.0 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. For all the samples analysed, no significant chromium purification was demonstrated. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Europium*: The concentration of europium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit in Lewatit TP 260 and Lewatit TP 208 chelating resin-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of europium was lowered from 0.6 ppm in the original coal to 0.008 ppm in Lewatit TP 214 chelating resin-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of europium was lowered from 0.6 ppm in the original coal to 0.005 ppm in Lewatit TP 260 chelating resin-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of europium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit in Lewatit TP 208 and Lewatit TP 214 chelating resin-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only. It appears that Lewatit TP 208 chelating resin gives better purification for europium than Lewatit TP 260 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

*Hafnium:* The concentration of hafnium was lowered from 2.8 ppm in the original coal to 0.1 ppm, 0.1 ppm and 0.08 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of hafnium was lowered from 2.8 ppm in the original coal to 0.06 ppm, 0.2 ppm and 0.05 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 214 gives better purification for europium than the Lewatit TP 208 and Lewatit TP 260 chelating resins. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Iron:* The concentration of iron was lowered from 3400 ppm in the original coal to 10 ppm in Lewatit TP 260 chelating resin-treated Refcoal coal and to 50 ppm in both Lewatit TP 208 and Lewatit TP 214 chelating resin-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of iron was lowered from 3400 ppm in the original coal to 200 ppm and 100 ppm in both Lewatit TP 208 and Lewatit TP 214 chelating resin-treated Refcoal and to a concentration that is close to the detection limit in Lewatit TP 208 chelating resin-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. It appears that Lewatit TP 208 chelating resin gives better purification for iron than Lewatit TP 260 and Lewatit TP 214 chelating resins for the Refcoal derived from the extraction with sodium hydroxide only. Purification appears to be better for the Refcoal derived from the extraction with sodium hydroxide only than for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

*Lanthanum:* The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 0.3 ppm, 0.6 ppm and 1.8 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the hydrofluoric acid-treated Refcoal, there was an increase in the lanthanum concentration for the chelating resin-treated Refcoal, which suggests contamination. The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 0.03 ppm, 0.1 ppm and 0.04 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 260 chelating resin gives better purification for lanthanum than the Lewatit TP 208 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

*Scandium:* The concentration of scandium was lowered from 5.7 ppm in the original coal to 0.09 ppm, 0.08 ppm and 0.08 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the hydrofluoric acid-treated Refcoal, there was an increase in scandium concentration for the Lewatit TP 260 chelating resin, which suggests contamination. The concentration of scandium was lowered from 5.7 ppm in the original coal to 0.05 ppm, 0.2 ppm and 0.05 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that Lewatit TP 214 chelating resin gives better purification for scandium than Lewatit TP 260 and Lewatit TP 208 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

*Samarium:* The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.05 ppm, 0.4 ppm and 0.3 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With respect to the hydrofluoric acid-treated Refcoal, there was an increase in samarium concentration for the Lewatit TP 208 and Lewatit TP 214 chelating resins, which suggests contamination. The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.03 ppm, 0.03 ppm and 0.04 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that Lewatit TP 260 chelating resin gives better purification for samarium than Lewatit TP 208 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

*Tantalum:* The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm, 0.6 ppm and 0.3 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm, 0.6 ppm and 0.3 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Terbium:* The concentration of terbium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit for all the Refcoal derived from the extraction with sodium hydroxide only, treated Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. The concentration of terbium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit for all the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

*Thorium:* The concentration of thorium was lowered from 4.9 ppm in the original coal to 1.1 ppm, 0.7 ppm and 1.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of thorium was lowered from 4.9 ppm in the original coal to 0.07 ppm, 0.07 ppm and 0.1 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that Lewatit TP 208 chelating resin gives better purification for thorium than Lewatit TP 260 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

*Uranium:* The concentration of uranium was lowered from 2.0 ppm in the original coal to a concentration that is close to the detection limit for the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260 chelating resins. The concentration of uranium was lowered from 2.0 ppm in the original coal to0.3 ppm and 0.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of uranium was lowered from 2.0 ppm in the original coal to 0.1 ppm, 0.6 ppm and 0.4 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. Purification appears to be better for the Refcoal derived from the extraction with sodium hydroxide only than for that derived from the extraction with both sodium hydroxide and sodium sulphide.

#### 4.3.4.1 Conclusions

The above observations are summarised below:

With regard to the original coal, the degree of purification of the Refcoal gel treated with chelating resins is as follows for the extraction with sodium hydroxide only:

- ✏ High purification, with purification values of 20 and above, is observed for Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Tb and U.
- ✏ Purification values below 5 are observed for Br, Co, Cr, Ta and Th.

The degree of purification of the Refcoal gel treated with chelating resins is as follows for the extraction with both sodium hydroxide and sodium sulphide:

- High purification, with purification values of 20 and above, is observed for Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Tb, Th, and U.
- Purification values below 5 are observed for Br, Co, Cr and Ta.

Precipitating Refcoal solution in water, followed by treating the resulting gel with acids and finally with chelating resins, appears to remove the elements Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Tb, Th and U. This suggests that these elements are either present as cationic ions in the coal matrix or are mainly present in inorganic association with the coal matrix. Elements such as cobalt, chromium and tantalum show little or no purification. This suggests that these elements are either strongly held in organometallic compounds in the coal matrix or are present as anionic ions in the coal matrix. The cobalt concentration appears to be lowered if the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide is first treated with acids, followed by resins. The elements Ba, Cs, Eu, Fe, Hf, La, Sc, Tb and Th are removed better with the chelating resin Lewatit TP 208, the elements Cs, Eu, Fe, La, Sm, Tb and U are removed better with the chelating resin Lewatit TP 260 and the elements Ba, Cs, Fe, Hf, La, Sc, Sm, Tb and Th are removed better with the chelating resin Lewatit TP 214. The chelating resin Lewatit TP 208 appears to be more effective than the other two chelating resins, i.e. Lewatit TP 260 and Lewatit TP 214, in lowering the amount of impurities in the Refcoal gel and or solution. Lewatit TP 208 is the sodium form of the iminodiacetic acid resin, which suggests that most of the elements that are removed by this resin are cations.

### 4.3.5 Extraction of trace elements with sulphonic acid resins

Initial experiments were conducted to determine whether sulphonic acid resins could be used in a Refcoal purification process. The experiments involved treating Refcoal solution and Refcoal gel with the resins, as explained in the procedure. Table 4.12 below lists the average concentrations of the elements monitored in the Refcoal samples derived from treating the Refcoal solution with the resins, usually at 140 to 145 °C, and in the samples derived from treating the Refcoal gel with the resins, usually at about 80 °C. The concentrations given in Table 4.12 are averages of two determinations. The Refcoal gel was obtained by precipitating the Refcoal solution in distilled water, followed by treatment with hydrochloric acid and hydrofluoric acid, as explained before.

For the Refcoal samples derived from treating the Refcoal gel with sulphonic acid resins, the degree of purification in relation to the original coal is as follows, for the Refcoal gel derived from the extraction with sodium hydroxide only:

- High purification, with purification values of 20 and above, is observed for Cs, Eu, Fe, Hf, La, Sc, Sm, Tb, Th and U.
- Purification values below 5 are observed for Br, Co, Cr and Ta.

The degree of purification in relation to the original coal is as follows, for the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide:

- High purification, with purification values of 20 and above, is observed for Cs, Eu, Fe, Hf, La, Sc, Sm, Ta, Tb, Th and U.
- Purification values below 5 are observed for Br, Co and Cr.

The samples derived from treating the Refcoal solution with the sulphonic acid resins did not show any purification for the rare earth elements and cobalt. However, tantalum, which did not show any purification with chelating resins, appears to be lowered for the both the Refcoal solution and the Refcoal gel derived from the extraction with sodium hydroxide only. The use of sulphonic acid resins appears to give better than the chelating resins for cobalt which may be because of the high temperature to which the resins can be taken. Sulphonic acid resins are cheaper than chelating resins, therefore future work should look into the application of the sulphonic acid resins in place of the chelating resins.

**Table 4.12: Concentrations of trace elements in Refcoal derived from Refcoal gel and Refcoal solution treated with sulphonic acid resins (ppm)**

| | Refcoal extracted with NaOH only | | Refcoal extracted with NaOH and $Na_2S$ | |
|---|---|---|---|---|
| Element | Derived from treating Refcoal solution | Derived from treating Refcoal gel | Derived from treating Refcoal solution | Derived from treating Refcoal gel |
| Br | 1.6 | 0.8 | 10.6 | 4.5 |
| Co | 5.6 | 1.5 | 4.9 | 2.5 |
| Cr | 10.1 | 2.1 | - | 3 |
| Cs | nd | nd | 0.2 | nd |
| Fe | 300 | nd | 100 | nd |
| Hf | 2.2 | 0.07 | 1.7 | 0.07 |
| La | 1.9 | nd | 3.3 | 0.09 |
| Sc | 3 | 0.04 | 2.4 | 0.07 |
| Sm | 1.06 | 0.02 | 0.9 | 0.03 |
| Ta | 0.2 | 0.2 | 0.6 | nd |
| Tb | 0.2 | nd | 0.1 | nd |
| Th | 2.2 | 0.1 | 2.6 | 0.1 |
| U | 1.3 | nd | 1.4 | - |

Note: - = not determined; nd = undetected

### 4.3.6 Extraction of cobalt with ammonia hydroxide solution, sodium nitrite solution and anion exchange resins

Initial experiments were conducted to investigate the effect of ammonium and sodium nitrite on cobalt. As it was reported in the literature that cobalt(III) ions have greater affinity for $NH_3$ and $NO_2$, we reasoned that treating the Refcoal solution with these compounds would complex the cobalt(III) ions present in the coal matrix. The results of these experiments are listed in Table 4.13 below. The concentrations given in Table 4.13 are averages of two determinations. The samples obtained by treating with *ammonium hydroxide* the Refcoal gel derived from the extraction with sodium hydroxide only, and the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide, did not show any lowering of the cobalt concentration, which suggests that cobalt is present in a more stable complex in the Refcoal. The samples obtained by treating with *sodium nitrite* the Refcoal gel derived from the extraction with sodium hydroxide only, and the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide, did show some lowering of the cobalt concentration, which suggests that the nitrite ion ($NO_2$) forms a complex with the cobalt that is more stable than the complex in which cobalt exists in the coal. The Refcoal derived from treating the Refcoal gel extracted with sodium hydroxide only with ammonia solution, followed by anionic resins, shows some purification for most of the elements, with the cobalt concentrations in particular being reduced from 7.45 ppm to 4.29 ppm.

The lowering of the cobalt concentration appears to be better with the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide, treated in the same way. In this case, the cobalt concentration is reduced from 7.52 ppm to 3.70 ppm. This suggests that sodium sulphide aids in the demetalation of cobalt from its complex in the Refcoal, and future work should be directed towards the use of sodium sulphide in the extraction and purification of coal. Just as observed with the chelating resins, the anion resins also introduced some bromine into the sample. Tantalum, which did not show any purification with chelating resins, appears to be lowered with anion resins. This suggests that tantalum is in anionic form in the Refcoal and for this reason could not be removed by the chelating resins. The rare earth metals did not show any purification with anion resins, which suggests that they are present in cationic form in the Refcoal.

**Table 4.13: Concentrations of trace elements in Refcoal derived from Refcoal gel treated with $NH_3$, $NaNO_2$ and anion resins (ppm)**

| | **Refcoal extracted with NaOH only** | | | **Refcoal extracted with NaOH and $Na_2S$** | | |
|---|---|---|---|---|---|---|
| **Element** | **$NH_3$-treated** | **$NaNO_2$-treated** | **Resin-treated** | **$NH_3$-treated** | **$NaNO_2$-treated** | **Resin-treated** |
| Br | 1.1 | 1.8 | 12.6 | 1.5 | 2.3 | 14.4 |
| Co | 7.8 | 6.3 | 4.3 | 7.2 | 7.8 | 3.7 |
| Cr | 9.4 | 6.4 | 5.9 | 7.2 | 7.5 | 6.3 |
| Cs | 0.2 | 0.1 | 0.05 | 0.2 | 0.1 | 0.1 |
| Eu | 0.2 | 0.2 | nd | 0.2 | 0.08 | 0.1 |
| Hf | 2.7 | 2 | 0.8 | 2.4 | 0.9 | 1.1 |
| La | 3.1 | 2.6 | 1.13 | 2 | 2.1 | 0.8 |
| Sc | 3.9 | 2.9 | 0.03 | 3.2 | 1.3 | 1.6 |
| Sm | 0.8 | 0.8 | 0.4 | 0.7 | 0.7 | 0.3 |
| Ta | 0.5 | 0.6 | 0.6 | 0.5 | 0.2 | 0.2 |
| Th | 2.4 | 2.6 | 0.1 | 2.7 | 1.2 | 1.5 |
| U | 1.2 | 2.8 | 1.3 | 1.2 | 3.8 | 1.4 |

Note: nd = undetected

### 4.3.7 Colorimetric determination of cobalt

The analysis of coal is normally done by either ICP-AES, ICP-MS, INAA or XRF to obtain reasonable and acceptable data. These instruments are, however, very expensive and not every institution can afford its own. The University of Pretoria did not have such instruments at the time of this work. Samples had to be sent to the University of the Witwatersrand for analysis, which usually took about six to eight weeks before results were obtained. The only instruments available at the University of Pretoria that could be used for this work were the AA and UV/VIS. We therefore selected cobalt as an indicator element, and its rapid determination by the colorimetric method using a UV/VIS spectrophotometer was investigated. The calibration curve (Figure 4.9) obtained using the published method showed that the method could indeed be used successfully for the determination of cobalt. However, determinations using representative samples (Table 4.14) gave inconsistent results. This could be attributed to a number of factors. First, the digestion method, which employs an open vessel, is not reproducible as we had thought, leading to some samples being digested completely and others not. Secondly, contamination from the atmosphere, the vessel and the reagents used could be the cause of the inconsistency. Furthermore, the loss of analyte, due to volatilisation during digestion and to incomplete extraction of the cobalt complex into the chloroform solution, could be the cause of the low concentration values obtained in some samples. Finally, because of the complex matrix we are dealing with in coal and because the level of impurities is not well known, interference from elements such as iron, nickel, tin, copper and the platinum group metals cannot be ruled out.

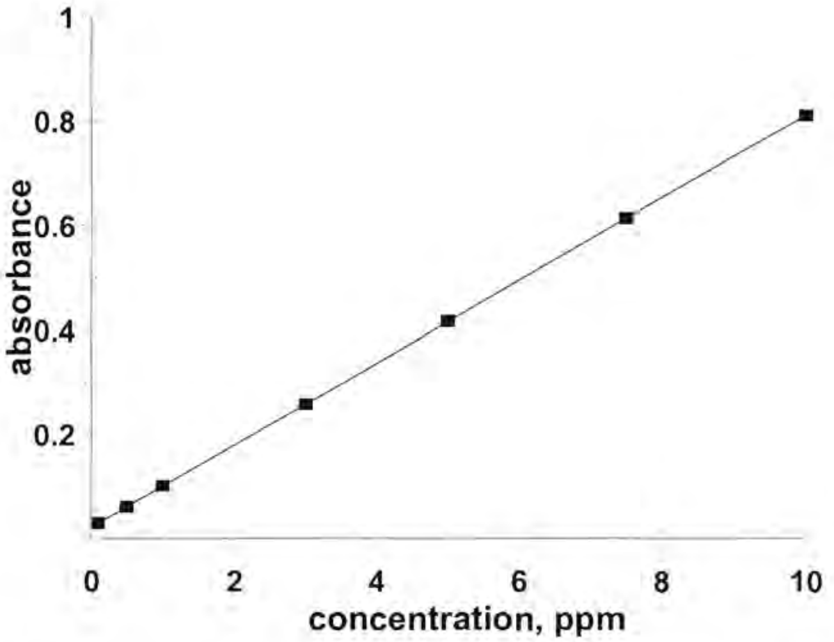

**Figure 4.9: Calibration curve for the colorimetric determination of cobalt**

**Table 4.14: Cobalt concentration in Refcoal as determined by colorimetric method**

| **Sample** | **RCO** | **RCB** | **RCR6** | **RCR9** | **RCR13** | **RCR14** | **RCR15** |
|---|---|---|---|---|---|---|---|
| Concentration, ppm | 6.3 | 6.6 | 2.1 | 17.3 | 15.4 | 7.2 | 6.2 |
| | 4.3 | 10.8 | 8.5 | 12.9 | 12.5 | 5 | 10.8 |
| | 6.1 | 15.6 | 1.7 | 5.8 | 16.6 | 5.8 | 6.7 |
| | 4.3 | 7.3 | 3.5 | | | | |
| | 0.8 | 7.7 | 9.7 | | | | |
| | 2.1 | 7.3 | 3.1 | | | | |
| | 5.6 | 2.1 | | | | | |
| | 2.3 | 15.1 | | | | | |
| | 3.6 | 9.8 | | | | | |
| Average | 3.9 | 9.1 | 4.8 | 12 | 14.8 | 6 | 7.9 |
| Standard deviation, δ | 1.8 | 4 | 3.1 | 4.7 | 1.7 | 0.9 | 2.1 |

# CHAPTER 5

## GENERAL CONCLUSIONS

The Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide appears to be lower in cobalt but higher in almost all the elements determined. Future work should be geared towards the extraction of carbon from coal with as little as possible amount of sodium sulphide to improve the coking of the Refcoal. High amounts of sodium sulphide should be avoided. A proper washing process for the recovery of the Refcoal from the Refcoal solution needs to developed.

Refcoal solution treated with chelating resins did not remove rare earth metals as well as cobalt but tantalum appears to be lowered. There is no significant difference in terms of impurities between the Refcoal solution derived from the extraction with both sodium hydroxide and sodium sulphide treated with resins, and the Refcoal solution derived from the extraction with sodium hydroxide only also treated with the resins.

The hydrochloric acid treated Refcoal samples derived from the extraction with both sodium hydroxide and sodium sulphide appear to be low in the rare earth and cobalt than the Refcoal samples derived from the extraction with sodium hydroxide only. The hydrofluoric acid treated samples also show a similar trend, which suggests that the sodium sulphide is necessary for the demetalation of the metal complex in the coal matrix. Future work has to be geared towards this approach. Both hydrochloric acid and hydrofluoric acid treated samples show an increase in the concentration of Br, which suggests contamination by the acids. A similar increase in Br concentration is demonstrated when the Refcoal solution is treated with chelating resins which also suggests contamination by the resins.

Good purification is demonstrated for all the elements determined except for cobalt, chromium and tantalum if the Refcoal is first precipitated in water, followed by successive treatment with concentrated hydrochloric acid, concentrated hydrofluoric acid and chelating resins. Chromium and tantalum are not a problem with respect to nuclear carbon, the only real problem is cobalt. The Lewatit TP 208 chelating resins appear to be working better than the other two chelating resins, that is Lewatit TP 260 and Lewatit TP 208 chelating resins. The use of sulphonic acid resins appears to be even better than the Lewattit chelating resins as shown in Table 5.1 below.

**Table 5.1Concentration of trace elements in Refcoal derived from treating Refcoal gel with sulphonic acid resins and Lewatit TP 208 chelating resins (ppm)**

| Element | Coal | Refcoal extracted with NaOH only | | | Refcoal extracted with both NaOH and $Na_2S$ | | |
|---|---|---|---|---|---|---|---|
| | | Unpurified Refcoal | Lewatit TP 208 resins | Sulphonic acid resins | Unpurified Refcoal | Lewatit TP 208 resins | Sulphonic acid resins |
| Br | 4.1 | 0.7 | 2.2 | 0.8 | 0.9 | 2.9 | 4.5 |
| Co | 8.7 | 6.9 | 4.3 | 1.5 | 4.8 | 2.4 | 2.5 |
| Cr | 11 | 7.2 | 4.2 | 2.1 | 7.1 | 4.4 | 3 |
| Cs | 1.1 | 0.3 | 0.04 | nd | 0.1 | 0.03 | nd |
| Fe | 3400 | 1000 | 50 | nd | 4100 | nd | nd |
| Hf | 2.8 | 1.7 | 0.1 | 0.07 | 1.9 | 0.2 | 0.07 |
| La | 15.8 | 1.6 | 0.6 | nd | 4.8 | 0.7 | 0.09 |
| Sc | 5.7 | 2.7 | 0.08 | 0.04 | 2.2 | 0.2 | 0.07 |
| Sm | 2.7 | 0.6 | 0.4 | 0.02 | 2.3 | 0.03 | 0.03 |
| Ta | 0.6 | 0.5 | 0.6 | 0.2 | 0.3 | 0.6 | nd |
| Tb | 0.6 | 0.2 | nd | nd | 0.7 | nd | nd |
| Th | 4.9 | 2.6 | 0.7 | 0.1 | 1.7 | 0.07 | 0.1 |
| U | 2 | 0.4 | 0.3 | nd | 1.3 | 0.7 | |

Note: nd = undetected