

# GRAPHITIZABLE CARBON PRECURSORS BY ALKALI-INDUCED COAL EXTRACTION WITH POLAR APROTIC SOLVENTS

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## Abstract

Coal dissolves to a limited extent in pure polar aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAA), and N-methyl-2-pyrrolidinone (NMP). The addition of sodium hydroxide (NaOH) increases the degree of coal dissolution in organic solvents. Similar degrees of extraction were achieved with DMF. Sodium sulfide (Na<sub>2</sub>S) addition aided the recovery of carbon precursors that led to graphitizable cokes. Extraction experiments were conducted using coal, containing 10% ash, from the Tshikondeni mine in South Africa. Depending on the extraction conditions, carbon extraction efficiencies of up to 92% were obtained. Coal material was recovered from the solution as a gel by precipitation with water. Ash content was reduced from 10% in the coal to <1.6% in the coal extracts. Addition of Na<sub>2</sub>S, 1:1 molar ratio of NaOH to Na<sub>2</sub>S, further reduced ash content to 0.7%. The degree of graphitization of cokes derived from the extracts depends on the extraction conditions, temperature, NaOH/Na<sub>2</sub>S ratio.

**Keywords:** graphitizability, coal, coke, extraction, aprotic solvent.

## Introduction

Coal is readily available in South Africa and therefore in principle it ought to be an inexpensive precursor for the production of high purity carbon. High-purity carbon is required for the manufacture of pure graphite used as a moderator for nuclear reactors. Coal contains large and complex macromolecules and mineral matter as well as other organic entities entrapped within the macromolecular structure (Cappiello *et al.*, 1996). Therefore to be an effective source of graphitisable carbon it is essential to remove these impurities and generate a precursor capable of fusion and development of carbonaceous mesophase. The appropriate polynuclear aromatic species must be extracted from the coal network. Various forces hold the various organic entities that make up coal, together. They range from hydrogen and covalent bonds to  $\pi$ - $\pi$ , charge transfer and ionic interactions (Gorbaty, 1994; Slezinga & Marzec, 1983; Iino, 2000, Giri & Sharma, 2000b). Coal swells in organic solvents. The swollen coal shows rubber-like elasticity indicating a network structure (Gorbaty, 1994; Iino, 2000; Slezinga & Marzec, 1983). For an organic solvent to dissolve coal, it should be capable of breaking the  $\pi$ - $\pi$ , charge transfer and covalent bonds holding the coal molecules together.

The extraction of the organic part of coal may be achieved by physical or chemical methods (Mukherjee & Borthakur, 2001). Physical methods are based on the differences in the physical properties of the minerals and the carbonaceous part of coal.

Alkaline solutions, comprising a sodium or ammonium hydroxide and hydrosulfide or carbonate can be used for coal beneficiation processes (Stambaugh, 1978). The alkali extraction is followed by acid washing using formic, acetic, sulphuric or hydrochloric acid. In a typical procedure, coal is treated with aqueous NaOH at temperatures ranging from 100°C to 350°C. Under these conditions, aluminosilicate compounds (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>OH and (NaMg,Al)-Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>) react to form insoluble sodalite (Na<sub>8</sub>Si<sub>6</sub>Al<sub>6</sub>O<sub>24</sub>). Sodalite is fairly soluble in dilute mineral acids. This forms the basis for coal cleaning using a dilute alkali followed by washing with mineral acid.

Another chemical method involves extraction of the organic part in various solvents utilizing various additives. It has been shown that coal extraction with organic solvents or demineralization process strongly modifies the chemical composition of the treated sample, with an increase in the volatile matter, oxygen and nitrogen contents (Rubiera *et al.*, 2002). This indicates a change in the

organic structure of the treated samples, with the incorporation of nitro groups as was confirmed by mass spectroscopy (MS) and Fourier Transform Infrared (FTIR) spectroscopy. Recently Okuyama *et al.* (2004) supplied details on the cost-effective Hyper-coal coal extraction process. It de-ashes coal with coal derived solvents, e.g. two-ring aromatics such as methyl-naphthalenes. The latter solvent has a good affinity for coal and features good thermal stability. Coal extractions approaching 70 wt% daf (based on dry and ash-free coal) were achieved with various ranks of coals at 350°C.

Coal solubility improves with temperature and when mixed solvents, e.g. carbon disulfide (CS<sub>2</sub>) and NMP, are used (Takahashi *et al.*, 2001; Stansberry *et al.*, 2002). This increased the yield to up to 85%. Shui *et al.* (2006) performed similar extraction experiments using four Chinese rank bituminous coals.

Morgan (1996) developed the “Refcoal” coal solubilization process. It is based on the efficient dissolution of the organic component of coal in polar aprotic solvents (DMF or NMP) with addition of an alkali (KOH or NaOH) in solid or liquid form. The research reported here evaluates the graphitizability of cokes derived from extracts produced at different temperatures and with sodium sulfide additions. The role of the latter is to enhance the extraction kinetics and reduce the residual mineral content in the extracts.

## Experimental

The coal used was a flotation product from the Tshikondeni Mine, Limpopo Province, South Africa. The coal analysis is given in Table 1.

DMF (1000 g), coal (100 g) and NaOH (10 g) were stirred vigorously at room temperature (RT) or at 95°C in a 1 litre steel reactor fitted with a hot oil jacket. A stream of nitrogen was allowed to flow continuously into the reactor to maintain an inert environment. Extractions were conducted over a period of about 5-6 hours.

Inorganic mineral matter and undissolved coal were removed from the solution by centrifugation at 1000 rpm using a Beckmann model GPR centrifuge. The extraction progress was monitored by sampling ~2 ml of the slurry at certain intervals. About 0.1 g of the supernatant solution was weighed into a 50 ml volumetric flask and diluted to the mark using DMF. The absorbance (A) of the solution was measured at a wavelength of 600 nm on a Spectronic Genesis-5 Ultraviolet spectrophotometer. The absorbances were corrected to exactly 0.1 g of the sample per 50 ml diluent. Similar experimental procedures were carried out using (C<sub>4</sub>H<sub>9</sub>ONa), CH<sub>3</sub>ONa or C<sub>2</sub>H<sub>5</sub>OLi instead of NaOH. Mass yields of coal organic matter were also evaluated. The NaOH:Na<sub>2</sub>S molar ratios tested were 4:1 (6.30 g Na<sub>2</sub>S), 2:1 (12.59 g Na<sub>2</sub>S) and 1:1 (25.21 g Na<sub>2</sub>S) while maintaining the NaOH concentration at a constant level.

The extracts were carbonized at 900°C and then further graphitized at 2950°C.

## Results and Discussion

Tables 1, 2 and 3 provide details on the coal petrography and proximate analysis. The oxygen content (%) was obtained by difference. The coal used is classified as a meta-bituminous (medium rank B) and has a high vitrinite content of 93%. Silicon is the main constituent element in the ash.

**Table 1.** Proximate (air-dry-basis) and ultimate analysis of Tshikondeni coal

Proximate Analysis		Ultimate analysis (d.a.f)	
Moisture	0.9 %	Carbon	90.86 %
Ash	9.4 %	Hydrogen	4.88 %
Volatile matter	23.3 %	Nitrogen	2.07 %
Fixed carbon	66.4 %	Oxygen	2.19 %
Total sulphur	0.81 %		

**Table 2.** Ash analysis of Tshikondeni coal

Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	Total
Tshikondeni	51.4	25.5	6.00	0.82	2.24	5.05	2.52	1.46	0.36	4.45	99.79

**Table 3.** Major petrographic characteristics of Tshikondeni coal

	<b>Tshikondeni coal</b>
Rank (degree of maturity)	Meta-bituminous
ACE-UN in-seam classification	(Medium rank B)
Mean random reflectance (%)	1.33
Vitrinite-class distribution	V10 – V16
Standard deviation ( $\sigma$ )	0.117
Abnormalities	Extended vitrinite-class distribution
<b>Petrographic composition – Analysis of macerals</b>	
Vitrinite content (%)	93
Liptinite content (%)	<1
Total reactive macerals (%)	94
Total inertinite (%)	6
More highly reflecting materials (%)	1
Cracks and fissures	Occasionally observed
Signs of advanced weathering or thermal effects	Very occasionally seen

Results indicated that more than 90 % of the organic part of a 10 % ash flotation product dissolved in N, N-dimethylformamide on addition of 10 % NaOH. The bulk of the impurities are removed by centrifugation and the dissolved organic material is recovered by water precipitation. The addition of Na<sub>2</sub>S (the molar ratio of NaOH to Na<sub>2</sub>S was 1:1) lowered the ash level further to 0.70 %. Na<sub>2</sub>S releases S<sup>2-</sup> ions into the medium thereby forming insoluble metal-sulfide complexes (Iino & Matsuda, 1983). The intention was to precipitate any metal impurities to aid their removal with the ash residue separated from the Refcoal solution. The extraction time also appeared to have been shortened significantly and this could be attributed to the combined strength of the nucleophiles in the solution. Na<sub>2</sub>S is a weaker nucleophile than NaOH. It is considered that the coal matrix softened and the broken bonds instantly allowed organics into the solution. High Na<sub>2</sub>S dosage (1:1 ratio), however, adversely affected the degree of extraction.

The elemental analysis of Refcoal extracted at 95°C is given in Table 4. Without Na<sub>2</sub>S, the coal extracts showed an ash content of 1.6 % (by weight). Increasing the S<sup>2-</sup> dosage causes a gradual decrease in the ash content: The ash content values were 1.3, 1.0, 0.7 (wt %) corresponding to Na<sub>2</sub>S:NaOH molar ratios of 4:1, 2:1, 1:1 respectively. Thus Na<sub>2</sub>S addition provides for higher purity coal extracts more favorable for producing graphitizable carbon. The oxygen carbon ratio is also reduced with increasing sulfide addition.

**Table 4.** Elemental analyses of coal extracts on the addition of different amounts of Na<sub>2</sub>S.

Molar ratio	Elemental analysis (wt %)					Ash	C/H	O/C
	NaOH:Na <sub>2</sub> S	C	H	N	O			
1:0	85.2	4.43	2.06	7.49	0.86	1.60	1.602	0.066
4:1	84.5	5.53	3.35	5.78	0.82	1.30	1.273	0.051
2:1	85.2	5.45	2.80	5.72	0.85	1.00	1.303	0.050
1:1	86.5	5.53	2.19	5.04	0.75	0.70	1.303	0.044

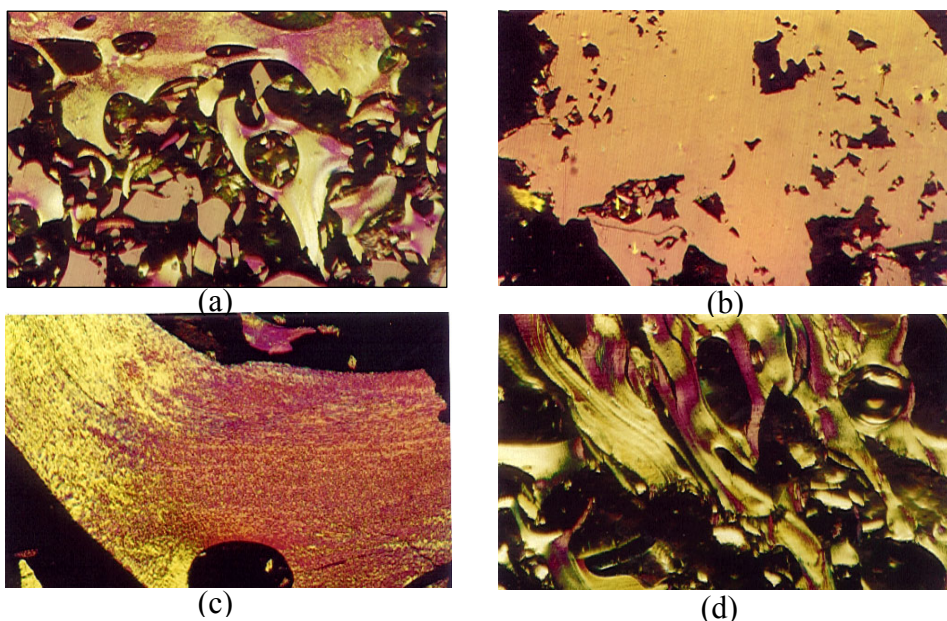
The Refcoal process can be summarized as follows:-

- DMF alone is a poor solvent for dissolving coal.
- An alkali is required for the solubilisation of coal to occur in polar organic solvents.
- More than 90% of the coal organic part can be recovered from a 10% ash flotation product (raw coal) from Tshikondeni mine.

- Ash level is reduced from 10% in the coal to <1.60% in the coal extracts. Addition of Na<sub>2</sub>S (the molar ratio of NaOH to Na<sub>2</sub>S was 1:1) further reduced ash content to 0.70%.
- Acid washing reduced inorganic mineral content considerably. Purification values above 20 for the elements were achieved.

### Carbonisation and Graphitisation of Refcoal Cokes

The heat-treatment of the coal extracts in nitrogen to 900°C produced a 75 % carbon yield. The optical texture of the subsequent cokes varied (Figure 1). The coke from the RT extracted sample without Na<sub>2</sub>S showed development of optical anisotropy with little evidence of extensive flow induced orientation of the anisotropic regions. The corresponding sample extracted at high temperature, however, exhibited no development of optical anisotropy at all and there appeared to have been little fusion of the material during carbonization. Clearly the molecular composition was significantly altered by the extraction temperature. The addition of Na<sub>2</sub>S, however, changed the situation markedly and both the RT and the higher temperature extracts gave cokes with extensive optical anisotropy. The RT/Na<sub>2</sub>S sample exhibited very fine domains whilst the HT/Na<sub>2</sub>S sample showed extensive flow orientation.



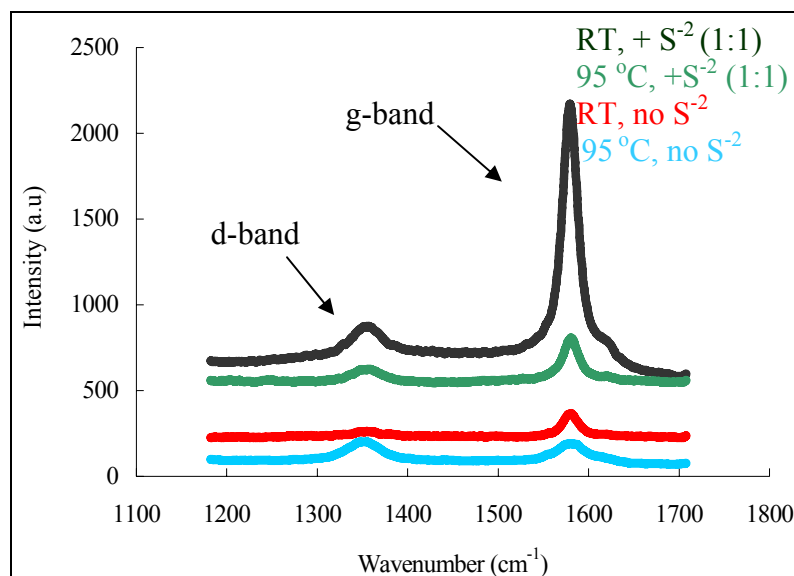
**Figure 1.** Micrographs of the cokes. (a) RT, no S<sup>-2</sup>, (b) 95 °C, no S<sup>-2</sup>, (c) RT, + S<sup>-2</sup> (1:1), (d) 95 °C, +S<sup>-2</sup> (1:1)

On graphitization to 2950°C the samples treated with Na<sub>2</sub>S showed a level of graphitization as did the RT sample with no Na<sub>2</sub>S addition. However, the higher temperature sample with no addition of Na<sub>2</sub>S did not graphitize at all. Table 5 shows the interlayer spacings deduced by XRD.

**Table 5.** XRD results of the graphitised cokes showing the interlayer thickness, d<sub>(002)</sub>

Extraction conditions	XRD, d <sub>(002)</sub> value
95 °C, no S <sup>-2</sup>	3.419
RT, no S <sup>-2</sup>	3.385
95 °C, +S <sup>-2</sup> (1:1)	3.376
RT, + S <sup>-2</sup> (1:1)	3.372

The corresponding Raman data is shown in Figure 2. The trend in the ratios of the Raman g to d peaks does not quite correspond with that in the interlayer spacings. However, It is clear from the results that graphitisable carbon can be produced by the Refcoal process and that the extraction conditions are critical in controlling the molecular composition of the extract and this in turn determines the development and coalescence of the microstructure during the mesophase stage, influencing the final coke optical textures and the subsequent graphitizability of the cokes themselves. Further work is required to determine the precise nature of these changes in chemical/molecular composition and also to further refine the process to reduce even further the residual level of inorganic impurity that remains in the extract and the subsequent carbons.



**Figure 2.** Raman spectra of the graphitised cokes showing bands at intensities of  $1360.5\text{ cm}^{-1}$  and  $1579.1\text{ cm}^{-1}$  for the d-peak and g-peak respectively.

## Conclusions

Untreated coals are not suitable carbon precursors owing to their high ash content and limited fusibility. The Refcoal coal solubilization process is effective at lowering the ash content of Tshikondeni coal. Relatively pure coal extracts were obtained and they may prove to be suitable starting materials for coking, carbonization and graphitization. The Refcoal process utilizes an alkali to aid the solubilization of coal in polar aprotic organic solvents. Carbon extraction efficiencies approaching ~92% were achieved. The strong alkali also increased the rate of coal dissolution. Addition of  $\text{Na}_2\text{S}$  further lowered the ash content but also significantly reduced the amount of organic extracted. The extracts produced with  $\text{Na}_2\text{S}$  addition gave cokes which were found to be graphitisable.

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