UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Coal Purification

by

Pabalala Meshack Mthembi

Submitted in partial fulfilment of the requirements for the degree

MAGISTER SCIENTIAE

in the Faculty of Natural and Agricultural Sciences

University of Pretoria

Pretoria

May 2003

© University of Pretoria

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

ACKNOWLEDGEMENTS

I wish to express my gratitude to the following people, without whom this thesis could not have been a success:

Prof. D L Morgan (promoter) for his assistance, supervision and informed guidance. Thank you also for giving me the MSc post.

Prof. W Focke, for his support and advice

Prof. R Hart of the Schonland Research Centre at the Witwatersrand University, for the analytical work he has done, was the cornerstone of the success of the project.

Eskom, Council for Scientific and Industrial Research (CSIR), Supra-Chem, The University of Pretoria and the National Research Foundation (NRF) for the financial assistance

All my students, for useful advice and encouragement

My wife and children for their wonderful love, understanding and encouragement

Pabalala Meshack Mthembi, May 2003

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Coal Purification

by

Pabalala Meshack Mthembi

Supervisor

Dr D L Morgan

Submitted in partial fulfilment of the requirements for the degree

MAGISTER SCIENTIAE

in the Faculty of Natural and Agricultural Sciences

University of Pretoria

Abstract

Coal is available in relative abundance worldwide and therefore can be used as 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. High-purity coal suitable for the production of high-purity carbon is produced by treating the coal to remove the bulk of the mineral matter content. Purifying the coal before usage has some cost advantage since it could eliminate the need for expensive high-temperature purification during graphitisation.

The aim of this study was to reduce the inorganic mineral content of coal. For this purpose, Tshikondeni coking coal floatation concentrate was used which had an ash content of 9.4% by mass and a sulphur content of 0.81%. This coal was subjected to step-wise purification. The concentration levels of Ba, Co, Cr, Cs, Eu, Fe, Hf, La, Sc, Sm, Ta, Tb, Th, and U were determined by instrumental neutron-activation analysis.

The bulk of the minerals was removed by extracting the organic part of the coal into a polar aprotic solvent. The resulting solution was then centrifuged to separate the inorganic mineral matter and the undissolved organic matter from the solution. The coal material was recovered as a gel by precipitation with water and was then washed thoroughly with water to remove water-soluble products. The resulting coal material had an ash value of 1.7% by mass. At this stage of the purification process, the concentration levels of the elements Ba, Co, Cr, Cs, Eu, Fe, Hf, La, Sc, Sm, Ta, Tb, Th, and U were still high in relation to nuclear carbon. The purification value of these elements was below 20. Most of these elements are unimportant with respect to nuclear-grade carbon, but the elements cobalt (Co), which becomes activated by neutron capture, the rare-earth elements (e.g. europium [Eu] and samarium [Sm]), which are neutron absorbers and sodium (Na), which is an oxidation catalyst, are undesirable.

An attempt was made to purify the coal extracts by either treating the coal solution with chelating resins and sulphonic acid resins, or treating the gel with anion exchange resins in a form of beads. In the latter case, the coal solution is filtered to separate the purified coal from the resin beads, followed by precipitation with water to recover the coal material. The purification values for all the elements determined are below 20 for sulphonic acid resins and chelating resins. Improved reduction in tantalum (Ta) concentration is observed with anion resins which suggests that tantalum exists as an anion in the coal matrix whereas the rare-earth metals exist as cations.

Recovered coal gel was first treated with concentrated hydrochloric acid to remove the acid-soluble products. These include the ions that form insoluble fluorides, e.g. calcium ions. The resulting coal gel was then treated with concentrated hydrofluoric acid to remove the silicates. Finally, the acid-treated gel was treated with chelating resin beads and sulphonic acid resin beads, and then filtered

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

to separate the purified coal material from the resin beads.

Purification values above 20 for the elements Cs, Eu, Fe, La, Sc, Sm, and Tb were achieved when the coal gel was treated with acid. Treatment with chelating resins gave purification values of 20 and above for the elements Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Tb, Th and U, while treatment with sulphonic acid resins resulted in purification values of 20 and above for the elements Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Ta, Tb, Th and U.

Treating the gel with concentrated acid followed by sulphonic acid resins was found to be the best method for reducing the concentration of alkali metals (represented by cesium [Cs]) and rare-earth elements (e.g. europium [Eu] and samarium [Sm]). Treating the gel with acid followed by chelating resins was the second best method. Solvent extraction alone did not yield satisfactory results and neither did ion-exchange treatment of the coal solution. No significant purification of cobalt could be achieved, suggesting that this element is held strongly in organometallic complexes in the coal matrix as a result of which the rate of exchange with the resins is slow.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE OF CONTENTS

ACKNOWLEDGEMENTS i

ABSTRACT ii

TABLE OF CONTENTS v

CHAPTER 1

General introduction 1

1.1. Introduction 1

1.2. Aim of the study 5

1.3. Contents of the study 5

CHAPTER 2

Literature survey 6

2.1. Coal: theoretical background 6

2.1.1. Introduction 6

2.1.2. Coal structure 7

2.1.3. Petrographic groups 8

2.1.3.1. The vitrinite goup 8

2.1.3.2. The liptinite group 9

2.1.3.3. The inertinite group 10

2.1.4 Mineral matter 11

2.1.4.1. Distribution and occurrence of mineral matter 11

2.2. Trace element analysis of coal 14

2.2.1. Introduction 14

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

2.2.2. Sample preparation 15

2.2.3. Coal standards 16

2.2.4. Analytical methods 17

2.2.4.1. Atomic absorption spectrometry 17

2.2.4.2. Atomic emission spectrometry 18

2.2.4.3. Inductively coupled plasma mass spectrometry 19

2.2.4.4. X-ray fluorescence spectrometry 20

2.2.4.5. Instrumental neutron activation analysis 21

2.2.4.6. Comparison of analytical methods 22

2.3. Refined coal 23

2.3.1. Introduction 23

2.3.2. Extraction of mineral matter using sodium hydroxide 23

2.3.3. Extraction of mineral matter using hydrofluoric acid 24

2.3.4. High-temperature solvent extraction of coal 25

2.3.5. Low-temperature solvent extraction of coal 26

2.3.5.1. Extraction of coal with mixed solvents 26

2.3.5.2. Extraction of coal with N-methylpyrrolidone 27

2.3.5.3. Extraction of coal with a polar aprotic solvent/alkaline mixture 28

2.4. Graphite 31

2.4.1. Introduction 31

2.4.2. The physical structure and purity of graphite 32

2.4.3. The manufacture of graphite 33

2.4.4. Graphite manufacture from refined coal 34

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

2.5. General chemistry 36

2.5.1. Ion-exchange 36

2.5.2. Specific elements 39

2.5.2.1. Iron 39

2.5.2.2. Cobalt 40

CHAPTER 3

Experimental procedures 42

3.1. Materials used 42

3.2. Coals studied 43

3.3. Dissolutions of coal with dimethylformamide-sodium hydroxide mixture 43

3.4. Dissolutions of coal with dimethylformamide-sodium hydroxide-sodium sulphide mixture 44

3.5. Dissolutions of coal with dimethylformamide-sodium sulphide mixture 44

3.6. Recovery of Refcoal 45

3.7. Extraction of mineral matter from Refcoal gel with hydrochloric and hydrofluoric acid 45

3.8. Extraction of mineral matter from Refcoal with ammonia hydroxide solution 46

3.9. Extraction of mineral matter from Refcoal with sodium nitrite solution 46

3.10. Extraction of trace elements from Refcoal gel with chelating resins 47

3.11. Extraction of trace elements from Refcoal gel with sulphonic acid resins 47

3.12. Extraction of trace elements from Refcoal gel with anionic resins 47

3.13. Extraction of trace elements from Refcoal solution with chelating resins 48

3.14. Extraction of trace elements from Refcoal solution with sulphonic acid resins 48

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

3.15. Colorimetric determination of cobalt 48

CHAPTER 4

Results and Discussion

4.1. Coal studied 51

4.2. Dissolutions of coal and Refcoal recovery 53

4.3. Trace element analysis 60

4.3.1. Trace element analysis of unpurified Refcoal 61

4.3.1.1. Conclusion 71

4.3.2. Extraction of trace elements with hydrochloric and hydrofluoric acid 72

4.3.2.1. Conclusion 82

4.3.3. Extraction of trace elements from Refcoal solution with chelating resins 84

4.3.3.1. Conclusion 92

4.3.4. Extraction of trace elements from Refcoal gel with chelating resins 94

4.3.4.1. Conclusion 101

4.3.5. Extraction of trace elements with sulphonic acid resins 103

4.3.6. Extraction of cobalt from Refcoal gel with ammonia hydroxide solution, sodium sulphide solution and anion exchange resins 105

4.3.7. Colorimetric determination of cobalt 107

CHAPTER 5

General Conclusions 109

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

CHAPTER 6

References 111

APPENDICES 125

Appendix 1 125

Appendix 2 137

Appendix 3 140

Appendix 4 145

Appendix 5 149